



# MassDEP

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## Massachusetts Department of Environmental Protection Division of Watershed Management

### STANDARD OPERATING PROCEDURE

#### Ambient Trace Metal Sampling

CN 101.2  
October, 2012

Prepared by:	_____	Date:	_____
	Richard Chase, Quality Assurance Analyst		
Approved by:	_____	Date:	_____
	Arthur Johnson, Monitoring Coordinator		
Approved by:	_____	Date:	_____
	Dennis Dunn, Program Supervisor		

*\* see pdf version for valid signatures*



**Disclaimer:** References to trade names, commercial products and manufacturers in this SOP does not constitute endorsement by MassDEP.

### **List of Revisions**

Revision Date	Revision	Pages #s
July, 2007	---	---
Oct., 2012	Added alternative field sampling protocol 2b to Appendix A	21-23
April, 2013	Added alternative field sampling protocol 2c to Appendix A	
May, 2013	Added Appendix X for preservation of samples at DWM lab	



## 1.0 SCOPE AND APPLICATION

Low-level metals sampling of ambient waters can be confounded by sample contamination during collection, transport and laboratory analysis, if appropriate steps to avoid contaminant pathways are not taken. Contamination pathways include airborne particulates (dust, vehicle exhaust, human breath, clothing, etc.), cross-contamination between stations and inadvertent contact with samples. In order to provide a means to generate reliable data at water quality criteria levels, EPA has developed recommended field and analytical methods. EPA Method 1669 provides performance-based guidance for “clean” field collection of ambient water samples for total recoverable and dissolved metals under a variety of conditions, and references new EPA analytical methods for the determination of specific metal analytes. This SOP for “clean” metals sampling is designed to meet the intent of EPA Method Guidance 1669, including the use of the “clean hands-dirty hands” technique.

## 2.0 SUMMARY

This SOP describes the necessary survey preparation and field procedures for the collection of uncontaminated aqueous trace metals samples from rivers and streams. It also includes relevant information regarding analytical determination of dissolved and total recoverable metal analytes, such as Al, Ag, As, Pb, Hg, Cd, Cu, Cr, Zn, Ni and Se.

## 3.0 SAFETY CONSIDERATIONS

Survey crews shall use best professional judgment at all times regarding personal safety, and follow safety precautions outlined in DWM’s general sample collection SOP, CN 1.21. All sampling personnel have been trained what to do in the event of an emergency. A complete First Aid Kit containing basic first aid equipment shall be brought (in the vehicle) on each field survey. At least one member of the survey team shall be trained in cardiopulmonary resuscitation (CPR) and basic first aid procedures. Each crewmember shall bring personal protective gear, such as protective clothing and footgear (i.e., hip boots). Some potentially-needed items are provided in the standard Field Kit, which shall accompany each survey. Orange, reflective safety vests shall be available for use as needed (e.g. when sampling in high vehicular traffic areas). A portable, cellular phone may be brought on each trip.

Based on testing performed in 2002, indications are that HNO<sub>3</sub>-acid-washing of new, pre-cleaned glass bottles (with certificate of metals analysis) is unnecessary. If acid-washing is performed (e.g. on used glass bottles), disposable gloves and safety glasses shall be worn when handling bottles containing 5-10% HNO<sub>3</sub> (v/v), and waste acid shall be disposed of properly using a waste acid container for transport to WES.

Extreme care must be used if samples are preserved with concentrated HNO<sub>3</sub> in the field or in the lab.



## **4.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING**

All field sampling for aqueous trace metals shall follow the intent of EPA guidance (Method 1669) detailing the use of “clean” (including the “clean hands-dirty hands” protocol) sampling techniques for low-level metals sampling.

All equipment and materials in contact with sample media shall have minimal exposure to the open atmosphere and potentially-contaminating surfaces in the field (and in the lab). Using a two-three person crew, only the one-two persons designated “clean hands” shall touch the sample bottle prior to, during and after sampling. The other, designated “dirty hands”, shall perform tasks not involving direct contact with the sample.

A PVC-frame/plastic bag sampling chamber (no metal parts) is used as a portable glove box at each sampling site for sample filtering and processing (to minimize sample contamination due to dry/wet atmospheric deposition). This device, based on a USGS schematic for “clean” metals sampling, can be constructed and dismantled at each site using the re-usable PVC pipe frame parts and new, translucent, large plastic bags.

Plastic, 60 ml. disposable syringes shall be used (one per site) with 0.45 u Supor® capsule filters or similar (prepared by pre-filtering/discarding 125-250 mls of DI through the filter immediately prior to sample collection) to filter samples for dissolved metal analytes. The syringes shall be filled several times to get the desired sample water volume (approx. 500 mls.). Based on ease of use and discussions with EPA-New England (Tom Faber, pers. comm., April, 2002) regarding their use of syringes, this method is currently preferred over the use of a peristaltic pump and tubing.

As allowed in Method 1669, samples shall be acidified with high purity, ultra-trace (e.g. Fisher “Optima”) HNO<sub>3</sub> at the analytical lab. Alternatively, as a contingency measure if samples cannot be delivered to the lab the same day, a small amount of ultra-trace grade HNO<sub>3</sub> can be procured from WES for use at DWM (using the “clean” fume hood), and the samples can be delivered the next day.

Additional analytes measured or determinations made that should be included when performing metals sampling are: Hardness (Ca+Mg; total or dissolved; for determination of hardness-specific State ambient water quality standards), pH (speciation of metal complexes), temperature, turbidity, total suspended solids, and total/dissolved organic carbon (relates to biotic ligand modeling).

## **5.0 MATERIALS AND EQUIPMENT**

The following materials are needed for this sampling (and analysis). A trip checklist (Appendix E) should be used prior to departure.

1. For Alternative Protocol #3 (Appendix A) only: PVC-frame/plastic bag sampling chamber (no metal parts) is designated for clean metals sampling only and made using standard schedule 40, ½ inch ID PVC pipe. This device shall be constructed (un-glued) and dismantled at each site using the re-usable PVC pipe frame parts and new, translucent, large



plastic bags (approx. 48"x48" non-clean can liners or Secovac 140 clear polyethylene clean room bags).

2. Plastic, 60 ml. disposable syringes (BD Co.) shall be used repeatedly (as needed) with 0.45 u Supor® capsule filters (Pall/Gelman/Geotech, hydrophilic polyethersulfone), and filter adaptors (Geotech). Filters shall be pre-soaked by pre-filtering/discarding 125-250 mls of DIW through the filter immediately prior to sample collection. Use of these filters shall result in filtered samples ready for dissolved metals analysis. The syringes shall be filled several times as needed to get the desired sample water volume (approx. 500 mls.).
3. Two new, large coolers have been purchased and designated for "Clean Metal" sampling ONLY. Cooler #1 contains "clean" materials and equipment needed for field surveys, such as syringes, filters, sampling suits, disposable gloves and the portable glove box (no metal-bearing objects). Cooler #2 shall contain wet ice for sample transport at 4 deg. C. A cooler thermometer should be used with the cooler containing samples to record sample temperatures at lab receipt.
4. New (or reusable, if acid-washed), 500 ml. "Trace-Clean" (VWR Scientific) amber glass sample bottles or HDPE, trace-clean bottles can be used. New, VWR TraceClean, re-usable, acid-washable, 4-liter, amber glass jugs shall be used to store ambient field blank water and as sample collection vessels for the taking of split samples. Glass is required when sampling for Hg (EPA 1669).
5. White "Hazmat" jump suits
6. Disposable sampling gloves (shoulder-length polyethylene and other)
7. Sample bottle labels, COC forms, fieldsheet forms, notebook
8. Misc. analyte sample bottles (e.g. HDPE, 1 l) for non-metal analyte samples
9. Field and Lab SOPs, and QAPP (on-hand)
10. Plastic Tarp as ground cover and/or protection from the rain
11. Extra sample bottles, assorted clean plastic bags, filters, syringes, adaptors, etc.
12. Misc. field probes as needed, such pH meter and turbidity meter (w/ Kim Wipes)
13. DIW for ambient field blanks
14. Ultra-trace grade HNO<sub>3</sub> and disposable pipettes for lab acidification. A smaller bottle can be prepared for use in the field or at DWM's lab for field acidification if preferred.



15. WES laboratory Inductively Coupled Plasma/Atomic Emission Spectrophotometer (ICP/AES) unit: P.E. Optima 3000 XL with cyclonic spray chamber and Gemcone nebulizer, quartz torch module and AS-90 autosampler. (EPA 200.7)
16. WES laboratory Inductively Coupled Plasma/Mass Spectrometry (ICP-MS) unit: (EPA 200.8). As of 2007, this ICP-MS is the preferred method for most metal analytes.
17. If needed, WES lab Stabilized Temperature Graphite Furnace Atomic Absorption Spectrophotometer (STGF/AA) unit: Zeeman 5100 with single-element hollow cathode lamps, 99.99% high purity argon gas, AS-60 autosampler and refrigerated recirculator (NESLAB CFT-75). (EPA 200.9)
18. WES lab's Cold Vapor Atomic Absorption (CVAA) unit for Hg analysis: Perkin-Elmer Flow Injection Mercury System (FIMS) with 21 cm long absorption cell, hollow cathode mercury lamp, AA detection set at 253.7 nm, AS-90 auto-sampling, 99 % pure Argon carrier gas, and water bath set to 95 deg. C. (EPA 245.1)
19. Alternate analytical lab equipment (as applicable)

## 6.0 REAGENTS

The primary reagents related to field samples are:

1. WES/DWM lab reagent water: Barnstead Nanopure Type I (deionized) reagent water (DIW).
2. WES trace grade HNO<sub>3</sub> for acid-washing (as needed)
3. WES high-purity Nitric Acid (HNO<sub>3</sub>) for preservation and analysis: "Optima" ultra trace-grade HNO<sub>3</sub> (Fisher Scientific) or equivalent

## 7.0 CALIBRATION

Not applicable to field operations.

## 8.0 PROCEDURES

**NOTE:** *The following set of procedures is based in part on the clean metals sampling employed by EPA-New England, OEME. Alternative field sampling procedures are provided in Appendix A.*

### Equipment and Supplies:

One sampling kit per sample. They will be assembled in the lab ahead of time by a handler wearing gloves. Each kit will consist of the following items placed inside new, clean plastic bags.

- One 500 ml pre-cleaned, certified-clean bottle per site
- One new 60 ml syringe in the original packaging



- One high volume disposable capsule or disk filter (large diameter)
- One pair of “powder free” (class 100 clean room class preferred) disposable gloves in clean plastic bag

For field work, you will also need:

- Spare new capsule filters in sealed plastic bag
- A box of regular powder-free gloves, a box of shoulder length polyethylene gloves and spare class 100 gloves in a clean sealed plastic bag
- Sealable clean plastic bags to hold filled sample bottles in ice chests
- Spare new 60 ml syringe in the original packaging in a clean sealed plastic bag
- DI water in amber glass (500 mls. bottle and 4 liter glass jug as spare water)
- Spare sampling kits
- General equipment: Site logbooks, indelible marker, waterproof pen, field data sheets, chain of custody forms, etc.
- Chest waders with belt, hip boots
- One clean “metals” ice chest with ice
- One clean “metals” cooler to hold dry materials

### 8.1 Pre-sampling Prep:

1. Determine the number of samples (including QC samples) to be taken and prepare bottle labels, COC, fieldsheets, etc... Fieldsheets must describe all sample information in detail. COC must include only that information the lab needs to have.
2. Prepare cart with materials needed for survey, load truck...
3. QC samples: field dups @ 20-50 % of total; field filter blanks @ 1-2 per crew; trip blanks @ one per project (at a minimum)

### 8.2 Sample Collection for Dissolved Metals

Sample will be collected using a clean-hands/dirty-hands (CH/DH) type procedure. The specific procedure at each stream/river site is as follows.

1. Sampling is done in teams of two. The person taking the sample is designated the “clean hands” person (CHP), and the assistant is designated the “dirty hands” person (DHP). The CHP is not to touch anything except the syringe, filter, and adaptor until sampling is complete.
2. Immediately before entering the water to collect the sample, the DHP and CHP don shoulder-length plastic gloves from the glove box.
3. Approach the sampling location slowly from the downstream. Once you have reached the sampling location allow the water to return to a pre-disturbed condition. Avoid contacting the syringe with the bottom or adjacent rocks and stream debris.
4. DHP then opens the sample kit, then extracts the bag containing the disposable gloves and opens it, allowing the CHP to take them out and put them on over the shoulder-length gloves. NOTE: in some cases the clean filter adaptor will be in this bag, so make sure to grab it as well.





5. Next, the DHP removes the syringe package from the kit and opens it. The CHP now takes the syringe out of the package, fills it up with ambient water from about 0.1 meter below the surface, places the tip of it into the adaptor and wastes downstream (**to rinse syringe**). 3X rinse.
6. Next, the DHP takes out and opens the filter package. The CHP then removes the filter and adaptor. At the first site, the adaptor is fitted onto the capsule filter on the syringe side (so the syringe will fit into it snugly; note the flow arrow on the filter and hook the adaptor up to the inlet).
7. Next the DHP takes the sample bottle from the kit and opens it with out touching the inside. The cap is held in one hand (without touching the inside) and is capped in-between successive additions.
8. CHP then fills the syringe with stream water from about 0.1 meter below the surface, places the tip of it into the adaptor/filter assembly and empties it into the sample bottle. DHP caps bottle, shakes 5-10 times, removes cap and empties contents downstream (**to rinse filter and bottle**). 3X rinse.
9. Then the sample is collected. CHP fills the syringe multiple times (always from about 0.1 meter below the surface), connects filter assembly to syringe, and pushes site water into the open bottle held by DHP. Do this until about 400-500 mls. is collected. Be careful not to drip any unfiltered stream water from gloves, etc into the sample bottle!
10. The DHP then caps the sample bottle and places it into the plastic kit bag.
11. CHP places the used sampling gear in the kit bag. NOTE: save used capsule filters and adaptors.
12. At vehicle, remove and dry sample bottle and place completed bottle label on the bottle. Place in plastic bag for samples on ice in the cooler. Repeat above steps at all sites.



Field filter apparatus



Inter-group replicate sampling using CH/DH

### 8.3 Sample Handling/Preservation/Storage and QC Samples

1. All samples are placed in clean plastic bags in wet ice (4 deg. C) and delivered to WES within 24-48 hours (preferably same day/next day).
2. Preservation of samples with conc. HNO<sub>3</sub> can be done immediately after sampling, continuing with the “dirty hands/clean hands” technique, OR at the lab within 48 hours from collection.
3. For **field dups**, use same filter for both dup samples at the same site (one filter per site).





4. For **field filter blank(s)**, reuse the capsule filter for the blank and the sample by performing the following procedure: CHP takes the blank by drawing ~200 mls (4 syringes) of DIW from the blank water bottle and pushing it through the new, unused filter to waste; then more blank water (~250-500 mls.) is drawn and pushed through the filter into the sample bottle. To then take the ambient sample: CHP pushes air through the filter using the empty syringe until the filter flow (DIW) stops. CHP then fills the syringe with sample water (as above) and pushes it thru the filter. This is done 4X (~250 mls. total) to rinse the filter thoroughly with sample water. Finally, CHP then takes the sample (as above). NOTE: if using less expensive, large diameter disk filters, it is not necessary to reuse the filter.

## 9.0 QUALITY CONTROL

To evaluate overall field precision, co-located and simultaneous or same-location and sequential field duplicates (or split samples using large volume glass jug sampler) shall be taken at approx. 10% of total survey samples for the same analytes (dissolved metals). Duplicate/split sampling at every station is preferred, due to the site-specific nature of potential contamination sources.

To evaluate the possibility of sample contamination from sampling activities, ambient field blanks (AFB) for both total recoverable (unfiltered) and dissolved (filtered) shall be taken. AFBs for total metals shall be taken at a minimum of one per survey and filtered AFBs for dissolved metals at approx. 10% of total survey samples (filtered AFBs at every station is preferred).

In addition, a trip blank (one per survey) is recommended to evaluate if any sample contamination found took place in transport.

Laboratory quality control samples shall include reagent water blanks, lab-fortified blanks, lab-fortified matrix and matrix duplicate samples, and internal quality control samples.

Training of the survey crew in grab sampling and the clean metals issues and approach will also ensure that samples are taken consistent with this DWM SOP. Following each survey, the survey crew(s) shall perform a self-evaluation to highlight potential improvements in the SOP or in the field performance. The survey crew will also discuss analytical issues with each lab for possible improvements in coordination, logistics and/or performance.

## 10.0 INTERFERENCES

Use of the sampling procedures outlined in this SOP is designed to avoid or reduce the potential for field interferences affecting the samples.

There is some evidence that acid-washing sample bottles prior to use (vs. using new certified bottles directly with just field-rinsing) reduces the potential for Al and Cu contamination. Provided adequate time, need and resources, acid-washing with trace-grade HNO<sub>3</sub> can be done.

The WES lab has previously documented accurate, precise and acceptable analysis for trace metals (initial and historical demonstration of capability). Their SOPs for metal analysis include necessary quality



control steps to address potential interferences, such as matrix modifications and minimizing airborne metals (e.g. Hg from COD, TKN analyses) in the lab during sample handling and analysis.

## **11.0 PREVENTIVE MAINTENANCE**

Not applicable for field operations. See WES Quality Assurance Plan (QAP) and specific WES SOPs for laboratory preventative maintenance.

## **12.0 CORRECTIVE ACTIONS**

Survey crew self-evaluations, performance audits by DWM's QA/QC Analyst and assessment of raw/draft laboratory data may result in the need for corrective actions. Actions to correct field sampling deficiencies shall be the responsibility of DWM, and for laboratory analytical deficiencies shall be the responsibility of the WES lab.

DWM's data validation report with regard to metals data, in addition to recommending specific data for qualification or censoring, may suggest corrective actions where necessary. Upon completion of all field sampling, the final project report shall note recommended changes to future QAPPs and the SOP, as appropriate.

## **13.0 WASTE AND POLLUTION PREVENTION**

The following provisions shall ensure the prevention of unnecessary waste and avoid pollution to the maximum extent practicable.

1. Re-use of large amber glass jugs for deionized water storage from one survey to the next. These vessels can be acid-washed between surveys (uses less containers).
2. Use of the same disposable, high volume capsule filters for same-site duplicate samples (uses less filters for same amount of samples).
3. Acid-washed bottles will be filled with DIW for delivery to survey sites (and the water disposed of in the field), rather than dilute HNO<sub>3</sub> (reduces amount of waste water).
4. Re-use of amber glass sample bottles (acid washing required)



## 14.0 REFERENCES

USEPA- *Methods for Chemical Analysis of Water and Wastes*, EPA 600/4-79-020, Revised 1983. Clesceri, L.S., A.E. Greenberg, and A.D. Eaton, (editors).

USEPA – Method 1638: *Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry*, EPA 821-R-95-031, April, 1995

USEPA – Method 200.8: *Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry*, Revision 5.4 EMMC version, 1995

USEPA – *Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities* (Draft), EPA 821-B-96-001, January, 1996

USEPA – *Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*, July 1996

USEPA – *The Volunteer Monitor's Guide to Quality Assurance Project Plan*, EPA 841-B-96-003, September 1996. Office of Wetlands, Oceans and Watersheds.

Virginia Dept. of Environmental Quality – *Quality Assurance Project Plan for Clean Metals* (Draft), July, 1997

MADEP -- *Draft 1.1 Work/Quality Assurance Project Plan, An Evaluation of Drinking Water Supply Contributions of Copper and Lead to Selected Wastewater Systems in the Commonwealth of Massachusetts*, December, 1997

1998 *Standard Methods for the Examination of Water and Wastewater*, 20<sup>th</sup> Edition, American Public Health Association, American Waterworks Association and Water Environment Federation, Washington.

USEPA – *Compendium of Quality Assurance Project Plan Guidance*, September 1998. Office of Environmental Measurement and Evaluation, New England, Region 1.

USEPA – *National Recommended Water Quality Criteria--- Correction*, EPA 822-Z-99-001, April, 1999

MADEP – Wall Experiment Station SOP for USEPA Method 200.7 *Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma—Atomic Emission Spectrometry*, Revision 1.1, November, 2000

MADEP – Wall Experiment Station SOP for USEPA Method 200.8 *Determination of Metals and Trace Elements in Water by Inductively Coupled Plasma—Mass Spectrometry*, Revision 1.6, January, 2010



MADEP - Laboratory Quality Assurance Plan and Standard Operating Procedures, 2008 Revision 4.1.  
Massachusetts Department of Environmental Protection, Wall Experiment Station.

MA DEP. CN 1.21 *Sample Collection techniques for DWM Surface Water Monitoring*, 2001;  
Massachusetts Department of Environmental Protection, Division of Watershed Management, Worcester,  
MA.

MADEP – Wall Experiment Station SOP for USEPA Method 245.1 *Determination of Mercury in Water  
by Cold Vapor Atomic Absorption Spectrometry*, Revision 1.1, December, 2001

MADEP – Wall Experiment Station SOP for USEPA Method 200.9 *Determination of Trace Elements by  
Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry*, Revision 2.4, February, 2002

USGS – National Field Manual for the Collection of Water Quality Data, TWRI Book 9; September, 1998



## Appendices

- APPENDIX **A**: Alternative Field Sampling Protocols
- APPENDIX **B**: Bottle Type/ Specifications, Preservation Methods & Holding Times for Metals Analytes
- APPENDIX **C**: Certificates of Analysis for “Optima” HNO<sub>3</sub> reagent, sample bottles and capsule filters
- APPENDIX **D**: WES Analytical Method SOPs
- APPENDIX **E**: Field Equipment List
- APPENDIX **F**: Hardness-Dependent CCC/CMC Calculator



## APPENDIX A

### Alternative Field Sampling Protocol #1

(based on excerpts from EPA-NE's 2007 clean metal SOP)

SOP Title: Low Level Metals Sampling

Revision #: 1

9/04/03

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#### STANDARD OPERATING PROCEDURE FOR THE COLLECTION OF LOW LEVEL METALS AMBIENT WATER SAMPLES

The Office of Environmental Measurement and Evaluation  
EPA New England - Region 1  
11 Technology Dr  
North Chelmsford, MA 01863

#### **7.0 Equipment and Supplies:**

7.1 One sampling kit per site and blank to be sampled and an extra kit or two as backup. They will be assembled in the lab ahead of time by a handler wearing gloves. Each kit will consist of the following items placed inside two sealed plastic Zip-Lock bags, one inside the other.

7.1.1 One 500 ml pre-cleaned bottle per site (a 1000 ml bottle for the filter blank) that has been demonstrated to be free of contaminants. (Bottles are purchased from Eagle Pitcher; part number C50-500/NM/LP. They have been washed with dilute acid and rinsed in a clean room with hot distilled water. Bottles are delivered capped in a sealed plastic bag.)

7.1.2 One pair of "powder free" shoulder length polyethylene gloves which have been stored in their commercial packaging or in a sealed Zip-Lock plastic bag.

7.1.3 One clean filter, syringe, and adaptor in their original packaging.

You will also need:

7.2 A box of regular powder-free gloves.

7.3 Ultrex-grade nitric acid and clean, packaged pipettes.

7.4 pH paper, preferably measuring a range of pH from 0 to 2.5.

7.5 General equipment: Site logbooks, indelible marker, waterproof pen, field data sheets, chain of custody forms.

7.5 Chest waders with belt, hip boots

7.6 Boat



## **8.0 Pre-sample Collection:**

8.1 Determine the number of samples (including QC samples) specified in QAPP. Refer to section 3.0 for QC sample definitions. At a minimum, a filter/equipment blank must be conducted for each sampling event or for each day.

8.2 Determine the sample locations, analytical sampling parameters, the sampling methods to be employed, and which equipment and supplies are needed.

8.3 Prepare a schedule and coordinate with the staff, clients, laboratory and regulatory agencies.

8.4 If possible, perform a general site survey prior to the site entry in accordance with the health and safety plan and QAPP.

8.5 Use GPS, topographic maps, stakes, flags, or buoys to identify and mark all sampling locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

## **9.0 Sample Collection**

When collecting samples, the field location should be recorded in detail (on fieldsheet, using GPS, etc.). The date and time of sample collection, field measurements and ambient conditions must be recorded. Water chemistry measurements should be made by a separate team, after sample collection is complete, unless the measurements can be made in a way that will not contaminate or influence the samples (i.e, if there is a strong flow).

### **9.1.0 Collection from a Boat**

9.1.1 Use only a fiber-glass boat for sampling.

9.1.2 Approach the sampling point from a downstream or down-wind position and then motor slowly toward the sampling point. The motor should be turned off prior to reaching the sampling location and the boat allowed to coast a short distance to the anchoring point to prevent sampling of water affected by motor exhaust.

9.1.3 Allow the boat to come to a complete stop and lower the anchor slowly to prevent bottom sediments from being disturbed. Do not drop or toss the anchor overboard. If there is no wind or current you may not need to anchor.

9.1.4 Allow the boat to drift into anchored position before beginning sampling.

### **9.2.0 Sample Collection From Shore or Using Waders**

9.2.1 Don waders with belt

9.2.2 Where there is flow or current, always approach the sampling location slowly from the downstream. Once you have reached the sampling location allow the water to return to a pre-disturbed condition. Avoid contacting the syringe with the bottom or adjacent rocks and stream debris. If the water depth is less than 0.2 meters, record this condition and sample the water at mid depth.

### **9.3 Collection Procedure**

9.3.1 Sampling is done in teams of two. The person taking the sample is designated the "clean hands" person (CHP), and the assistant is designated the "dirty hands" person (DHP). The CHP is not to touch anything except the syringe, filter, and adaptor until sampling is complete.

9.3.2 Immediately before collecting the sample, the DHP dons regular powder-free gloves. They then opens the sample kit, extracts the bag containing the shoulderlength





gloves and opens it, allowing the CHP to take them out and put them on.

9.3.2 Next, the DHP takes out and opens the filter package. The CHP then removes the filter.

9.3.3 The CHP next removes the adaptor from the kit and connects it to the filter (Note the flow arrow on the filter and hook the adaptor up to the inlet).

9.3.5 Next, the DHP removes the syringe package from the kit and opens it.

9.3.6 The CHP now takes the syringe out of the package, fills it up with water from about 0.2 meters below the surface, places the tip of it into the adaptor and empties it into the filter. (If necessary, rather than holding the filter while drawing the sample, the CHP may place the filter and adaptor on the opened syringe packaging or pass the filter to the DHP while filling the syringe. Do not, however, allow the filter to contact any unclean surfaces such as a stream bank or the boat.)

9.3.7 The CHP now draws another syringe of water (always from about 0.2 meters below the surface), places the tip of it into the adaptor, and empties it into the filter, purging the water out of the filter downstream from the sampling site.

9.3.8 Next the DHP takes the sample bottle from the kit and opens it with out touching the inside. The cap is held in one hand (without touching the inside) or may be placed in the open syringe packaging.

9.3.9 The CHP places the filter and adaptor onto the bottle allowing the DHP to hold it in place.

9.3.10 The CHP draws a syringe of sample from the water and empties it into the filter. They continue to do this until the bottle is nearly full, leaving enough room for about 1 ml of preservative to be added.

9.3.12 The DHP then removes the filter and caps the sample bottle.

## **10.0 Sample Handling, Preservation, and Storage**

Preservation of samples with conc. HNO<sub>3</sub> can be done immediately after sampling, continuing with the “dirty hands/clean hands” technique, OR at the lab. For field preservation:

10.1 The CHP dons safety glasses, shoulder-length gloves and any other necessary safety equipment. Have a neutralizing agent (such as baking soda) and rinse water readily available.

10.2 The DHP opens the pipette package and the CHP removes the pipette.

10.4 Next, the DHP opens the bottle containing Ultrex-grade nitric acid and the sample bottle.

10.5 The CHP draws about 1 ml of acid per 500 ml sample and adds it to the bottle. The pipette may be placed back in its original wrapper.

10.6 The DHP caps the sample bottle and shakes it gently to mix the preservative with the sample.

10.7 The CHP takes out a piece of pH paper and the DHP pours a drop of the sample onto it. To avoid contamination, do not dip the pH paper in the sample bottle.

10.9 If the pH does not register < 2.0, add a drop more acid, to the sample, cap and shake the bot, and retest the pH using the above protocols until the correct acidity is achieved (no glove changes needed).

10.6 Once the sample has been preserved properly, the DHP caps the sample bottle (using a custody seal if the sample is for enforcement), places it in a Zip-lock plastic bag



(optional), and places the bottle in a cooler of ice, ensuring that the bottle is in the ice but not totally immersed in water.

10.8 Record all pertinent data in the site logbook and on the field data sheet. At a minimum this includes date, time, station number, sampling number and sampling conditions.

### **13.0 Quality Control/Quality Assurance and Decontamination:**

13.1 Representative samples are required. The sampler will evaluate the site specific conditions to assure the sample will be representative.

13.2 All sampling equipment must be completely decontaminated prior to and after use.

13.3 Between each station, any sampling equipment used shall be washed with a phosphate free soap and rinsed three times with distilled water. If sampling vertical profiles at the same station, sampling equipment will not be washed unless deemed necessary by the project data quality objectives.

13.4 All field QC sample requirements outlined in the SOP must be followed. These may involve trip blanks, equipment blanks, field duplicates and the collection of extra samples for the laboratory's quality control.



## **Alternative Field Sampling Protocol #2**

(generally consistent with EPA-NE's SOP, but tailored for use by DWM/WES  
and re-use of high-volume capsule filters)

**NOTE:** This alternative protocol is NOT RECOMMENDED, due to the potential for cross-contamination (ref. Steps 9.13-9.15).

### **7.0 Equipment and Supplies:**

7.1 One sampling kit per sample. They will be assembled in the lab ahead of time by a handler wearing gloves. Each kit will consist of the following items placed inside new, clean plastic bags.

- One 500 ml pre-cleaned, certified-clean bottle per site
- 500 ml DI water in pre-cleaned, certified-clean bottle
- One pair of "powder free" shoulder length polyethylene gloves
- One pair of "powder free" class 100 clean room vinyl gloves in clean plastic bag
- One new 60 ml syringe in the original packaging

For field work, you will also need:

- One 0.45 micron high capacity capsule filter in a clean sealed plastic bag. This filter will be re-used at multiple sites after thorough pre-rinsing with DI water and sample water at each site.
- Spare new capsule filters in sealed plastic bag
- A box of regular powder-free gloves, a box of shoulder length polyethylene gloves and spare class 100 gloves in a clean sealed plastic bag
- Sealable clean plastic bags to hold filled sample bottles in ice chests
- Spare new 60 ml syringe in the original packaging in a clean sealed plastic bag
- Spare DI water in 4 liter glass jug
- Spare sampling kits
- General equipment: Site logbooks, indelible marker, waterproof pen, field data sheets, chain of custody forms, etc.
- Chest waders with belt, hip boots
- One clean "metals" ice chest with ice
- One clean "metals" cooler to hold dry materials

### **8.0 Pre-sampling Prep:**

- 8.1 Determine the number of samples (including QC samples) to be taken and prepare bottle labels, COC, fieldsheets, etc...
- 8.2 Prepare cart with materials needed for survey, load truck...
- 8.3 QC samples: field dups @ 20-50 % of total; field filter blanks @ one per crew; trip blanks @ one per project (at a minimum)



## 8.4

### 9.0 Sample Collection for Dissolved Metals

Sample will be collected using a clean-hands---dirty-hands type procedure. The specific procedure at each stream/river site is as follows.

2. Sampling is done in teams of two. The person taking the sample is designated the “clean hands” person (CHP), and the assistant is designated the “dirty hands” person (DHP). The CHP is not to touch anything except the syringe, filter, and adaptor until sampling is complete.
3. Immediately before entering the water to collect the sample, the DHP dons regular powder-free gloves.
4. Approach the sampling location slowly from the downstream. Once you have reached the sampling location allow the water to return to a pre-disturbed condition. Avoid contacting the syringe with the bottom or adjacent rocks and stream debris.
5. DHP then opens the sample kit, extracts the shoulder-length gloves, allowing the CHP to take them out and put them on.
6. DHP then extracts the bag containing the class 100 clean vinyl gloves and opens it, allowing the CHP to take them out and put them on over the shoulder-length gloves.
7. Next, the DHP removes the syringe package from the kit and opens it. The CHP now takes the syringe out of the package, fills it up with ambient water from about 0.2 meters below the surface, places the tip of it into the adaptor and wastes downstream (to rinse syringe). 1X rinse.
8. Next, the DHP takes out and opens the filter package. The CHP then removes the filter and adaptor. At the first site, the adaptor is fitted onto the capsule filter on the syringe side (so the syringe will fit into it snugly; note the flow arrow on the filter and hook the adaptor up to the inlet). The adaptor remains on the filter for the duration of the survey.
9. CHP then fills it up with stream water from about 0.2 meters below the surface, places the tip of it into the adaptor and empties it into the filter to waste downstream. Do this 4X (~250 mls) to thoroughly rinse the filter with site stream water. (Do not allow the filter to contact any unclean surfaces).
10. Next the DHP takes the sample bottle from the kit and opens it without touching the inside. The cap is held in one hand (without touching the inside) and is capped in-between successive additions.
11. The CHP now draws multiple syringes of water (always from about 0.2 meters below the surface) to filter site water into the open bottle held by DHP. They continue to do this until about 400-500 mls. is collected. Be careful not to drip any unfiltered stream water from gloves, etc into the sample bottle!
12. The DHP then caps the sample bottle and places it into the plastic kit bag.



13. After sample collection, the re-usable filter must be purged of sample water. First, CHP pushes air through the filter using the syringe until the filter flow stops. Then, DHP removes the 500 ml bottle of DI water from the kit and opens it. CHP fills the syringe with DI water and pushes it thru the filter. This is done 4X (~250 mls.) to rinse the filter thoroughly. Finally, CHP pushes air through the filter again (using the syringe) until the filter flow stops.
14. CHP places the rinsed and emptied capsule filter into its original bag in the kit bag. This filter can filter large volumes of water and is re-used at successive sites (following thorough rinsing and purging).
15. At the next site, the gloved DHP opens the kit bag from the previous site, removes the bag containing the used filter and places it into the new kit.
16. Repeat above steps at all sites. If filter becomes clogged or malfunctions, use a spare filter.

#### **10.0 Sample Handling, Preservation, and Storage**

1. All samples are placed in clean plastic bags in wet ice (4 deg. C) and delivered to WES within 24 hours (next day).
2. Preservation of samples with conc. HNO<sub>3</sub> can be done immediately after sampling, continuing with the "dirty hands/clean hands" technique, OR at the lab within 48 hours from collection.



## **Alternative Field Sampling Protocol #2b** (same as Protocol#2, and adapted for lake sampling)

General equipment and supplies needed for TOTAL and DISSOLVED metals sampling include:

- Spare new disk/capsule filters in sealed plastic bag; spare new 60 ml syringe in the original packaging in a clean sealed plastic bag; spare sampling kits
- A box of regular powder-free gloves, and a box of shoulder length polyethylene gloves
- Sealable clean plastic bags to hold filled sample bottles in ice chests
- Spare DI/RO water in 4 liter glass jug (for rinsing and field blanks)
- One clean “metals” ice chest with ice for samples (and one clean “metals” cooler to hold dry materials)
- One clean Van Dorn (VD) sampling bottle (w/ no direct metal contacting sample water)

### **TOTAL METALS**

#### **Sampling Kit:**

One TOTAL METALS sampling kit per sample. They will be assembled in the lab ahead of time by a handler wearing gloves. Each kit will consist of the following items placed inside new, clean plastic bags.

- One 500 ml pre-cleaned, certified-clean bottle per site
- One pair of “powder free” Class 100 clean room vinyl gloves in clean plastic bag

#### **Sample Collection for TOTAL METALS**

Sample will be collected generally using a clean-hands---dirty-hands (CH/DH) type procedure. The specific procedure is as follows.

1. Sampling is done in teams of two. The person taking the sample is designated the “clean hands” person (CHP), and the assistant is designated the “dirty hands” person (DHP).
2. The DHP dons regular powder-free gloves and grabs a sampling kit. CHP dons shoulder-length PE gloves from box of gloves in plastic zip-bag. DHP opens the sample kit (without touching the inside), allowing the CHP to take and put on the class 100 clean vinyl gloves (over the shoulder-length gloves).
3. Next, the DHP opens the kit and CHP removes the sample bottle.
  - A. Manual Method (surface samples only): CHP inserts the capped bottle below the surface and then uncaps about 6-12” below the surface to fill the bottle. CHP caps bottle below the surface tightly. Above the surface, CHP immediately removes cap briefly to pour off 5-10 mls for headspace.
  - B. Van Dorn Method (any depth): DHP uses a clean/rinsed Van Dorn sampling bottle to collect a sample at the desired depth (any depth from 6” below the surface to 18” off the bottom), then opens the valve and lets the sample flow out/overboard. After a few seconds, CHP uncaps sample bottle (holding cap) and places bottle below the flow to collect sample, leaving approx. 1” headspace. Cap tightly.
  - C. Reserved.
4. DHP opens the 2 gallon plastic bag from the cooler and CHP inserts the filled sample bottle into the bag.
5. DHP places the plastic bag back into the 4 deg. C cooler for delivery to WES within 24 hours (next day).
6. Preservation of samples with conc. HNO<sub>3</sub> is performed using clean technique (preferably in a Class 100 clean room) at the lab within 24 hours from collection.



**Alternative Field Sampling Protocol #2b (continued)**  
(same as Protocol#2, and adapted for lake sampling)

## **DISSOLVED METALS**

### **Sampling Kit:**

One DISSOLVED METALS sampling kit per sample. They will be assembled in the lab ahead of time by a handler wearing gloves. Each kit will consist of the following items placed inside new, clean plastic bags.

- One 500 ml pre-cleaned, certified-clean bottle per site
- One pair of “powder free” shoulder length polyethylene gloves
- One pair of “powder free” class 100 clean room vinyl gloves in clean plastic bag
- One new 60 ml syringe in the original packaging
- One 0.45 micron high capacity disk or capsule filter in a clean sealed plastic bag. This filter can be used for multiple samples at the same site as long as CH/DH is used, or a new kit can be used (e.g., field duplicates).

### **Sample Collection for DISSOLVED METALS:**

Sample will be collected using a clean-hands---dirty-hands (CH/DH) type procedure. The specific procedure is as follows.

1. Sampling is done in teams of two. The person taking the sample is designated the “clean hands” person (CHP), and the assistant is designated the “dirty hands” person (DHP). The CHP is not to touch anything except the syringe and filter, until sampling is complete. CHP dons shoulder-length PE gloves from box of gloves in plastic zip-bag. The DHP dons regular powder-free gloves, then opens the sample kit (without touching the inside), allowing the CHP to take and put on the class 100 clean vinyl gloves (over the shoulder-length gloves).
2. Next, the DHP removes the syringe package from the kit and opens it (without touching the syringe itself). The CHP now takes the syringe out of the package, fills it up with ambient water from about 3-6” below the surface, inserts plunger and wastes to other side of boat to rinse syringe. 2-3 rinses.
3. Next, the DHP removes the filter package from the kit bag and opens the filter package (w/o touching). The CHP then removes the filter and holds it.
4. Samples are then collected as follows, depending on method chosen.
  - A. Manual Method (surface samples only): CHP then collects ambient lake water from about 3-6” below the surface, inserts filter and wastes approx. 20 mls. thru the filter. DHP retrieves sample bottle, and opens (holding cap). Following the filter waste, CHP directs filtrate into bottle being careful not to drip any unfiltered lake water from gloves into the sample bottle. CHP repeats water collection and filtering using the syringe/filter assembly until the required sample volume (200-240 mls) is reached. DHP can cap bottle in-between fills.
  - B. Van Dorn Method (any depth): DHP retrieves sample bottle, and places capped bottle in a clamp firmly attached to the boat. DHP uses Van Dorn (VD) sampler to collect sample water in the VD at desired depth. The 1<sup>st</sup> volume is wasted to other side of the boat (including a rinse of the outflow tube). DHP then collects the VD sample at desired depth. After collection, DHP opens VD air valve to dispense sample water into the syringe/filter assembly (via the outflow tube) held by CHP. DHP then removes the cap on the sample bottle in the clamp (holding cap). CHP wastes approx. 20 mls. thru the filter, then directs the filtrate into sample bottle. The syringe is filled again and the water filtered into the sample bottle until the required sample volume (200-240 mls) is reached. DHP can cap bottle in-between fills.
5. The DHP then caps the sample bottle and places it into the plastic cooler bag, and into the cooler. Sample are delivered to WES within 24 hours (next day), where they are preserved with conc. HNO<sub>3</sub> using clean technique (preferably in a Class 100 clean room) at the lab within 24 hours from collection. NOTE: If desired, filters can be reused as needed for field duplicates and sample replicates from the same sampling station (and at different depths if pre-rinsed), depending on study needs. In general, a new filter should be used for each new station.





## Alternative Field Sampling Protocol #2c

(generally consistent with EPA-NE's SOP, but tailored for use by DWM/WES)

*CH/DH=Clean hands-Dirty Hands technique*

### 7.0 Equipment and Supplies:

7.1 One sampling kit per sample. These will be assembled in the lab ahead of time using CH/DH approach. Each kit will consist of the following items placed inside new, clean plastic bags.

- One 250 ml pre-cleaned, certified-clean bottle per site ("DUP" kits will contain 2 bottles per kit)
- One pair of "powder free" shoulder length polyethylene gloves
- One pair of "powder free" vinyl gloves in clean plastic bag
- One new 60 ml syringe
- One new high-volume capsule filter (preferred) or disk filter
- One barb adaptor (for use with capsule filters)

For field work, you will also need: **TAKE TO STREAM IF IN BOLD**

- A **bag containing a box of new vinyl gloves** (for dirty-hands to glove up)
- A bag of new large disk filters (in case the site is very clear, in which case the disk filter can be used in place of the more expensive capsule filter).
- A bag of spare sampling kits (if you need an extra item, take it from a spare kit)
- **DI water in new 500 ml sample container (for field blank)**
- One clean "metals"-only cooler to hold dry materials
- A bag of sealable clean plastic bags to hold filled sample bottles in ice chests
- A wet-ice chest for preserving/storing samples
- General equipment: Site logbooks, indelible marker, waterproof pen, field data sheets, chain of custody forms, chest waders with belt, hip boots, etc.

### 8.0 Pre-sampling Prep [in the lab]:

- 8.1 Determine the number of samples (including QC samples) to be taken and prepare bottle labels, COC. fieldsheets, etc.
- 8.2 To affix labels before site work (optional), remove sample bottle(s) from each kit bag to affix survey-specific bottle OWMID labels, with CH (gloves), then replace bottle(s) inside kit bag. Sharpie-label kit bags with site#, OWMID# or other.
- 8.3 QC samples: field dups @ ~10-20% of total; field filter blanks @ one per crew; trip blanks @ one per project (at a minimum)

### 9.0 Sample Collection for Dissolved Metals

**NOTE:** Aluminum criteria are defined as total metal. Except for special cases, total metals samples will generally not be collected due to resource limitations (it would double the sample load to the lab). So, in cases where dissolved aluminum results are less than the criteria, it will not be known if the total aluminum meet or exceed the criteria. If dissolved aluminum results exceed the criteria, however, then it is assumed that total aluminum would also have exceeded the criteria.

Dissolved metals samples will be collected using a CH-DH type procedure.

- 9.1 Sampling is done in teams of two. The person taking the sample is designated the "clean hands" person (CHP), and the assistant is designated the "dirty hands" person (DHP). The CHP is not to touch anything except the syringe, filter, and adaptor until sampling is complete.
- 9.2 If the metals sampling crew is also involved in other site activities, SAMPLE FOR METALS USING CH/DH FIRST, PRIOR TO OTHER ACTIVITIES.
- 9.3 Immediately before entering the water to collect the sample, the DHP dons regular powder-free gloves contained in a sealed bag. DHP carries the plastic bag sampling kit containing items that are needed.



- 9.4 Approach the sampling location slowly from the downstream to upstream direction. Once you have reached the sampling location allow the water to return to a pre-disturbed condition. Avoid contacting the syringe with the bottom or adjacent rocks and stream debris.
- 9.5 DHP then opens the sample kit, extracts the shoulder-length gloves, allowing the CHP to put them on.
- 9.6 DHP then extracts the bag containing the new vinyl gloves and opens it, allowing the CHP to take them out and put them on over the shoulder-length gloves.
- 9.7 Next, the CHP removes the syringe from the kit (DH opens the package if needed, since some syringes are plastic-wrapped), and fills the syringe with ambient water from about 0.2 meters below the surface, and wastes downstream (to rinse syringe). **2-3 X rinse.**
- 9.8 Next, the DHP takes out and opens the new capsule filter package. The CHP then removes the filter and the adaptor. The adaptor is screwed onto the capsule filter on the syringe side (so the syringe will fit into it snugly; note the flow arrow on the filter and hook the adaptor up to the filter inlet side---opposite the flow direction). *NOTE: at very clean sites, samplers may elect to use a large disk filter (from a separate plastic bag), in lieu of the more expensive capsule filter.*
- 9.9 CHP then fills the syringe with stream water from about 2-4 inches below the surface, places the tip of it into the adaptor and empties the syringe contents into the filter (wasted downstream). **Do this 3-4X (~150-200 mls) to thoroughly rinse the filter with site stream water.** (Do not allow the filter to contact any unclean surfaces).
- 9.10 Next the DHP takes the sample bottle from the kit and opens it without touching the inside. The cap is held in one hand (without touching the inside of the cap) and the bottle is capped in-between successive additions. Prior to collecting the sample, rinse inside of sample bottle 1-2X with filtered site water. CHP draws water into the syringe, attaches to filter and filters site water into the open bottle held by DHP. DHP caps, shakes, uncaps and discharges the rinsate downstream.
- 9.11 The CHP now draws multiple syringes of water from about 2-4 inches below the surface to filter site water into the open bottle held by DHP. Continue to do this until about 200-225 mls. is collected. Be careful not to drip any unfiltered stream water from gloves, etc into the sample bottle! After sufficient volume has been collected, DHP caps the sample bottle and places it into the plastic kit bag.
- 9.12 For QC duplicates, use the same capsule filter to fill the duplicate bottle. Collect field blanks as equipment blanks by collecting water from the DIW bottle using the syringe and filtering into the field blank bottle.
- 9.13 All waste plastic, including the syringe and filter, is placed in a separate, used plastic bag for later disposal. The adaptors, however, are placed in a "Used Adaptors" bottle and are retained for later cleaning.
- 9.14 At the vehicle, dry bottle and affix OWMID# label (if not already affixed beforehand). Place the sample bottle(s) in the designated plastic bag in the cooler (separate from the other, loose bottles). Repeat above steps at all sites.

## 10.0 Sample Handling, Preservation, and Storage

- 10.1 All samples are placed in clean plastic bags in wet ice (4 deg. C) and delivered to the WES or EPA lab within 48 hours (next day) for acidification. Alternatively, samples can be acidified at the DWM lab within 48 hours, then delivered to the analytical lab.
- 10.2 For DWM acidification, use CH/DH to dispense 0.3 ml of conc. HNO<sub>3</sub> OR 1 ml of 1:1 HNO<sub>3</sub> per ~200 ml sample, via micropipetter and one disposable pipette tip per survey batch of samples. Perform preservation in a hood to minimize contamination potential. CH protects hands with neoprene gloves. See also Appendix G.



### Alternative Field Sampling Protocol #3

When sample contamination risks require the use of extraordinary steps to minimize contamination, metals sampling (including “Clean Hands (CH)-Dirty Hands (DH)” procedure and the use of a portable chamber) can be performed as follows.

It is assumed that all samples shall be taken to the Wall Experiment Station (WES) for analysis. Samples collected in the field will be transported on ice (4 deg. C.) and preserved at the WES lab (not in the field). Different procedures are used depending on what type of ambient samples and QC samples are desired. (See “V” below)

- A. Construct portable glove box; disassemble and place all parts in a clean double-plastic bag (at DWM)
- B. Acid-Washing of Containers (as necessary if non-pre-cleaned and/or non-certified bottles are used): Clean the required number of used/non-certified glass bottles and glass DI water jugs using dilute (5%) trace-grade HNO<sub>3</sub>. At WES’s “clean” work area, fill 500 ml bottles with DIW  $\frac{3}{4}$  full and then dispense 20 mls. concentrated trace-grade HNO<sub>3</sub> into each bottle to make a 5% HNO<sub>3</sub> solution (v/v). Store for 24-72 hours until needed for samples. Alternatively, after 24-72 hours, rinse 3X with DIW, and then fill with Type I DIW and store until used (at WES).
- C. Sample Bottle Preparation & Labeling: Based on the sampling design/QAPP, label all new, pre-cleaned and/or acid-washed bottles with DWM and WES sample ID #s. First, rinse the outsides of the bottles by removing (four at a time) from the original box and placing in the designated plastic wash basket, rinsing the outsides of the bottles thoroughly with DIW, and then, using CH, placing in the DWM “clean” fume hood (turned “ON”). Allow the bottles to completely dry at the DWM “clean” hood (Captair ductless filtration hood). When dry, affix completed labels, using CH, to each bottle. Place containers in labeled, double-plastic-bags and place in the designated “clean” cooler #1 (at DWM).
- D. Using CH, fill cleaned glass jugs with Type I DIW for use in taking ambient field blanks (at DWM). Also, fill sample bottle trip blanks, if taken. Put all blank water containers in new, clean double-plastic bags. (at DWM)
- E. Assemble all survey equipment, materials and staff and conduct equipment/material inventory, using CH for any sample container/bottle contact (at DWM)
- F. Using demonstration materials, perform a complete “dry run” of “clean hands-dirty hands” field procedures as they will be executed in the field for the particular survey, with one-two persons designated “clean hands” and one person “dirty hands”. This is especially needed for the first few surveys of the year where exact field procedures have not been actually practiced (at DWM)
- G. Notify the WES lab of sample delivery schedule (at DWM)
- H. Fill out Fieldsheets and COCs to the maximum amount possible to minimize that required in the field (at DWM)
- I. Prior to departure, fill “clean” cooler #2 with cube ice (at DWM)
- J. Site Selection: A protected work area that is hard, flat, out of the wind, on the ground and away from vehicles and metal objects is desirable for sample processing. The closer to the river/stream shore, the better for rapid field filtration. Proper site and sample collection point selection is critical to ensure sample representativeness and to support the assumption of complete lateral and vertical mixing (see 8.2.1) (on-site)
- K. Upon arrival at each site, CH constructs the portable PVC “glove box” (on a clean flat surface (30”x30” untreated plywood can be used) using a new translucent plastic bag and places new, un-opened items needed for filtration inside. Orient the box with its back to the wind.



- L. Prior to CH/DH metals sampling, sample for and take field measurements for other analytes (e.g. pH, temp., turbidity, TSS, etc.). DH takes notebook notes as appropriate and fills out site-specific fieldsheet. (on-site).
- M. All sampling personnel must put on clean gloves and hats before commencing sample collection activity, with "clean hands" donning shoulder-length disposable polyethylene gloves and "dirty hands" putting on PVC gloves (on-site).
- N. Because mercury analysis is usually desired, CH puts on a new, white "hazmat" suit. "Clean hands" also puts his/her waterproof boots on at this time (if CH takes sample). A protective suit for DH is optional (DH needs to keep away from samples as much as possible to minimize the risk of contamination), especially in hot weather conditions. (on-site).
- O. CH should replace disposable polyethylene gloves at this time. (on-site)
- P. DH readies the sample worksheet and opens the outer bags for sample bottle retrieval by CH. DH checks off samples on the worksheet as they are taken and makes sample notes as appropriate (e.g. sample times). (on-site). CH puts all sample bottles to be used at the site inside the glove box.
- Q. Retrieval/insertion of clean bottles and equipment (general): DH opens the equipment cooler to retrieve/open the double-bagged sample bottles and washed equipment from storage, and unzips the outer bag. CH opens the inside bag containing the sample bottles, syringes, filters, etc., removes/inserts items as needed, and reseals the inner bag. DH then reseals the outer bag. (on-site)
- R. Acid-wash solution disposal (as necessary): With safety glasses on, CH pours the dilute HNO<sub>3</sub> from the container into a waste-acid jug (uncapped/capped by DH) carefully, rinses the container insides thoroughly with DIW 3 times, then uses container as needed.
- S. Trip/Bottle Blanks: DH removes the double-plastic-bag containing the trip blank (if any) from Cooler #1 and places the bag on ice in Cooler #2.
- T. Taking river/stream samples: Because of the need for chest/hip waders and to keep CH as "clean" as possible, DH dons disposable gloves (double-gloved PE) and enters the water for a wade-in grab sample using a 4 l DIW rinsed amber glass jug (see W below). But first, take blank QC sample(s).
- U. Ambient blank sampling (total recoverable): See Q above. CH removes a sample bottle and DIW jug (and reseals the inside bags). CH unscrews the sample bottle cap and, while holding the cap upside down, discards the dilute acid or DIW (if any) from the bottle into a carboy/jug for waste-acid/wastewater (cap removed/replaced by DH). CH then uncaps the DIW jug and holds the cap while DH holds bottom of jug and pours DIW into sample bottle (held by CH) 3X for rinsing (capped and shaken). After rinsing, DH pours DIW into sample bottle held by CH for the "total recoverable metals" ambient blank sample. CH caps the bottles and places the sample bottle back into the inner bag.
- V. Ambient blank sampling (dissolved): See Q above. CH prepares the filtration apparatus (use one capsule filter and one syringe per site (blanks and samples), unless problems arise; use a filter adaptor if available attached to the syringe). CH removes a sample bottle (and reseals the inside bags). CH unscrews the sample bottle cap and, while holding the cap upside down, discards the dilute acid or DIW (if any) from the bottle into a carboy/jug for waste-acid/wastewater (cap removed/replaced by DH). CH then uncaps the DIW jug and holds the cap while DH holds bottom of jug and pours DIW into sample bottle (held by CH) 3X for rinsing (capped and shaken). After rinsing, CH caps the sample bottle (inside the glove box) sets up the filtration apparatus (syringe with capsule filter), removes and holds the sample bottle cap while DH pours approx. 50 mls. of DIW at a time from the jug into the syringe for about 10-12 times until the desired sample volume of about 450-475 mls is attained. The syringe plunger is used to push the water through the 0.45 u capsule filter into the sample bottle. At least 150 mls is initially filtered and wasted to rinse filter media (filter retention is approx. 120 mls prior to flow-through). Care is taken not to drip any unfiltered water into the sample bottle, and to only touch the top of the syringe during use. Once the desired volume is reached in the sample bottle, the sample bottle cap is replaced by CH and



placed in the inner bag by CH. The filter assembly is reused for other station blanks and same-station dissolved samples. (on-site)

- W. **Ambient river samples (total recoverable and dissolved):** *See J, O and R above. CH readies all bottles to be used and places inside the "glove box" as needed prior to grab sampling.* DH enters the river/stream in a downstream-to-upstream direction, with minimal disturbance, and samples looking upstream and standing downstream of sample bottles. DH (with double-gloved PE) carries capped sample bottles (for duplicates), a clean, large volume container (for splits), or a syringe (for integrated or time-composited samples). DH waits for any bottom disturbance to dissipate prior to sample collection. The sample container(s) is uncapped underneath the water surface and partially filled at a depth of 3-6 inches below the surface for rinsing (fill 1/4 full---replace cap underwater---lift out of water---shake contents---uncap---empty contents downstream---recap---and repeat). Again, DH attains a position looking upstream and waits for any disturbance to dissipate (minimum 1 minute). DH then uncaps underwater and allows them to fill with sample water at about 3-6 inches below the surface. After the bottle has filled (i.e., when no more bubbles appear), and while the bottle is still submerged, DH replaces the cap(s) of the bottles underwater. In this way, the sample water has never contacted the air. DH delivers the sample(s) to shore ASAP for the taking of samples for total recoverable and dissolved metals (with DH as the pourer and CH working the filtration unit and holding sample bottles). Grab sampling employing the split sampling procedures outlined below (intra-laboratory or inter-laboratory splits) is preferred, but other methods can be employed. Splits allow comparisons of total recoverable concentrations and the dissolved fractions using the same sample, in addition to providing quality control data (i.e. precision estimates).

**Total recoverable (split-sampling):** DH dons new clean gloves. Work with samples is performed inside or near the opening of the glove box. CH retrieves the appropriate sample bottles from the inner bag(s) and places inside the "glove box". For each sample, CH removes the sample container cap and each sample bottle cap, holding them or placing in a clean plastic baggie, as DH pours from the large volume container into the sample bottle. Swirl-rinse split sample bottles 3X as above, then take each sample as follows: Fill splits 1/3 full, swirl large container; fill 2/3 full, swirl large container; fill to 3/3 full with some head space. Cap each sample and container. Place samples in inner bag and proceed ASAP to take filtered samples using large container sample water. Place all finished samples in cooler ice to 4 deg. C. ASAP.

**Dissolved (split-sampling):** DH dons new clean gloves. DH opens the filter capsule and syringe packages and CH reaches in to get each item. CH uncaps the appropriate sample bottle caps inside the "glove box" and holds the caps. DH swirls sample container for successive 50-60 ml pours into the syringe throughout the filtration process. CH plunges one pour through the filter into one split and plunges the succeeding pour into the second split until the desired sample volume (450-475 mls) is reached in each split. In this way, splits are filtered at the same time. At least 150 mls is initially filtered and wasted to rinse filter media with sample water and dispense remnant DIW in filter capsule. Care is taken not to drip any unfiltered water into the sample bottle, and to only touch the top of the syringe during use. Once the desired volume is reached in the sample bottles, the sample bottle caps are replaced by CH and placed in the inner bag by CH. A second CH person may be used to facilitate more rapid filtration. DH places the spent large volume sample container and cap into a "waste" plastic bag. The capsule filter assembly is reused for other station replicates. Once handling is completed, samples are double-plastic bagged and placed in ice to 4 deg. C. ASAP (on-site).

**Total Recoverable and Dissolved (co-located&simultaneous (or sequential) duplicate sampling):** As in total recoverable and dissolved above, but using two separate sample bottles, side-by-side at the same time (or sequential). Co-located duplicates can be used to estimate overall precision (two of the same---total or dissolved), or to compare total/dissolved concentrations (by using one duplicate for total recoverable and one for dissolved). The exact field protocols for this type of sampling is consistent with that outlined above, but should be worked at CH and DH together prior to sampling.





**Total Recoverable and Dissolved (space-time integrated sampling):** The dissolved procedure involves taking ambient sample water directly from the river/stream with the sampling syringe. Multiple 50-60 ml. draws over several minutes are filtered for one dissolved sample. Total recoverable samples can be taken in a similar fashion over time and/or space. More complicated, integrated sampling techniques can also be employed using depth-integrated samplers or by flow- or width-compositing.

**Field Acidification (optional):** Although not required by EPA Method 1669, samples can be acidified in the field using 1 ml. of concentrated ultra-trace-grade HNO<sub>3</sub> (“Ultrex”, “Optima”) per 500 ml sample. This procedure can be done consistent with the approach outlined above, but must be specifically worked out by CH and DH prior to sampling. Use of this procedure requires greater attention to safety (i.e safety glasses, proper acid storage and use, waste disposal, etc.)

- X. **For non-metal analyte sampling:** Once all metals samples have been taken (or prior to, see L above), CH and/or DH can proceed to take grab samples for other analytes, such as TSS and the use of portable field instruments (e.g. for pH, D.O., temperature, turbidity and specific conductance). (on-site).
- Y. Once sample handling is completed and all samples are on ice in coolers, CH disassembles portable glove box and re-bags the plastic pieces, discarding the large plastic frame bag to the “waste” bag. DH assists in clean-up to prepare for the next site (without touching anything that will come into contact with samples). (on-site).
- Z. Both proceed to the next sampling site and perform similarly. (on-site).





## **Alternative Field Sampling Protocol #4**

### **Clean-Hands/Dirty-Hands Dissolved Metals Sampling Using Peristaltic Pump**

Reserved.





## APPENDIX B

### Bottle Type/Specifications, Preservation Methods & Holding Times

Group Designation	M	C
<b>Analytes Groups</b>	<b>Metals</b>	<b>Hardness</b>
<b>Analyte/Method</b>	Hg (EPA245.1)	Ca (ICP) SM3120B (EPA200.7)
<b>Analyte/Method</b>	Ag, Al, As, Be, Cd, Cr, Cu, Ni, Pb, Sb, Se, Tl, Zn (EPA200.8)	Mg (ICP) SM3120B (EPA200.7)
<b>Analyte/Method</b>	Fe, Ca, Mg (EPA200.7)	
<b>Bottle Type</b>	500-1000 ml NM/WM HDPE Teflon-lined caps; pre-cleaned; (flouropoly or borosilicate glass for Hg-only)	Same as for metals bottles
<b>Preservative</b>	1:1 HNO <sub>3</sub> (at the lab <24 hours) Field-filtered for diss. metals	Same as for metals bottles
<b>Holding Time</b>	6 months (Cr <sup>+6</sup> - 24 hr) (Hg -28 day)	6 months



## **APPENDIX C**

### **Certificates of Analysis for “Optima” HNO<sub>3</sub> reagent, sample bottles and capsule filters**

INCLUDED BY REFERENCE AND AVAILABLE AS STAND-ALONE DOCUMENTS AT DWM QA OFFICE.



## I-CHEM<sup>TM</sup> Brand Products

A Division of Chase Scientific Glass, Inc.

## CERTIFICATE OF ANALYSIS



PRODUCTION NUMBER : 036636



Item Number: 313-0250

Item Description: BOTTLE HDPE NM CR  
Group 1 is applicable

\*This is your Certificate of Analysis for I-CHEM Certified<sup>TM</sup> product which has been prepared in accordance with I-CHEM Performance-Based Specifications. This product meets or exceeds analyte specifications established in the U.S. EPA "Specification and Guidance for Contaminant-free Sample Containers" for use in Superfund and other hazardous waste programs.

### Group 1. Glass and HDPE/LDPE Sample containers for use in the analysis of Metals

Analyte	Detection Limit (µg/L)	Analyte	Detection Limit (µg/L)	Analyte	Detection Limit (µg/L)	Analyte	Detection Limit (µg/L)
Aluminum	<80	Calcium (all HDPE)	<100	Magnesium	<100	Selenium	<2
Antimony	<5	Chromium	<10	Manganese	<10	Silver	<5
Arsenic	<2	Cobalt	<10	Mercury	<0.2	Sodium	<500
Barium	<20	Copper	<10	Nickel	<20	Sodium (all HDPE)	<100
Beryllium	<0.5	Iron	<50	Potassium	<750	Thallium	<5
Cadmium	<1	Lead	<2	Potassium (all HDPE)	<100	Vanadium	<10
Calcium	<500					Zinc	<10

### In addition to the above analytes, NALGENE® containers are certified for these analytes:

Analyte	Detection Limit (µg/L)	Analyte	Detection Limit (µg/L)	Analyte	Detection Limit (µg/L)	Analyte	Detection Limit (µg/L)
Chloride	<100	Fluoride	<20	Nitrite	<50	Sulfate	<100
Cyanide	<10	Nitrate	<20	Paraquat (amber only)	<0.4	Sulfide	<30
Diquat (amber only)	<1.0					Sulfite	<1000

### Group 2. Glass Sample Containers for use in the analysis of Semivolatiles and Pesticides/PCBs

Compound	Quantitation Limit (µg/L)	Compound	Quantitation Limit (µg/L)	Compound	Quantitation Limit (µg/L)
Acenaphthene	<5	Acenaphthylene	<5	Anthracene	<5
Benzo(a)anthracene	<5	Benzo(a)pyrene	<5	Benzo(b)fluoranthene	<5
Benzo(k)fluoranthene	<5	Benzo(g,h,i)perylene	<5	Benzoic Acid	<20
Benzyl Alcohol	<5	4-Bromophenyl-phenylether	<5	Butylbenzylphthalate	<5
4-Chloroaniline	<5	4-Chloro-3-methylphenol	<5	bis-(2-Chloroethoxy) methane	<5
bis-(2-Chloroethyl)ether	<5	bis-(2-Chloroisopropyl)ether	<5	2-Chloronaphthalene	<5
2-Chlorophenol	<5	4-Chlorophenyl-phenylether	<5	Chrysene	<5
Di-n-butylphthalate	<5	Di-n-octylphthalate	<5	Dibenzo(a,h)anthracene	<5
Dibenzofuran	<5	1,2-Dichlorobenzene	<5	1,4-Dichlorobenzene	<5
1,3-Dichlorobenzene	<5	3,3'-Dichlorobenzidine	<5	2,4-Dichlorophenol	<5
Diethylphthalate	<5	Dimethylphthalate	<5	2,4-Dinitrotoluene	<5
4,6-Dinitro-2-methylphenol	<20	2,4-Dinitrophenol	<20	Fluoranthene	<5
2,6-Dinitrotoluene	<5	bis-(2-Ethylhexyl)phthalate	<5	Hexachlorobutadiene	<5
Fluorene	<5	Hexachlorobenzene	<5	Indeno(1,2,3-cd)pyrene	<5
Hexachlorocyclopentadiene	<5	Hexachloroethane	<5	2-Methylphenol	<5
Isophorone	<5	2-Methylnaphthalene	<5	3-Nitroaniline	<20
4-Methylphenol	<5	2-Nitroaniline	<20	N-Nitrosodimethylamine	<5
4-Nitroaniline	<20	N-Nitroso-di-n-propylamine	<5	Nitrobenzene	<5
N-Nitrosodiphenylamine	<5	Naphthalene	<5	Pentachlorophenol	<20
2-Nitrophenol	<5	4-Nitrophenol	<20	Pyrene	<5
Phenanthrene	<5	Phenol	<5	2,4,6-Trichlorophenol	<5
1,2,4-Trichlorobenzene	<5	2,4,5-Trichlorophenol	<20	Aldrin	<0.01
Azobenzene	<5	Carbazole	<5	Alpha-BHC	<0.01
4,4-DDD	<0.02	Endosulfan II	<0.02	Beta-BHC	<0.01
4,4-DDE	<0.02	Endosulfan Sulfate	<0.02	Delta-BHC	<0.01
4,4-DDT	<0.02	Endrin	<0.02	Gamma-BHC	<0.01
Dieldrin	<0.02	Endrin Aldehyde	<0.02	Heptachlor Epoxide	<0.01
Endosulfan I	<0.01	Heptachlor	<0.01	Alpha-Chlordane	<0.01
Methoxychlor	<0.10	Endrin Ketone	<0.02	Aroclor-1016	<0.20
Gamma-Chlordane	<0.01	Toxaphene	<0.30	Aroclor-1242	<0.20
Aroclor-1221	<0.20	Aroclor-1232	<0.20	Aroclor-1260	<0.20
Aroclor-1248	<0.20	Aroclor-1254	<0.20	2,4-Dimethylphenol	<5
Aroclor-1262	<0.20	Aroclor-1268	<0.20		

### Group 3. Glass Sample Containers for use in the analysis of Volatiles

Compound	Quantitation Limit (µg/L)	Compound	Quantitation Limit (µg/L)	Compound	Quantitation Limit (µg/L)
Acetone	<5	1,3-Dichloropropane	<1	Benzene	<1
2,2-Dichloropropane	<1	Bromobenzene	<1	1,2-Dichloropropane	<1
Bromodichloromethane	<1	trans-1,3-Dichloropropene	<1	Bromoform	<1
cis-1,3-Dichloropropene	<1	Bromomethane	<1	1,1-Dichloropropene	<1
2-Butanone	<5	Ethylbenzene	<1	tert-Butylbenzene	<1
Hexachlorobutadiene	<1	sec-Butylbenzene	<1	2-Hexanone	<5
n-Butylbenzene	<1	Isopropylbenzene	<1	Carbon Disulfide	<1
p-Isopropyltoluene	<1	Carbon Tetrachloride	<1	4-Methyl-2-pentanone	<5
Chlorobenzene	<1	Methylene Chloride	<2	Chloroethane	<1
Naphthalene	<1	Chloroform	<1	n-Propylbenzene	<1
Chloromethane	<1	Styrene	<1	2 & 4 Chlorotoluene	<1
1,1,2,2-Tetrachloroethane	<1	1,2-Dibromo-3-chloropropane	<1	Tetrachloroethene	<1
Dibromochloromethane	<1	Toluene	<1	1,2-Dibromoethane (EDB)	<1
1,2,3-Trichlorobenzene	<1	Dibromomethane	<1	1,2,4-Trichlorobenzene	<1
1,4-Dichlorobenzene	<1	1,1,2-Trichloroethane	<1	1,3-Dichlorobenzene	<1
1,1,1-Trichloroethane	<1	1,2-Dichlorobenzene	<1	Trichloroethene	<1
Dichlorodifluoromethane	<1	Trichlorofluoromethane	<1	1,2-Dichloroethane	<1
1,2,2-Trichloroethane	<1				



## Disposable Capsule Filters



### Geotech dispos-a-filter™ Filter Capsule Specifications

Micron size.....	0.45, 1.0, 5.0, 10.0
Effective Filter Area.....	700 cm <sup>2</sup> , (High Capacity)
	350 cm <sup>2</sup> , (Medium Capacity)
	20 cm <sup>2</sup> , (Low Capacity)
Thickness.....	191 µm
Tensile strength.....	3000 PSI
Void volume.....	>80%
Extractables (boiling water).....	<3%
Water flow (ASTM:F-317-72)	
(ml/min/cm2 @ 10 psi).....	4
Bubble point (ASTM: F-316-80)	
Kerosene (psi).....	11
Water (PSI).....	23
Versapor filter membrane.....	White acrylic copolymer coating over a nonwoven substrate
Maximum operating temperature.....	190°F (88° C)



In-line filtration using the Geotech Hand Pump, pressurized bailer and dispos-a-filter™

### CERTIFICATION

Rest assured, our dispos-a-filters are certified to exhibit non-detectable levels when a metals analysis is performed on their effluent using ICAP, ICP-MS or GFAA instrumentation. In a Class 100 clean room, ICP-MS instrumentation was used to perform a NEW certification of metals (see list below). All manufactured lots are tested using an independent laboratory using EPA-approved test methods.

Element	LOD (µg/L) (ppb)	Element	LOD (µg/L) (ppb)	Element	LOD (µg/L) (ppb)	Element	LOD (µg/L) (ppb)
Aluminum (Al)	0.2	Gallium (Ga)	0.04	Osmium (Os)	0.02	Thallium (Tl)	0.05
Antimony (Sb)	0.02	Germanium (Ge)	0.05	Palladium (Pd)	0.06	Thorium (Th)	0.02
Arsenic (As)	0.2	Gold (Au)	0.05	Platinum (Pt)	0.08	Thulium (Tm)	0.01
Barium (Ba)	0.01	Hafnium (Hf)	0.03	Potassium (K)	25	Tin (Sn)	0.2
Beryllium (Be)	0.04	Holmium (Ho)	0.01	Praseodymium (Pr)	0.01	Titanium (Ti)	0.05
Bismuth (Bi)	0.04	Indium (In)	0.02	Rhenium (Re)	0.06	Tungston (W)	0.2
Boron (B)	2	Iridium (Ir)	0.06	Rhodium (Rh)	0.02	Uranium (U)	0.02
Cadmium (Cd)	0.03	Iron (Fe)	1	Rubidium (Rb)	0.1	Vanadium (V)	0.03
Calcium (Ca)	25	Lanthanum (La)	0.01	Ruthenium (Ru)	0.05	Ytterbium (Yb)	0.03
Cerium (Ce)	0.01	Lead (Pb)	0.05	Samarium (Sm)	0.04	Yttrium (Y)	0.02
Cesium (Cs)	0.02	Lithium (Li)	0.03	Scandium (Sc)	0.2	Zinc (Zn)	1
Chromium (Cr)	0.03	Lutetium (Lu)	0.01	Selenium (Se)	7	Zirconium (Zr)	0.05
Cobalt (Co)	0.02	Magnesium (Mg)	10	Silicon (Si)	0.5	Chloride (Cl)	50
Copper (Cu)	0.5	Manganese (Mn)	0.03	Silver (Ag)	0.03	Sulfate (So4)	10
Dysprosium (Dy)	0.04	Mercury (Hg)	0.05	Sodium (Na)	25	Flouride (F)	2
Erbium (Er)	0.02	Molybdenum (Mo)	0.05	Strontium (Sr)	0.01	Nitrite (NO2)	10
Europium (Eu)	0.02	Neodymium (Nd)	0.02	Tantalum (Ta)	0.02	Bromide (Br)	5
Gadolinium (Gd)	0.04	Nickel (Ni)	0.5	Tellurium (Te)	0.04	Nitrate (NO3)	10
		Niobium (Nb)	0.02	Terbium (Tb)	0.02	Phosphate (HPO)	5

\*LOD: Limits of Detection (ppb)

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## CERTIFICATE OF ANALYSIS

### FISHER OPTIMA™ NITRIC ACID

ATOMIC NUMBER	ELEMENT	VALUE (in ppt)	ATOMIC NUMBER	ELEMENT	VALUE (in ppt)
13	Aluminum	<20	60	Neodymium	<0.05
51	Antimony	<10	28	Nickel	<20
33	Arsenic	<10	41	Niobium	<1
56	Barium	<1	46	Palladium	<10
4	Beryllium	<5	78	Platinum	<1
83	Bismuth	<0.1	19	Potassium	<10
5	Boron	<50	59	Praseodymium	<0.05
48	Cadmium	<1	75	Rhenium	<1
20	Calcium	<20	45	Rhodium	<1
58	Cerium	<0.05	37	Rubidium	<1
55	Cesium	<0.05	44	Ruthenium	<10
24	Chromium	<10	62	Samarium	<0.01
27	Cobalt	<1	21	Scandium	<1
29	Copper	<5	34	Selenium	<20
66	Dysprosium	<0.01	47	Silver	<2
68	Erbium	<0.01	11	Sodium	<10
63	Europium	<0.01	38	Strontium	<1
64	Gadolinium	<0.01	73	Tantalum	<10
31	Gallium	<1	52	Tellurium	<5
32	Germanium	<1	65	Terbium	<0.01
79	Gold	<10	81	Thallium	<0.1
72	Hafnium	<0.05	90	Thorium	<0.05
67	Holmium	<0.01	69	Thulium	<0.01
49	Indium	<1	50	Tin	<20
26	Iron	<20	22	Titanium	<10
57	Lanthanum	<0.05	74	Tungsten	<5
82	Lead	<1	92	Uranium	<0.01
3	Lithium	<1	23	Vanadium	<1
71	Lutetium	<0.01	70	Ytterbium	<0.01
12	Magnesium	<5	39	Yttrium	<1
25	Manganese	<2	30	Zinc	<5
80	Mercury	<100	40	Zirconium	<1
42	Molybdenum	<10			

SEE REVERSE SIDE FOR MORE DETAILED INFORMATION

Lot Number: 1201060





## **APPENDIX D**

### **WES Method SOPs (and MDLs/RLs)**

INCLUDED BY REFERENCE AND AVAILABLE AS STAND-ALONE DOCUMENTS AT WES.



### Laboratory Method Detection Limits and Reporting Limits (as of 2007):

For metals analysis (EPA 200.8), the following reporting limits have been added for ICP-MS and ICP at EPA's lab and ICP-MS at WES.

	EPA		WES
Analyte	ICP RL (ug/l)	ICP-MS RL (ug/l)	ICP-MS RL (ug/l)
Ag	4.0	0.2	0.9
Al	110	5	50
As	20	0.5	1.5
Be	8	0.5	0.6
Ca	110	100	0.60 (200.7)
Cd	10	0.1	0.5
Cr	20	0.5	0.8
Cu	20	0.2	0.6
Fe	40	50	---
Hg			0.5 (245.1)
Mg	100	100	0.03 (200.7)
Ni	20	0.2	0.5
Pb	20	0.2	0.5
Sb	10	0.5	0.5
Se	20	1.0	8.0
Tl	20	0.5	0.5
Zn	20	5.0	0.9





## APPENDIX E

### Field Equipment Checklist (depends on protocol used)

*Note: The following list includes all items for all alternative protocols. Use of individual protocols will require a sub-set of those listed. **Protocol 2c shaded/bolded***

#### Laboratory (sample receipt and handling, washing):

1. Trace Metal Grade HNO<sub>3</sub> (for acid-washing as necessary)
2. Ultra-trace grade HNO<sub>3</sub> preservation ampoules (if used)
3. Ultra-trace grade ("Optima") HNO<sub>3</sub> preservative and reagent
4. Clean bench/hood

#### Field Sampling:

1. Portable glove box (2'x2'x2' ½ inch PVC frame with disposable 48"x48" translucent/clear plastic bags) with plywood board support
2. Large "clean" coolers (2), one with kits, extra gloves, field blank water, etc. and one with wet ice
3. New (and extra) disposable, sealable plastic bags (12"x 18") and large plastic bags
4. Amber glass sample bottles (500 ml.) and DIW/sampling container jugs (4 l), both pre-labeled
5. Extra sample kits
6. Plastic syringes (60 ml. or greater) with adaptors
7. 0.45u Supor capsule filters
8. White "Hazmat" jump suits
9. Extra Disposable sampling gloves (assorted, inc. shoulder length PE)
10. Sample bottle labels, COC forms, fieldsheets
11. Misc. analyte sample bottles (e.g. HDPE, 1 l) for other (e.g. TSS)
12. Field and Lab SOPs, and QAPP (on-hand)
13. Waste acid container (if needed)
14. Field Kit (including First Aid Kit)
15. Chest waders, hip waders, knee boots
16. Large traffic cone
17. Maps, vehicle book, station directions, GPS, camera, phone, etc.
18. Field probes (e.g. pH, turbidity, temperature)
19. DIW for field blanks (in sample container(s))
20. Trip blank (if necessary)
21. Food, change of clothes, hats
22. Large plastic tarp
23. Large umbrella (if rain)
24. Suitable vehicle (two large coolers must fit inside vehicle; 4-door sedans, x-tra cab trucks and vans can be used. Do not put coolers in uncovered truck beds.)
25. Kim Wipes box and/or paper towels
26. Binoculars (to read distant staff gages as needed)
27. Pre-calls to landowner(s) as needed



## **APPENDIX F: Hardness-Dependent CCC/CMC Calculator**

[CN 101.5 - SOP\\_Metals Criteria Calculations.xls](#)

(DWM network access)



## Appendix G

### Preservation of Metals Samples at DWM-Worcester Lab

- 1) Sample preservation requires 2 persons. CH and DH must wear PPE (safety glasses, lab coat, gloves) as appropriate.
- 2) Place the following items in the 229 Fume Hood for use:
  - a. Conc. HNO<sub>3</sub> ampoule OR 1:1 HNO<sub>3</sub>
  - b. Box of pipette tips
  - c. Finnpiquette
  - d. Neoprene gloves (e.g., Black “Marigold” gloves in lab)
  - e. Box of nitrile gloves
- 3) Turn ON outside vent (switch in Room 228)
- 4) Remove samples from fridge and place near the hood. Also, remove any acetone in the 229 hood to the flammables cabinet temporarily.
- 5) At the fume hood (Light ON, Vent OFF, since there is no filter for acid vapor), CH dons black neoprene gloves, then another pair of nitrile gloves over them. NOTE: Although not used as a fume hood per say, the Room 229 fume hood is a good lab bench work area and less busy than the one in Room 228.
- 6) CH removes cap on HNO<sub>3</sub> ampoule, then loads a pipette tip
- 7) DH uncaps each sample and places it into the hood, then removes his/her hand from the area.
- 8) CH pipettes 300 ul of conc. HNO<sub>3</sub> OR 1 ml of 1:1 HNO<sub>3</sub> from container into 200-250 ml sample. If air bubbles, dispense back into ampoule and re-try.
- 9) DH then caps sample.
- 10) REPEAT FOR EACH SAMPLE.
- 11) Place un-used acid and used pipette tip into a HAZ WASTE container for temporary storage at the satellite haz waste storage tray in Room 229.
- 12) Complete sample preservation log to document samples have been acidified. Bottle caps can also be labelled with an “A”.
- 13) Place sample back into fridge. Amend COC forms as needed to indicate sample preservation.
- 14) Remove all metals sample preservation materials from the 229 fume hood to the designated storage area until needed again (e.g., 228 fume hood for storage). NOTE: 229 hood is used mainly for acetone handling---acetone and nitric acid are not compatible.