Trace Metal and Mercury Sampling Methods for Lake Michigan Tributaries

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Revision 2

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1.0 Bottle Labeling and Supply Sorting

Prior to boat deployment, all sample bottles must be selected, labeled, and sorted into a cooler for easy access during sampling. Consult the master sampling plan, and/or specific instructions for a given sampling trip to determine what samples should be obtained. Remove the requisite number of Teflon Sampling Bottles from each of the Trace Metal and Mercury Bottle storage containers. With a black Sharpie label the outer bag with the site code, date, and type of sample (unfiltered, filtered, replicate, blank, spike, etc.). Record this same information on the Field Data Sheet, which is to be consulted during the sampling process to prevent mixup of sample bottles and bags. A sample bottle label can be affixed to the outer bag *after* sampling is completed. Remove a 1000 mL poly bottle from the storage bag and using a black Sharpie label it as a SPM/DOC Trace Metal Composite, and with site code.

The following sampling supplies should also be placed into the cooler for transport:

1. Calyx Filters
2. Pump Head Tubing
3. Trace Metal Acidification Kit
4. Mercury Acidification Supplies (Acid and Vials)
5. Bagged Wrench

The 1 gallon tubing rinse container must be filled full with 2% HNO_3 from the 20 L carboy and then placed into the egg crate for use on the boat.

2.0 Boat Deployment and Anchoring

The Boston Whaler must always be transported with cover intact. Periodically wash cover in a manual car wash to prevent build-up of contaminants.

The inside surfaces of the Boston Whaler should have been rinsed after completion of previous sampling (see clean-up), if not, rinse them now before loading and launching.

Position equipment containers into the Boston Whaler in a manner which will minimize reorganization out on the river. Review equipment checklist to verify that all necessary supplies have been loaded. Prior to launching, all required (consult sample bottle manifest) sample

bottles should be organized and labeled (see above).

Anchor Boston Whaler at sampling site (above centroid of river) using two anchors, bow and stern. The bow anchor line is threaded through metal eye and tied-off on port cleat. Transport anchors, especially bow anchor, in plastic bags. Upon completion of sampling, thoroughly wash anchors with river water before bringing on-board, and place directly into plastic bags to avoid muddying up the boat.

3.0 Set-Up

Steps 3.1-3.3 may be performed without clean suits.

3.1 Equipment Organization

Position tubs, and other sampling equipment in appropriate locations in boat.

3.2 Boom Installation

Hook fiberglass cleat adaptor into place on bow cleat. Remove plastic protective bags (place in bag container) from bow sampling boom and put boom in place by resting in fiberglass cleat adaptor, hooking straight end under bungie cord, and securing boom in fiberglass cleat by tieing with an arm-length glove.

3.3 Sampling Platform - Pump Installation

Wrap a large PE bag over the starboard gunnels of the boat. Hook the plexiglass sampling platform over the gunnels on top of the plastic bag. Insert the canopy frame into the sampling platform. Place a plastic bag over the canopy frame, and secure with split tubing clamps. Attach power cord to Geo-pump, wrap pump with an arm-length glove, and set into sampling platform. Run power cord to stern of boat and attach to pump battery.

4.0 Sampling

Clean Suits and Gloves Must Be Worn For All The Following Steps.

4.1 Lowering Tubing Line

Open plastic cartons containing sampling line and kevlar support rope. Tie kevlar rope to loop of Teflon string attached to sampling-line

weight. (The end of the rope is two feet above sampling intake). Slowly and carefully begin removing lower end of sampling line (i.e. Teflon weight end) from plastic bag (use extreme caution to avoid kinking and contamination), insert weight through receptacle on end of boom and lower into river to first depth (0.2 x River Depth). Secure kevlar support rope onto starboard plastic cleat. Keep remainder of sampling line tubing in plastic bag until pump head tubing is attached.

Note: Rope is marked in one foot increments - beginning six inches from the end. Use the six inches to tie off to Teflon string. The distance from sampling ports to top of Teflon string is two feet. A double line is marked every five feet, and a triple line is marked every 10 feet.

To drop the sampling line to the lower depth, the kevlar rope is un-cleated, and both rope and Teflon sampling line slowly let out to (0.8 x River Depth). It is usually necessary to uncouple Sampling Line from pump-head tubing before lowering line. Clean-hands uncouples and re-couples sampling line from pump-head tubing.

4.2 Geo-Pump Loading and Sample Line Connection

Load pump-head tubing into Geo-Pump using clean protocol. {Gloved dirty hands opens pump head clamp lever and holds outer bag of pump-head tubing, while gloved clean hands removes inner bag and loop of tubing. Clean hands inserts closed tubing loop into pump head and dirty hands closes clamp lever making sure that tubing is properly positioned. Dirty hands makes sure that Teflon Tubing Adaptor Fitting (TTAF) and plexiglass clamp ring (PCR) are ready. At this point dirty hands re-gloves, and retrieves open end of sampling line from storage bag, while clean hands opens pump head tubing loop. Dirty hands gives clean hands sampling line who inserts it into pump head tubing. Dirty hands collects TTAF bag and opens outer bag, while clean hands opens inner bag and removes TTAF and tightly inserts it into the long end of the pump head tubing. The TTAF bags should be kept in the sample transport cooler during sampling (inner bag is always kept inside dirty outer bag. Dirty hands, with new gloves, collects PCR from storage bag, removes PCR, and holds it while clean hands inserts TTAF into PCR. Dirty hands then inserts assembly into groove in sampling platform. The PCR bag should also be kept in the cooler during sampling to minimize contamination and prevent it from being blown away.

4.3 Sample Collection

Place the appropriate sample bottles into the plastic sample organizing container using the following protocol. The outer bags should have been previously labeled with site and sample type information. The outer bags are removed using clean techniques and sample bottles with inner bag are placed in the organizing container. Dirty hands (with new gloves) retrieves appropriate double bagged Teflon sample bottle and opens outer bag. Clean hands (with new gloves) pulls inner-bag out of outer bag and places single-bagged bottles in the organizing container. Outer bags are stowed in the sample transport cooler, out of the wind.

The typical sampling sequence will be:

[1] 250 mL Unfiltered sample for Trace Metals
[2] 500 mL Unfiltered sample for Mercury
[3] 125 mL Unfiltered sample for Methyl Mercury (see Note)
[4] 1000 mL Unfiltered sample for SPM and DOC
[5] 250 mL Filtered sample for Trace Metals
[6] 500 mL Filtered sample for Mercury
[7] 125 mL Filtered sample for Methyl Mercury (see Note)

Filling each bottle ½ full.

Note: For Methyl Mercury; Sheboygan, Manistique, Pere Marquette, and Grand rivers only.

This sequence will be repeated at the lower depth (except that filtered samples will be collected first) to fill the remaining ½ of bottle and then samples are acidified, and double-bagged.

4.3.1 Upper Depth

4.3.1.1 Unfiltered Sample Collection

Dirty hands starts Geo-pump and adjusts to moderately high speed to flush lines (Verify that water flow is correct, through platform hole, and not splashing sides). Sampling lines are flushed for a minimum of five minutes before unfiltered samples are collected.

Sample Bottle Handling: Clean hands (with new gloves) pulls appropriate bottle out of inner-bag leaving inner-bag in organizing container.

Trace Metal Sample Collection: Teflon bottles are supplied empty and dry. Clean hands reaches under water stream and partially ( ) fills bottle. The bottle is loosely capped and gently shaken to rinse. This process is repeated for a total of three bottle rinses. On the fourth collection the bottle is filled ½ full. *Do Not Touch Bottle Mouth To TTAF Or Any Other Surface*. Clean hands then returns sample bottle to inner-bag in organizing container. The bags do not have to be sealed at this point. Dirty hands removes and replaces organizing container lid during sampling.

Mercury Sample Collection: Teflon bottles are supplied filled with dilute HCl. Clean hands dumps acid into waste container. *Do Not Touch Bottle Mouth To Waste Container Or Any Other Surface*. Clean hands reaches under water stream and partially ( ) fills bottle. The bottle is loosely capped and gently shaken to rinse. This process is repeated for a total of four bottle rinses. On the fifth collection the bottle is filled ½ full. Clean hands then returns sample bottle to inner-bag in organizing container. The bags do not have to be sealed at this point.

SPM - Carbon Sample Collection: One-Liter polyethylene bottles are supplied empty and dry. Clean hands reaches under water stream and partially fills bottle. The bottle is loosely capped and gently shaken to rinse. This process is repeated for a total of three bottle rinses. On the fourth collection the bottle is filled ½ full. Clean hands re-gloves after handling the poly bottle.

4.3.1.2 Filtered Sample Collection

After all unfiltered samples are obtained from the upper depth, dirty hands reduces pump speed and then shuts off pump. Dirty hands re-gloves, retrieves a bagged Calex filter, and opens outer bag. Clean hands opens inner bag, removes filter capsule, opens vents, and drains off storage MQ into river (The filter bags may be discarded - the filter capsule is a disposable, single-site use, item). Dirty hands removes PCL/TTAF assembly from sampling platform, and clean hands uncouples TTAF and screws filter capsule onto TTAF. Clean hands inserts filter capsule into support on sampling platform. Dirty hands starts Geo-pump and adjusts to moderate speed to flush capsule (Verify that water flow is correct,

through platform hole, and not splashing sides). The filter capsule is flushed for five minutes or approx. 3 L before filtered samples are collected. At this point Filtered Trace Metal samples and Filtered Mercury samples are collected in an identical manner to Unfiltered samples as described above. To minimize the potential for filter clogging, dirty hands shuts off pump after each rinse or sample has been obtained. Upon completion of Filtered sample collection from the upper depth, clean hands un-couples Teflon sampling line from pump-head tubing and dirty hands lowers tubing to 0.8 depth. When at depth, the sample tubing line is then reattached to the pump-head tubing using the clean technique.

4.3.2 Lower Depth

The collection process is identical to that described above for Upper Depth, except that obviously ½ full bottles are not rinsed and filtered samples are collected first. The protocol for flushing and equilibration of sampling line and filter is similar to Upper Depth, except that here one is flushing the line and filter as a unit. Flushing as a unit for five minutes should not present a problem except under conditions of very high suspended solids levels. If during Upper Depth sampling or early stages of Lower Depth flushing, significant reduction of sample flow rate through the filter is noted, do the following to minimize filter clogging. Uncouple filter capsule from the TTAF and flush the sample tubing line for the full five minutes. While tubing is flushing, drain the river water from the capsule filter. After tubing is flushed, connect to drained filter and flush filter for 90 seconds. Clean techniques must be followed. Bottles are filled to near capacity, leaving space for preservation acid. After each sample bottle is filled, and before re-bagging, preservation acid is added to the sample.

4.4 Acidification

4.4.1 Trace Metal Sample Acidification (250 mL Sample Bottles)

Acid (50% Ultrex HNO_3) is supplied pre-measured in small Teflon Vials, one for each sample. Acid transfer to the sample must be quantitative. Dirty hands (with new gloves) retrieves the bag containing acid vials and opens it. Clean hands reaches in and removes a vial. Dirty hands wrenches open the vial while clean hands holds it. Clean hands then removes vial cap and pours acid into sample bottle which should be available and loosely capped on work surface. Used acid vials are re-capped and placed into a designated Zip-bag, to be returned to Water Chemistry Lab along with metal samples. Note the acid batch number on the field data sheet. The acidified sample is ready to be double-bagged using clean-hands protocol after the cap is wrenched tight. Clean hands holds bottle tightly while dirty-hands takes a double-bagged channel-lock pliers to cap. Clean-hands twists bottle to secure cap. Place new bags on the wrench before use at each site, and during a sampling period if the bags appear worn.

4.4.2 Mercury Sample Acidification (500 mL Sample Bottles)

Acid (50% HCl) is supplied in a 250 mL double-bagged Teflon bottle. Also supplied is a Teflon measuring vial into which acid is poured to measure out 10 mL aliquots. Before starting the acidification process, verify that the samples to be acidified are

organized on the clean work surface, and that their bottle caps are loose. Dirty-hands retrieves acid bottle and opens outer bag. Clean hands opens inner bag and removes Teflon acid bottle, setting it on plastic covered work surface. Dirty-hands retrieves Teflon measuring vial and opens outer bag. Clean hands opens inner bag and removes vial. Temporarily place acid and vial bags (inner bag inside outer bag) in the sample organization box. Clean hands pours acid into the vial up to the etched line and then quickly pours contained volume into the sample bottle. *Do not let acid measuring vial touch lip of sample bottle*. Clean-hands - dirty-hands procedures are then used to wrench shut and double-bag sample bottles, and to double bag acid bottle and measuring vial.

Do not acidify 125 mL methyl Hg bottles.

Verify that Everything Has Been Recorded and that Bags are Labeled.

5.0 Clean-up

5.1 Tubing-Line and Weight

Upon completion of lower depth sampling, the sampling line and support line are retrieved by slowly pulling on the Kevlar line (Dirty-hands person) while the clean-hands person coils the tubing into the storage bag. The sample line tubing should be un-coupled from the pump-tubing before retrieval so that the river water drains out. Untie the support line and seal in storage box. The weight and tubing must be flushed with dilute acid to prevent cross-contamination and to prevent contaminant build-up. A dilute acid solution is supplied in a 1 gallon PE bottle. Before inserting the tubing weight into the acid bottle, wipe the top outer surfaces of the weight with a clean-room wiper. Insert the tubing weight into the acid bottle, connect the free end of the sampling line to the pump-head tubing, and flush at moderate-high pump speed. Pump until all of the acid solution has flushed through the tubing, and then continue pumping until a majority of the tubing has been pumped dry (you may have to lift the tubing weight out of the acid jar to ensure that the tubing pumps dry). Remove the weight from the acid bottle, place in a *new* plastic bag, and wipe the top outer surfaces with a new clean room wiper. Recoil the tubing, tie with an arm length glove, and place in plastic bag. Store in dedicated storage container. Tubing will be periodically resupplied from the Water Chemistry Lab.

5.2 Sampling Platform

Calex filter is discarded.
Rinse PCL and TTAF with MQ, double-bag using clean techniques, and place in tubing storage container. (The TTAF fittings should be periodically returned to Madison along with samples for more rigorous cleaning).
Canopy bag is discarded.
Platform is rinsed with MQ and wiped with clean-room wipers.

Canopy frame and platform are bagged and placed in rubbermaid container.

5.3 Boom

Bagged in two large PE bags.
Fiberglass cleat adaptor is bagged and stored in supplies container.

5.4 Anchors and Anchor Line

Any sediment on anchors or line is washed off in the river before bringing into the boat. When anchor is clean, remove from water and place directly into a plastic bag.

5.5 Boat Rinsing

The inside surfaces of the boat must be rinsed with water after sampling is completed. If simple flushing with water is not sufficient to remove grime, then use the supplied brush to loosen dirt.

6.0 Additional Trace Metal (Non-Hg) QC Procedures

6.1 Trip Bottle Blank

With every batch of bottles a field bottle blank is created. The bottle blank is a 250 mL Teflon bottle, prepared identically to the sample bottles, except that before double-bagging it is filled with MQ water in the lab. This bottle travels to the field along with the sample bottles (In the field keep this bottle in the QC sample container). The bottle blank is to be acidified in the field with the same pre-measured acid vials as supplied for the samples. Soon after receipt of a batch of samples bottles, include the associated bottle blank with the set of sample bottles that are taken out in the boat. Handle the bottle/sample using clean techniques, and acidify in an identical manner as described for actual samples. Send bottle blank immediately back to Madison along with samples from that site.

6.2 Analyte Spiking

At a frequency of approximately 10% (see master sampling schedule), duplicate un-filtered and filtered river water samples, as well as a MQ water blank will be spiked with an acidified solution of the analytes of concern. The MQ water blank for spike addition (Blank Spike) and spiking solutions are kept in the QC sample container. The large 6 mL vials are used for the *un-filtered* river water, and the small 3 mL vials are used for the *filtered* river water and *MQ blank*. These vials contain sufficient acid to properly stabilize the sample - Do Not Acidify Again with Normal Acid Vials. The spike addition must be quantitative. The procedure is to simply collect sequential duplicate un-filtered and filtered samples in the standard 250 mL Teflon bottles using clean protocols (i.e. fill an additional 250 mL bottle for the un-filtered spike and an additional 250 mL Teflon bottle for the filtered spike *at the same time* you are collecting normal filtered and un-filtered samples. Composite 0.2 and 0.8 as usual). It is important for the duplicate samples to be as similar as possible These samples along with the Blank Spike MQ bottle are then acidified in the boat using clean techniques with the spiked acid solution in place of the normal acid. Send the three spiked samples back to Madison along with other samples from that site.

7.0 Field Blanking Procedure

Field blanking is performed to estimate the level of metal contamination from the sample tubing line, filter cartridge, and general handling of the sampling apparatus. In addition these blanks are used as field diagnostic tools, and to generate method detection limits.

The field blank kit consists of the following gear:

1 5000 mL Teflon bottle filled with Milli-Q water.
1 3000 mL Teflon bottle filled with Milli-Q water.
3 250 mL Teflon bottles for trace metal samples.
3 500 mL Teflon bottles for mercury samples.
Short length (3 ft) of Teflon Tubing.
Zip-lock bags for 5 L bottle caps.
Plastic bags.

Blank collection will follow the sequence:

Source Water.
Filter Blank.
Tubing Blank.

Please perform the blanking procedure *before* beginning normal sampling.

Trace Metal Clean Procedures Must be Followed.

[1] Label three sets (250 mL trace metal, 500 mL mercury) of bottles as follows:

Source Water Filter Blank Tubing Blank
Record bottle numbers and type on field data sheets.

[2] Set up filtration platform as usual. Install a new section of pump head tubing in peri-pump. Attach TTAF and lock in PCL. Uncouple tubing weight from sample line.

[3] Remove Teflon cap/insert from 5 L bottle, place caps in zip-lock bag. Insert short length of Teflon tubing into bottle and connect other end to pump head tubing in peri-pump. Place a plastic bag over 5 L bottle to isolate during blanking procedure.

[4] Flush approx. 500 mL of blank water through pump head tubing. Collect Source Water samples as per protocol, with appropriate number of rinses. Conserve water! Shut off peri-pump when not collecting samples or flushing.

[5] Remove Teflon tubing from 5 L bottle and place into 3 L bottle (Rinse MQ). Connect a filter cartridge to TTAF and lock into holder. Flush approx. 1500 mL of Rinse MQ through filter cartridge. Place tubing back into 5 L blank water bottle and collect

Filter Blank samples as per protocol.

[6] Remove filter cartridge (save for later use). Uncouple short Teflon line - rebag. Insert one end of sampling line into 3 L bottle, connect other end to peri-pump. Flush approx. 1500 mL of Rinse MQ through line. Place sample tubing line into 5 L blank water bottle and collect Tubing Blank samples as per protocol.

[7] Acidify samples as per protocol.

[8] Cap 3 L and 5 L bottle. Place samples bottles, 3 and 5 L bottles, short Teflon tubing in Blank Kit Cooler and return to Water Chemistry in Madison.

[9] Re-couple tubing weight to sample line (Fasten Securely).

8.0 Equipment List

[1] Plastic bow boom packaged in two large PE bags.
[2] Fiberglass boom cleat adaptor.
[3] Rubbermaid carton for plastic bags.
[4] Rubbermaid carton containing plexiglass sampling platform and canopy.
[5] Geo-pump and power cord.
[6] Deep-discharge battery in plexiglass case for running peri-pump.
[7] Rubbermaid container with kevlar support line (50 feet - marked in increments of one foot).
[8] Rubbermaid container with Teflon sampling line, Teflon sampling weight.
[9] Plastic container with insert to secure and organize sample bottles.
[10] Sampling Supplies.

a. Teflon sample bottles
b. Pump-head tubing (Double-bagged)
c. Teflon fitting for end of sampling line (TTAF)
d. Plexiglass clamp ring (PCR)
e. Calex Filter capsules
f. Acidification supplies
g. Double-bagged channel-locks
h. Arm-length gloves
i. Wrist-length gloves

[11] Dilute acid solution in 1 gallon container.

Electric Motor
Motor Battery
Oars
Two Plastic Coated Anchors with poly- line

Trace Metal Field Quality Assurance Plan Summary - 1994 and 1995

Sample Type	QAPjP Frequency	1994 Accomp.	1995 Goal	1995 # Samples	Comments
Field Replicates	15-20%	25 (13.7%) U 21 (11.5%) F	15% U 15% F	40 U 40 F	
Analyte Spike Sample Matrix	10%	18 (9.8%) U 18 (9.8%) F	10% U 10% F	27 U 27 F	
Analyte Spike Blank Matrix	5%	21 (4.7%)	2.5%	15	one every other bottle batch (20)
Field Bottle Blank	5%	23 (5.1%)	5%	30	one every bottle batch (20)
Filter Blank	2.5%	5 (1.1%)	2%	12	four per team
Tubing Blank	2.5%	5 (1.1%)	2%	12	four per team
Lab Bottle Blank	5%	28 (6.2%)	5%	30	one every bottle batch (20)

Replicate and spike percentages given as a percent of site visits (183 in 1994).
Blank percentages are expressed as a percent of non-blank samples (449 in 1994).

1995 QA samples based on 271 site visits (Jan- Nov) and 596 non-blank samples.

Trace Metal Field Quality Assurance Plan Summary - 1995

Site	Replicates				Spikes				Large Me-Hg Bottle Site Count
	Spring Runoff	Summer Event	Baseflow	3	Spring Runoff	Summer Event	Baseflow	3	
Manistique	1	0	1	2	1	0	1	2	
Menominee	1	2	1	4	1	0	1	2	
Fox	1	2	1	4	1	1	1	3	

Sheboygan	1	2	2	5	1	0	1	2	
Milwaukee	1	2	2	5	1	1	1	3	
Grand Cal.	1	0	1	2	1	0	1	2	
St. Joseph	1	1	2	4	1	1	1	3	
Kalamazoo	1	2	2	5	1	1	1	3	
Grand	1	2	2	5	1	1	1	3	
Muskegon	1	0	1	2	1	0	1	2	
P. Marquette	1	0	1	2	1	0	1	2	
3	11	13	15	40	11	5	11	27	

1. Replicates and Spikes are obtained from both Unfiltered and Filtered Samples. Hg samples are not spiked in the field.

2. Field Bottle Blanks are sent with each batch of 20 bottles and should be acidified as soon as possible and returned to lab.

3. Field Spike Blanks are sent with every other batch of 20 bottles and should be spiked when performing a sample spike.

4. The Blanking Kit (Filter and Tubing Blanks) will be rotated between field teams, and must be performed as soon as possible in order that each team can obtain four method blanks over the study year.

5. One 250 mL Teflon MeHg bottle must be substituted for one of the unfiltered or filtered 125 mL MeHg bottles every 5th site visit. Site visits can be recorded in MeHg site count column.

Trace Metal Sample Treatment Summary

Sample Type	Bottle Size	Treatment
Routine Field Sample		
-Unfiltered	250 mL	contents (3 mL) of one *acidification* vial
-Filtered	250 mL	contents (3 mL) of one *acidification* vial
Field Bottle Blank		
-milli-Q	250 mL	contents (3 mL) of one *acidification* vial
Field Sample Spike		
-Unfiltered	250 mL	contents (3 mL) of one *large spiking* vial
-Filtered	250 mL	contents (2 mL) of one *small spiking* vial
Field Blank Spike		
-milli-Q	250 mL	contents (2 mL) of one *small spiking* vial
Blank Kit		
-Feed Water	250 mL	contents (3 mL) of one *acidification* vial
-Filter Blank	250 mL	contents (3 mL) of one *acidification* vial
-Line Blank	250 mL	contents (3 mL) of one *acidification* vial

Field Acidification vials are packaged in zip-lock bags labeled Field Acidification Solution, Lot #FS95##. All vials are the large 6 mL capacity.

Field Spiking vials are packaged in zip-lock bags labeled as follows:

a. Unfiltered (or Total) Sample Spiking Solution, Lot #SPU95##. All vials are the large 6 mL capacity.

b. Filtered Sample Spiking Solution, Lot #SPF95##. All vials are the small 3 mL capacity. Both the Unfiltered and Filtered Spiking Solutions contain sufficient acid to stabilize the samples. *Do not* use an acidification vial in addition to spiking solution. Please do not interchange spiking solutions - they are designed for a specific matrix.

Field Bottle Blanks should be acidified in the boat in a manner identical to routine field samples, and returned to the lab within two to three weeks of receipt.

Field Blank Spikes should be spiked at the same time as sample spikes. If you have scheduled a sample spike and a blank spike bottle exists - spike it. Return to lab as soon as possible.

Field Sampling QA Final Project (1994-1995) Accounting

Blank Accounting

Source	QC Sample Type	Number of Samples	Percent of Non-Blank Samples (891)
Teflon Sample Bottle (prep. and sample storage)	Lab Bottle Blanks	56	6.3
Sample Bottle Handling in Field and Acidification	Field Bottle Blanks	54	6.1
Acidification Acid	Acid Batch Qualifier	14	Each Acid Batch
Filter	Dedicated Lab Study	----	----
Filter/Pump-Head Tubing and Filtering in Field	Field Filter Blanks	13	1.5
Pump-Head Tubing	Dedicated Lab Study	----	----
Field Sample Tubing	Field Tubing Blanks	13	1.5

	Number of Samples	Percent of Site Visits (356)
Recovery		
Field Analyte Spike (Blank Matrix)	41	4.6
Field Analyte Spike (Filtered Sample Matrix)	42	11.8
Field Analyte Spike (Unfiltered Sample Matrix)	42	11.8
Field Surrogate Spike (four rare metals in Sample)	1081	100
Precision		
Field Replicates (Filtered Sample Matrix)	46	12.9
Field Replicates (Unfiltered Sample Matrix)	50	14.0
Accuracy		
Interlab Studies (Prepared Samples)	3 studies	
Interlab Studies (Ambient Samples)	2 studies	

ICP-MS Batch Analysis QA Outline
15-18 Samples per Batch

Sample Type	Frequency
ICP-MS Qualification	
-Blank Levels	Before each sample batch
-Stability	Before each sample batch
-Sensitivity	Before each sample batch
-Resolution	Before each sample batch
-Interference Check	Once per week
Blanks Levels During Run	
Calibration Blank	One per batch
Check Blanks	Four per batch
Memory Check	One per batch
Recovery	
Lab Analyte Spike, Blank Matrix	One per batch
Lab Analyte Spike, Sample Matrix	Two per batch
Internal Standards, 3-metals	All samples
Precision	
Replicate Sample Acquisitions	Four per sample
Lab Sample Replicates (within batch)	Two per batch
Lab Sample Replicates (different batch)	20%
Accuracy	
Standard Reference Material (SLRS-3)	Three per batch
Laboratory Control Sample (Trib Matrix)	One per batch