ONONDAGA LAKE BASELINE MONITORING
BOOK 1
DEEP BASIN WATER AND ZOOPLANKTON MONITORING WORK PLAN FOR 2008

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INTRODUCTION

This work plan describes the samples and data to be collected during implementation of the deep basin water and zooplankton monitoring defined in the draft Baseline Monitoring Scoping Document for the Onondaga Lake Bottom Subsite (Parsons 2008). The work plan is comparable to the work plan for 2007 Deep Basin Water and Zooplankton Monitoring (UFI and SU, 2007b) approved by the New York State Department of Environmental Conservation (NYSDEC). This work plan describes sample locations, sample and data gathering methods, and sample analyses to be performed. A detailed description of the field and analytical methods and quality assurance program supporting the field work is described in the Quality Assurance Project Plan (QAPP), which is provided in Appendix B of this work plan. In subsequent years, it is anticipated that any changes to the field or analytical program described in this work plan will be documented by addenda to this work plan.

OBJECTIVES

As described in Section 3.0 of the Baseline Monitoring Scoping Document (Parsons 2008), the Baseline Monitoring Program for Onondaga Lake has three program objectives:

- establish a comprehensive description of baseline chemical conditions prior to remediation to assess remedy effectiveness and to facilitate remedy design;
- provide additional data for future understanding of remedy effectiveness in achieving PRGs; and
- provide habitat-related information.

Deep Basin Water Monitoring – Deep basin water monitoring is a component of water sampling, which is associated with the first objective. Deep basin water sampling supports three data uses as follows:

(1) provide basis to measure achievement of PRG3 (surface water quality standards);

(2) provide basis to measure success in controlling key processes (e.g., mercury methylation in the hypolimnion, sediment resuspension from the in-lake waste deposit, and mercury release from profundal sediment); and

(3) provide information on the generation of methylmercury in the hypolimnion for use in the design of nitrate addition/oxygenation pilot tests and basis to measure results.

With regard to the first data use, the only surface water quality standards for hazardous chemicals that were exceeded in previous years in the deep basin were the lowest mercury standards, specifically the New York State surface water quality standard for protection of wildlife (i.e., 2.6 nanograms per liter dissolved mercury) and the

standard for protection of human health [via fish consumption] (i.e., 0.7 nanograms per liter dissolved mercury). Consequently, deep basin water monitoring includes analysis of dissolved total mercury in a subset of samples.

Deep basin water monitoring supports the second data use by including analysis of methylmercury concentrations in the hypolimnion (i.e., a measure of mercury methylation), analysis of total mercury concentrations in the hypolimnion (i.e., a measure of mercury release from profundal sediment), and measurement of gas ebullition, which is a potential mechanism for mercury release from profundal sediment. The monitoring program described in this work plan is a continuation of 2006 and 2007 efforts (UFI and SU, 2007a: UFI and SU, 2007b).

The third data use supported by deep basin water monitoring necessitates analysis of mercury and redox parameters (i.e., oxygen, nitrate, sulfide) in the water column. The time period following oxygen depletion from when nitrate concentrations are low to after fall turnover is of particular interest because, based on 2006 and 2007 results, nitrate appears to limit methylmercury release from sediment at this time.

A fourth data use supported by water sampling (i.e., provide basis to establish goals for water quality during implementation of the remedy) will be addressed in a separate work plan currently being developed by the Dredging and Sediment Consolidation Area (SCA) Operations Technical Work Group. A scope for monitoring during implementation of the lake remedy has not yet been formulated, but it will likely include monitoring stations located near planned dredging/capping operations (near-field stations) and monitoring stations in SMU 8 (far-field stations).

Zooplankton Monitoring – Zooplankton monitoring is a component of other biota sampling (i.e., biota other than fish), which is associated with the second objective and specifically with assessing biological factors that may contribute to variations in fish mercury concentrations (see Section 4.7.1 in Parsons, 2008). Because the ROD specifies PRGs for fish mercury concentrations, achieving these concentrations will be a measure of remedy success; however, multiple factors beyond the scope of the remedy potentially influence fish mercury concentrations and will thus be evaluated in the monitoring program.

The primary data use for zooplankton sampling is to assess biological factors that may contribute to variability in fish mercury concentrations. Diet accounts for more than 90% of total methylmercury uptake in fish (Weiner et al. 2003). Mercury concentrations in and abundance of fish prey are therefore primary biological factors that affect fish mercury concentrations. Fish prey consists primarily of zooplankton, benthic macroinvertebrates, and prey fish. Methylmercury concentrations and community composition and abundance of each of these prey items are thus factors that influence fish mercury concentrations and are worthy of monitoring. This work plan (Book 1) addresses zooplankton monitoring and Book 2 addresses monitoring of benthic macroinvertebrates and prey fish.

FIELD COMPONENTS

The deep basin water column and zooplankton monitoring program described herein is partitioned into four components, water column, ebullition, *in situ/in vivo*, and zooplankton. The *in situ/in vivo* component will consist of profiles of total dissolved gas pressure (TDG) and spatially detailed monitoring with the ISUS rapid profiling instrument. A sampling schedule for the 2008 monitoring program is presented in Table 1. Sample locations and analyses for water column monitoring are summarized in Tables 2 and 3 and in Appendix A. *In situ* robotic measurements (dissolved oxygen, temperature, specific conductance, pH, fluorometric chlorophyll, and turbidity) will be made at one meter depth interval profiles at South Deep (Figure 1), at least daily during the April-November interval and, possibly, into December depending on weather.

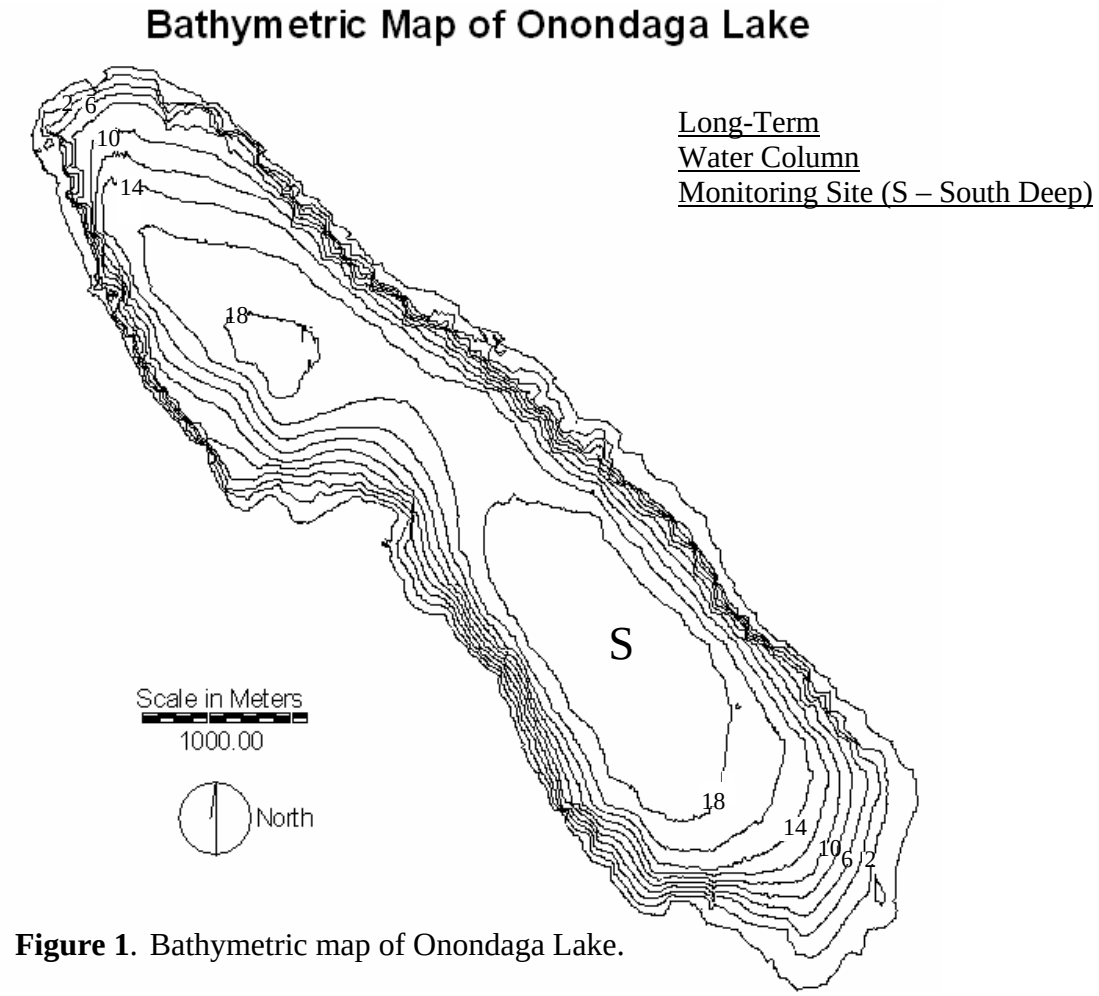

Figure 1. Bathymetric map of Onondaga Lake.

RATIONALE FOR STATION LOCATION, DEPTHS, FREQUENCY, AND PARAMETERS

The rationale for selection of station location, depths, frequency, and parameters is as follows:

Station Location – Water column and zooplankton monitoring will be conducted at South Deep, the long-term monitoring station used by both UFI and Onondaga County. Numerous studies, including data from the 2007 Nitrate Evaluation Study (UFI and SU, 2007b; see Appendix C), have indicated that South Deep is a representative station for water and zooplankton in the deep basins of Onondaga Lake. As was done in 2007, ebullition rates will be measured in both the north and south deep basins based on the 2006 data (Exponent, 2007), which showed greater variability between basins than within basins. *In situ/in vivo* monitoring is a rapid procedure and therefore involves multiple stations along a longitudinal transect and a lateral transect across the south basin.

Depths – Depths for water column monitoring were selected to provide a representative epilimnetic sample (2 m), a representative upper hypolimnetic sample (12 m), and a sample near the sediment-water interface (19 m). When the lake is stratified (typically July – October), samples will be collected at 16 m and 18 m to provide a gradient of concentrations from the sediment-water interface into the overlying water. Based on historical sampling, this region is where concentrations of mercury and electron acceptors change the most. In addition, 14 m water samples will be collected starting September 15, and 6 m water samples collected starting October 20. Sampling will continue into December for two weeks with water samples collected at 2, 6, 12, 14, and 19 m water depths on December 1 and 8, if field conditions allow samples to be collected on those dates. This plan will provide increased coverage during the critical fall turnover and post-turnover periods.

For filtered total mercury, samples will be collected at 2 m (i.e., the epilimnetic sample) because the purpose of the analysis is to compare to surface water quality standards based on protection of human health via fish consumption. The 2 m water depth represents water to which fish are exposed before and after stratification (when the water column is well-mixed) and during stratification when fish are confined to the epiliminion because of reduced oxygen concentrations in the hypolimnion. In addition, dissolved mercury samples will be collected at 14 m depth starting on September 15 through the end of the sampling. Gas ebullition measurements will be made in the deepest portions of the north and south basins. Because of rapid profiling capabilities, *in situ/in vivo* monitoring will occur at approximately 0.25 m intervals. The 13 m vertical tow for zooplankton sampling is sufficient to collect a representative sample of zooplankton in the epilimnion and upper hypolimnion.

Frequency – Timing for water column monitoring is designed to track conditions less frequently (biweekly) prior to the depletion of nitrate (April – July) and more frequently (weekly) starting when nitrate concentrations are depleted but not at zero and

continuing through fall turnover (August – mid-December). Samples for dissolved total mercury will be collected biweekly throughout the field season. Timing for the gas ebullition measurements is weekly, consistent with historical measurements by UFI. *In situ/in vivo* monitoring will occur weekly in order to track changes in key parameters. Timing for the zooplankton monitoring will be biweekly through most of the season and weekly from October 20 through December 8, which will allow for monitoring of seasonal dynamics in community composition and mercury concentrations.

Parameters – The parameters for water column monitoring are consistent with those measured during the 2006 and 2007 nitrate evaluation studies (UFI and SU 2007a, 2007b). They include total mercury, methylmercury, parameters indicative of redox status (i.e., oxygen, nitrate, and sulfide), and other general water quality parameters. For gas ebullition, the key parameter is the volume of gas collected, from which the rate of ebullition is calculated. Dissolved methane and total dissolved gas measurements in the water column samples will also contribute to the understanding of gas ebullition rates. The *in situ/in vivo* measurements include parameters that can be measured rapidly and that contribute to the understanding of nitrate, bisulfide, and turbidity. For zooplankton monitoring, total mercury and methylmercury are the main parameters as the purpose is to evaluate potential role of zooplankton in mercury bioaccumulation by fish. Taxonomic identification is also important as changes in community composition may indirectly affect bioaccumulation rates.

SAMPLING GOALS AND SPECIFICATIONS

Goals and specifications are summarized below for each of the monitoring subcomponents.

1. **Water Column Monitoring** - laboratory analyses of lake water samples
    a. Goals
        i. assess temporal and vertical patterns of mercury speciation in Onondaga Lake;
        ii. assess temporal and vertical patterns of an array of constituents that include important redox constituents and indicators of primary production and decomposition processes; and
        iii. further document the relationship(s) between the patterns of mercury and redox constituents.
    b. Specifications
        i. timing – specified in Table 1;
        ii. location - at long-term (South Deep) monitoring site (S, Figure 1); depths as specified in Table 2 according to analyte;

iii. sample collection as per NELAC and EPA specifications (see Appendix B); and

iv. parameters - listing, methods, and depths are presented in Table 2.

2. **Monitoring of Ebullition** – assessment of gas ebullition with inverted cones

   a. Goals:

      i. quantify the upward flux of ebullitive gas from the sediments; and

      ii. support the evaluation of the potential for increases in ebullition associated with a shift to an increased role for nitrate in supporting decomposition in the hypolimnion (a potential impact of nitrate treatment).

   b. Specifications:

      i. inverted cone design, LEXAN construction, 0.75 m diameter, inverted graduated separatory funnel collection (see Appendix B);

      ii. deployment/collection - 2 m above bottom, one unit at South Deep and one unit in the deep portion of north basin;

      iii. timing - weekly collections, April – November; and

      iv. parameters

         (1) upward flux for both cones.

3. ***In situ*/*in vivo* monitoring**

   a. Measurements with rapid profiling instrumentation

      i. Goals:

         (1) continue to validate ISUS measurements of nitrate (NO_3^-) and bisulfide (HS^-); and

         (2) assess spatial patterns of nitrate (NO_3^-), bisulfide (HS^-), beam attenuation coefficient (**c**; surrogate of TSS and turbidity), specific conductance (SC) and ancillary parameters, with high spatial resolution, over short time intervals (three dimensional resolution available within several hours).

      ii. Specifications

         (1) a transect along the long axis of the lake and a lateral transect at "South Deep" (~10 sites); see Figure 2 for example ISUS sampling locations;

         (2) vertical resolution ~ 0.25 m;

(3) frequency – weekly, April – mid-December; and

(4) parameters measured by sensors as specified in Table 3.

b. Measurements of total dissolved gas pressure (TDG)[1]

i. Goals:

(1) evaluate the potential for dissolved gas supersaturation and gas bubble trauma in fish through measurements of TDG.

ii. Specifications

(1) vertical profiles with a calibrated tensionometer at "South Deep" on 27 occasions in 2008 (see Table 1); and

(2) vertical resolution of 1 m.

4. **Zooplankton Monitoring -** zooplankton taxonomy and mercury concentrations

a. Goals:

i. specify seasonal patterns in the taxonomy and biomass of the pelagic zooplankton community through enumeration of samples to genus or species (in most cases) level;

ii. determine concentrations of total and methylmercury in the pelagic zooplankton assemblage on a seasonal basis; and

iii. if possible, determine concentrations of total and methylmercury in large daphnids.

b. Specifications:

i. "South Deep";

ii. Bi-weekly samplings from April to mid-October; weekly sampling from October 20 to mid-December, as feasible;

iii. 13 m vertical tows with a non-metallic 64µm mesh zooplankton net;

iv. three tows per sampling - two tows combined into one sample bottle for mercury analyses (i.e., composite sample)[2] and one tow for enumeration; and

v. the zooplankton assemblage samples will be analyzed for total mercury and methylmercury. If large daphnids are present, they will be picked from the sample and analyzed for total mercury and methylmercury.

Sample preservation and analytical requirements are provided in the QAPP (Appendix B). Field and analytical standard operating procedures (SOPs) are referenced in the QAPP and SOP L-16 is provided in Attachment 1.

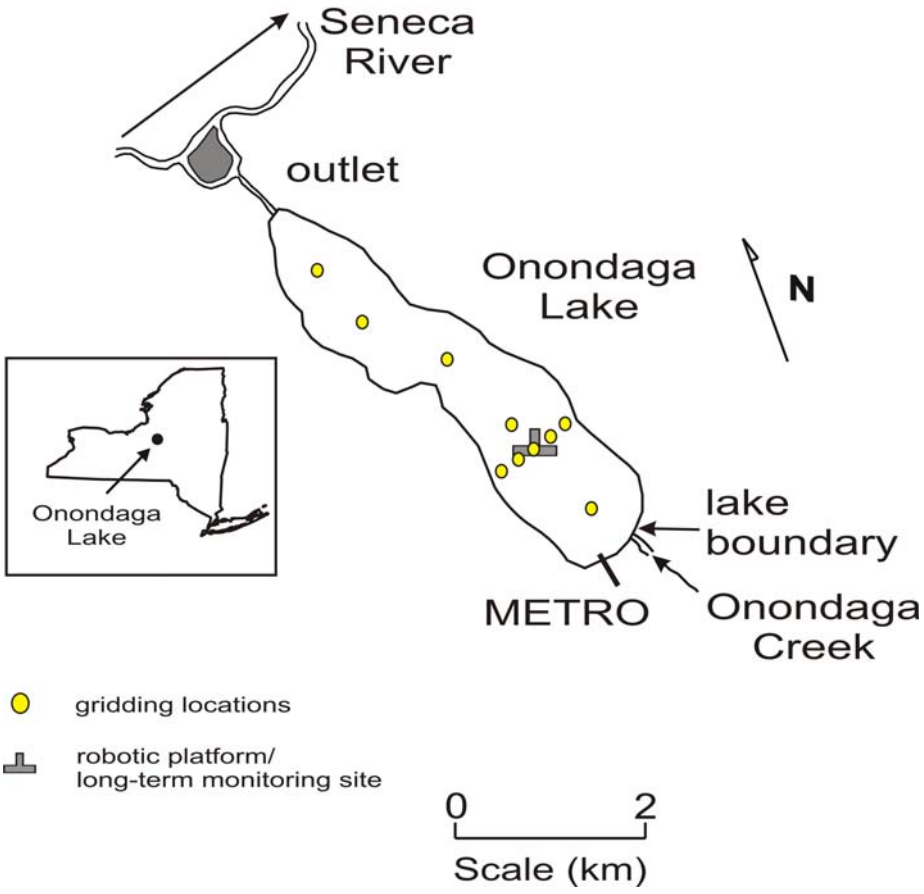

Figure 2. Example ISUS sampling locations.

[1] The tensionometer will be used to measure total dissolved gas (TDG). The primary components of TDG other than N_2 (i.e., oxygen, methane, and carbon dioxide) are measured independently. These measurements, in conjunction with TDG, allow an estimate of N_2 concentration by difference.

[2] The 2008 program includes two tows per event for analytical work and then combines them into one sample rather than submitting them separately for chemical analysis. This approach yields a composite field-averaged sample, which is appropriate because more variability is expected between duplicates as a result of field heterogeneity than due to sampling technique. It also ensures that there is enough sample mass to analyze.

Table 1: Water Column Sampling Schedule for 2008

Month	Water Column		
	Frequency	**Sampling Date**	**South Deep Depths (m)**
April	bi-weekly	4/14, 4/28	2, 12, 19
May	bi-weekly	5/12, 5/26	2, 12, 19
June	bi-weekly	6/9, 6/23	2, 12, 19
July	bi-weekly	7/7, 7/21	2, 12, 16, 18, 19
August	weekly	8/4, 8/11, 8/18, 8/25	2, 12, 16, 18, 19
September	weekly	9/1, 9/8	2, 12, 16, 18, 19
		9/15, 9/22, 9/29	2, 12, 14, 16, 18, 19
October	weekly	10/6, 10/13	2, 12, 14, 16, 18, 19
		10/20, 10/27	2, 6, 12, 14, 16, 18, 19
November	weekly	11/3, 11/10, 11/17, 11/24	2, 6, 12, 14, 16, 18, 19
December	weekly	12/1, 12/8	2, 6, 12, 14, 19

Note: This sampling schedule is based on the lake being stratified from early July until late October – early November. If the timing for stratification is significantly different during 2008, sampling frequency and depths may be adjusted. Any possible adjustments will be discussed with NYSDEC before being implemented.

Table 2: Specifications for Water Column and Zooplankton Monitoring at South Deep, Laboratory Analytes[x]

Parameter	Method	South Deep Depths (m) and Dates	Total Number of Analyses for 2008[x]
[@]Chl	EPA 445	2,12 (see Table 1 for dates)	135
NO_X	EPA 353.2	See Table 1	221
NO_2^-	EPA 353.2	See Table 1	221
T-NH_3	EPA 350.1	See Table 1	221
DOC	SM 18-20 5310C	See Table 1	221
TIC	SM 18-20 5310C	See Table 1	221
Cl^-	SM 18-20 4500 Cl^- C	See Table 1	221
[+*]Total Hg	EPA 1631E	See Table 1	194
[+*]Total Hg, dissolved	EPA 1631E	2 m biweekly, 14 m biweekly starting 9/15	43
[+*]CH_3Hg	EPA 1630	See Table 1	194
[#]H_2S method 1	SM 18-20 4500 S^{2-} E	anoxic depths: 1 m intervals (mid-Jul-mid-Nov)	221
°method 2	SM 18-20 4500 S^{2-} G	anoxic depths: 1 m intervals (mid-Jul-mid-Nov)	221
Fe^{2+}	Heaney and Davison (1977)	anoxic depths; 12,16,18,19 (mid-Jul-mid-Nov)	119
CH_4	Addess 1990	anoxic depths; 12,16,18,19 (mid-Jul-mid-Nov)	119
[*] Zooplankton Total Hg	EPA Method 1631	13 m vertical tows bi-weekly 4/14 – 10/13, weekly 10/20 – 12/8	24
[*] Zooplankton CH_3Hg	EPA Method 1630	13 m vertical tows bi-weekly 4/14 – 10/13, weekly 10/20 – 12/8	24

[@] Higher resolution data will be provided by the *in situ* robotic monitoring, which will be measuring chlorophyll *a* at 1m depth intervals every day at the same location (South Deep). The main purpose of the chlorophyll analyses at 2 and 12 m is to provide confirmation of the RUSS data.

[x] Includes trip blanks and field triplicates at one depth for all analytes except total mercury and methylmercury (See Appendix A). Includes field blanks and field duplicates at one depth for total mercury and methylmercury, and field duplicates for dissolved total mercury. UFI trip blanks are sample bottles that are filled in the laboratory, transported to the field, and then back to the laboratory for analysis. Mercury field blanks are sample bottles that are filled in the laboratory, transported to the field, and then poured into a second sample bottle that is taken back to the laboratory for analysis. Total does not include matrix spikes or equipment rinsate blanks for mercury analyses. See QAPP Worksheet #20 for total number of samples to laboratory.

[+] Total mercury analysis of water will be performed by TestAmerica; total mercury analysis of zooplankton and methylmercury in all matrices will be performed by Brooks Rand as a subcontractor to TestAmerica; all other analyses will be performed by UFI.

* Includes one field duplicate and one field blank per sampling event for water samples. Includes two field duplicates for zooplankton. In addition, up to 10 samples of large *Daphnia* will be analyzed for total Hg and CH_3Hg if sufficient numbers are present to conduct laboratory analyses.

[#] Total number of samples will depend on the time of year and extent of anoxia. This estimate assumes 10 depths plus one field blank and two field replicates per sampling event.

Table 3: Specifications for ISUS Rapid Profiling Instrumentation

Parameter	Sensor[x]	Performance Accuracy/Resolution	Attribute/Value
$^{+}NO_3^-$	Satlantic ISUS V2	0.5 μM (dl[7])	status, preferred electron acceptor
$^{+}HS^-$	Satlantic ISUS V2		redox constituent, SO_4^- reduction
T[1]	SBE 3F	± 0.002 °C/0.0003 °C	stratification
SC[2]	SBE4	± 3 μS/cm/0.1 μS/cm	tracer/stratification
$\mathbf{c}_{660}$[3]	Wetlabs C-Star	± 0.1% transmission	particle indicator
OBS[4]	D&A OBS-3	± 0.25 NTU/0.1 NTU	particle indicator
Chl_f[5]	Wetlabs WETstar	± NA/0.1 μg/L Chl	vertical pattern of phyto
PAR[6]	Li-Cor LI-193	± 5% reading	light penetration

[x] factory calibrated annually, maintained according to manufacturers instructions
[+] as described in Johnson and Coletti (2002)
[1] temperature
[2] specific conductance
[3] beam attenuation coefficient at 660 nm
[4] optical backscattering
[5] chlorophyll fluorescence
[6] photosynthetically active irradiance
[7] detection limit

HEALTH AND SAFETY

Health and safety is the highest priority. The UFI Safety Plan (Appendix C of UFI and SU 2007a) prepared for previous Onondaga Lake field activities will be used for this investigation and will be strictly followed by all personnel. Any task outside of the current scope defined in the Safety Plan will have a new Job Safety Analysis (JSA) completed before the task begins. A summary of the roles/responsibilities and contact information is included in Appendix C of the UFI Safety Plan, which will be maintained at the support zone and on each vessel.

DATA MANAGEMENT AND REPORTING

Unvalidated data will be submitted to NYSDEC on a quarterly basis (e.g., April data will be submitted by late summer), unless agreed to otherwise by NYSDEC. Syracuse University will review all unvalidated mercury data and will conduct split analyses on 10% of the mercury samples, using laboratory SOPs provided in the 2007 work plan (UFI and SU, 2007b).

Analytical data generated during this investigation will be reviewed and validated as described in detail in Appendix B of this work plan. Consistent with the 2006 and 2007 nitrate evaluation studies (UFI and SU, 2007a and 2007b), all analytes will be subject to Level III validation as described in the PDI QAPP (Parsons, 2005). In addition, 10% of

the nitrate, total mercury, and methylmercury data will be validated based on Level IV protocols. The validated results will be incorporated into the Locus Focus database by Parsons following validation.

Once the data validation has been completed, a data usability and summary report (DUSR) will be prepared and submitted to NYSDEC as an attachment to the Annual Baseline Monitoring Report in June of the year following the field season, in accordance with the Consent Decree for the lake. The DUSR will present the results of data validation and data usability assessment. Data interpretation and trend analysis will be presented in the baseline monitoring report.

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Appendix A *Phase I Sampling And Analysis Plan*
Appendix B *Quality Assurance Project Plan*
Appendix C *Project Safety Plan*

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APPENDIX A

FIELD SAMPLING MATRIX

APPENDIX A

Field Sampling Matrix for Laboratory Analyses of Water Samples for April, May, and June[1] 2008:

Sampling Depth	Chl	NO_X	NO_2	$T\text{-}NH_3$	TIC	DOC	Cl^-	[3]Total Hg	[4]CH_3Hg
2m	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XX	XX
12m	X	X	X	X	X	X	X	X	X
19m		X	X	X	X	X	X	X	X

Field Sampling Matrix for Laboratory Analyses of Water Samples for July – September 8[1] 2008:

Sampling Depth	Chl	NO_X	NO_2	$T\text{-}NH_3$	TIC	DOC	Cl^-	[2] H_2S	Fe^{2+}	CH_4	[3]Total Hg	[4]CH_3Hg
2m	XXX	XXX	XXX	XXX	XXX	XXX	XXX				XX	XX
12m	X	X	X	X	X	X	X	anoxic depths	XXX	XXX	X	X
16m		X	X	X	X	X	X	anoxic depths	X	X	X	X
18m		X	X	X	X	X	X	anoxic depths	X	X	X	X
19m		X	X	X	X	X	X	anoxic depths	X	X	X	X

Field Sampling Matrix for Laboratory Analyses of Water Samples for September 15 – October 13[1] 2008:

Sampling Depth	Chl	NO_X	NO_2	$T\text{-}NH_3$	TIC	DOC	Cl^-	[2] H_2S	Fe^{2+}	CH_4	[3]Total Hg	[4]CH_3Hg
2m	XXX	XXX	XXX	XXX	XXX	XXX	XXX				XX	XX
12m	X	X	X	X	X	X	X	anoxic depths	XXX	XXX	X	X
14m		X	X	X	X	X	X	anoxic depths			X	X
16m		X	X	X	X	X	X	anoxic depths	X	X	X	X
18m		X	X	X	X	X	X	anoxic depths	X	X	X	X
19m		X	X	X	X	X	X	anoxic depths	X	X	X	X

Field Sampling Matrix for Laboratory Analyses of Water Samples for October 20 – November 24[1] 2008:

Sampling Depth	Chl	NO_X	NO_2	$T\text{-}NH_3$	TIC	DOC	Cl^-	[2]H_2S	[2]Fe^{2+}	CH_4	[3]Total Hg	[4]CH_3Hg
2m	XXX	XXX	XXX	XXX	XXX	XXX	XXX				XX	XX
6m		X	X	X	X	X	X				X	X
12m	X	X	X	X	X	X	X	anoxic depths	XXX	XXX	X	X
14m		X	X	X	X	X	X	anoxic depths			X	X
16m		X	X	X	X	X	X	anoxic depths	X	X	X	X
18m		X	X	X	X	X	X	anoxic depths	X	X	X	X
19m		X	X	X	X	X	X	anoxic depths	X	X	X	X

Field Sampling Matrix for Laboratory Analyses of Water Samples for December 1 – December 8[1] 2008:

Sampling Depth	Chl	NO_X	NO_2	$T\text{-}NH_3$	TIC	DOC	Cl^-	[3]Total Hg	[4]CH_3Hg
2m	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XX	XX
6m		X	X	X	X	X	X	X	X
12m	X	X	X	X	X	X	X	X	X
14m		X	X	X	X	X	X	X	X
19m		X	X	X	X	X	X	X	X

NOTES:

X Represents one field sample. XX and XXX represent duplicate and triplicate field samples, respectively.

[1] South Deep will be sampled on a total of 27 occasions as specified in Table 1.

[2] H_2S samples will be collected at all anoxic depths and one meter above the uppermost anoxic depth (oxic sample).

[3] Total mercury analysis will be performed by TestAmerica.

[4] Methylmercury analysis will be performed by Brooks Rand.

APPENDIX B
QUALITY ASSURANCE PROJECT PLAN
ONONDAGA LAKE BASELINE MONITORING
BOOK 1
DEEP BASIN WATER AND ZOOPLANKTON MONITORING WORK PLAN FOR 2008

Based on the Intergovernmental Data Quality Task Force
Uniform Federal Policy for Quality Assurance Project Plans

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May 2008

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Title and Approval Page

Site Name/Project Name: Onondaga Lake Baseline Monitoring
Site Location: Syracuse, New York

Title: Book 1 – Deep Basin Water and Zooplankton Monitoring for 2008
Revision Number: 1
Revision Date: May 13, 2008

Quality Assurance Project Plan, Book 1 – Deep Basin Water and Zooplankton Monitoring for 2008
Document Title

Parsons
Lead Organization

M.G. Perkins, Upstate Freshwater Institute (UFI)
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Preparer's Address, Telephone Number, and E-mail Address

April 30, 2008
Preparation Date (Day/Month/Year)

Co-Investigative Organization's Project Managers: _____
Signature

_____
Signature

Steven Effler, UFI, and Charles Driscoll, SU
Printed Name/Organization/Date

Co-Investigative Organization's Project QA Officer: _____
Signature

M.G. Perkins, UFI
Printed Name/Organization/Date

Lead Organization's Project Manager: _____
Signature

Ed Glaza, Parsons
Printed Name/Organization/Date

QAPP Worksheet #1
Title and Approval Page
(continued)

Site Name/Project Name: Onondaga Lake Baseline Monitoring
Site Location: Syracuse, New York

Title: Book 1 – Deep Basin Water and Zooplankton Monitoring for 2008
Revision Number: 1
Revision Date: May 13, 2008

Approval Signatures: _____
Signature

_____
Printed Name/Title/Date

_____
Approval Authority

Other Approval Signatures: _____
Signature

_____
Printed Name/Title/Date

Document Control Number: UFI 021

QAPP Worksheet #2
QAPP Identifying Information

Site Name/Project Name: Onondaga Lake Baseline Monitoring
Site Location: Syracuse, New York
Site Number/Code: N/A
Operable Unit: N/A
Contractor Name: UFI and SU
Contractor Number: N/A
Contract Title: N/A
Work Assignment Number: N/A

Title: Book 1 – Deep Water Basin and Zooplankton Monitoring for 2008
Revision Number: 1
Revision Date: May 13, 2008

1. Identify guidance used to prepare QAPP:
Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) Manual (505-B-04-900A) (Version 1)

2. Identify regulatory program: CERCLA

3. Identify approval entity:
New York State Department of Environmental Conservation (NYSDEC) and U.S. EPA Region 2

4. Indicate whether the QAPP is a generic or a project-specific QAPP. (circle one)

5. List dates of scoping sessions that were held: January 31, 2007 and others

6. List dates and titles of QAPP documents written for previous site work, if applicable:

Title	Approval Date
2007 Onondaga Lake Nitrate Evaluation QAPP	February 11, 2008

7. List organizational partners (stakeholders) and connection with lead organization:
NYSDEC, Earth Tech (consultant to NYSDEC), USEPA, Honeywell, Parsons (consultant to Honeywell), Exponent (consultant to Parsons/Honeywell) and SU (consultant to Honeywell), and UFI (consultants to SU/Honeywell)

8. List data users: NYSDEC, Earth Tech, U.S. EPA, Honeywell, Parsons, Exponent, UFI, SU

9. If any required QAPP elements and required information are not applicable to the project, then circle the omitted QAPP elements and required information on the attached table. Provide an explanation for their exclusion below:

QAPP elements and required information that are not applicable to the project are circled and an explanation is provided in the QAPP.

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
Project Management and Objectives		
2.1 Title and Approval Page	- Title and Approval Page	QAPP Worksheet #1
2.2 Document Format and Table of Contents 2.2.1 Document Control Format 2.2.2 Document Control Numbering System 2.2.3 Table of Contents 2.2.4 QAPP Identifying Information	- Table of Contents - QAPP Identifying Information	QAPP Worksheet #2
2.3 Distribution List and Project Personnel Sign-Off Sheet 2.3.1 Distribution List 2.3.2 Project Personnel Sign-Off Sheet	- Distribution List - Project Personnel Sign-Off Sheet	QAPP Worksheet #3 & #4
2.4 Project Organization 2.4.1 Project Organizational Chart 2.4.2 Communication Pathways 2.4.3 Personnel Responsibilities and Qualifications 2.4.4 Special Training Requirements and Certification	- Project Organizational Chart - Communication Pathways - Personnel Responsibilities and Qualifications Table - Special Personnel Training Requirements Table	QAPP Worksheet #5, #6, #7 & 8
2.5 Project Planning/Problem Definition 2.5.1 Project Planning (Scoping) 2.5.2 Problem Definition, Site History, and Background	- Project Planning Session Documentation (including Data Needs tables) - Project Scoping Session Participants Sheet - Problem Definition, Site History, and Background - Site Maps (historical and present)	QAPP Worksheet #9 & #10
2.6 Project Quality Objectives and Measurement Performance Criteria 2.6.1 Development of Project Quality Objectives Using the Systematic Planning Process 2.6.2 Measurement Performance Criteria	- Site-Specific PQOs - Measurement Performance Criteria Table	QAPP Worksheet #11 & #12
2.7 Secondary Data Evaluation	- Sources of Secondary Data and Information - Secondary Data Criteria and Limitations Table	QAPP Worksheet #13

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
2.8 Project Overview and Schedule 2.8.1 Project Overview 2.8.2 Project Schedule	- Summary of Project Tasks - Reference Limits and Evaluation Table - Project Schedule/Timeline Table	QAPP Worksheet #14 & #15
Measurement/Data Acquisition		
3.1 Sampling Tasks 3.1.1 Sampling Process Design and Rationale 3.1.2 Sampling Procedures and Requirements 3.1.2.1 Sampling Collection Procedures 3.1.2.2 Sample Containers, Volume, and Preservation 3.1.2.3 Equipment/Sample Containers Cleaning and Decontamination Procedures 3.1.2.4 Field Equipment Calibration, Maintenance, Testing, and Inspection Procedures 3.1.2.5 Supply Inspection and Acceptance Procedures 3.1.2.6 Field Documentation Procedures	- Sampling Design and Rationale - Sample Location Map - Sampling Locations and Methods/ SOP Requirements Table - Analytical Methods/SOP Requirements Table - Field Quality Control Sample Summary Table - Sampling SOPs - Project Sampling SOP References Table - Field Equipment Calibration, Maintenance, Testing, and Inspection Table	QAPP Worksheet #17, #18, #19, #20, #21, #22
3.2 Analytical Tasks 3.2.1 Analytical SOPs 3.2.2 Analytical Instrument Calibration Procedures 3.2.3 Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures 3.2.4 Analytical Supply Inspection and Acceptance Procedures	- Analytical SOPs - Analytical SOP References Table - Analytical Instrument Calibration Table - Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table	QAPP Worksheet #23, #24, #25 and SOPs in UFI and SU (2007) with the exception of SOPs L-16 through L-19 which are provided in Attachment 1 to this QAPP
3.3 Sample Collection Documentation, Handling, Tracking, and Custody Procedures 3.3.1 Sample Collection Documentation 3.3.2 Sample Handling and Tracking System 3.3.3 Sample Custody	- Sample Collection Documentation Handling, Tracking, and Custody SOPs - Sample Container Identification - Sample Handling Flow Diagram - Example Chain-of-Custody Form and Seal	QAPP Worksheet #19, #26, #27 and SOPs in UFI and SU (2007)
3.4 Quality Control Samples 3.4.1 Sampling Quality Control Samples 3.4.2 Analytical Quality Control Samples	- QC Samples Table - Screening/Confirmatory Analysis Decision Tree	QAPP Worksheet #28

Required QAPP Element(s) and Corresponding QAPP Section(s)	Required Information	QAPP Worksheet # or Crosswalk to Related Documents
3.5 Data Management Tasks 3.5.1 Project Documentation and Records 3.5.2 Data Package Deliverables 3.5.3 Data Reporting Formats 3.5.4 Data Handling and Management 3.5.5 Data Tracking and Control	- Project Documents and Records Table - Analytical Services Table - Data Management SOPs	QAPP Worksheet #29, #30
Assessment/Oversight		
4.1 Assessments and Response Actions 4.1.1 Planned Assessments 4.1.2 Assessment Findings and Corrective Action Responses	- Assessments and Response Actions - Planned Project Assessments Table - Audit Checklists - Assessment Findings and Corrective Action Responses Table	QAPP Worksheet #32, #28
4.2 QA Management Reports	- QA Management Reports Table	QAPP Worksheet #33
4.3 Final Project Report		
Data Review		
5.1 Overview		
5.2 Data Review Steps 5.2.1 Step I: Verification 5.2.2 Step II: Validation 5.2.2.1 Step IIa Validation Activities 5.2.2.2 Step IIb Validation Activities 5.2.3 Step III: Usability Assessment 5.2.3.1 Data Limitations and Actions from Usability Assessment 5.2.3.2 Activities	- Verification (Step I) Process Table - Validation (Steps IIa and IIb) Process Table - Validation (Steps IIa and IIb) Summary Table - Usability Assessment	QAPP Worksheet #34, #35, #36, #37
5.3 Streamlining Data Review 5.3.1 Data Review Steps To Be Streamlined 5.3.2 Criteria for Streamlining Data Review 5.3.3 Amounts and Types of Data Appropriate for Streamlining		

QAPP Recipients	Title	Organization	Telephone Number	Fax Number	E-mail Address	Document Control Number
Ed Glaza	Project Manager	Parsons	315-451-9560	315-451-9570	edward.glaza@ parsons.com	
Charles Driscoll	Project Manager	SU	315-443-3434	315-443-4936	ctdrisco@syr.edu	
Michelle Briscoe	VP of Analytical Services, Laboratory Director	Brooks Rand	206-623-6206	206-632-6017	michelle@brooksrand.com	
Jennifer Holmes	Client Services Manager, Project Manager	Brooks Rand	206-632-6206	206-632-6017	Jennifer@brooksrand.com	
Frank McFarland	Quality Assurance	Brooks Rand	206-632-6206	206-632-6017	frank@brooksrand.com	
Steven W. Effler	Project Manager	UFI	315-431-4962 ext. 102	315-431-4969	sweffler@ upstatefreshwater.org	
MaryGail Perkins	Quality Assurance Officer, Field Manager, Laboratory Director	UFI	315-431-4962 ext. 104	315-431-4969	mgperkins @upstatefreshwater.org	
David Matthews	Scientific/ Technical Manager	UFI	315-431-4962 ext. 107	315-431-4969	damatthews@ upstatefreshwater.org	
Betsy Henry	Project Manager	Exponent	518-370-5132	518-381-4115	henryb@exponent.com	
John McAuliffe	Project Manager	Honeywell	315-431-4443	315-431-4777	john.mcauliffe@ honeywell.com	
Tim Larson	Project Manager	NYSDEC	518-402-9767	518-402-9020	tjlarson@gw.dec.state.ny.us	
Robert Nunes	Project Manager	U.S. EPA Region 2	212-637-4254	212-637-3966	nunes.robert@epa.gov	

Organization: Syracuse University (SU)

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Charles Driscoll	SU Project Manager	315-443-3434		

Organization: Upstate Freshwater Institute (UFI)

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Steven W. Effler	UFI Project Manager	315-431-4962 ext. 102		
David Matthews	UFI Scientific/ Technical Manager	315-431-4962 ext. 107		
MaryGail Perkins	UFI Quality Assurance Officer, Field Manager, Laboratory Director	315-431-4962 ext. 104		

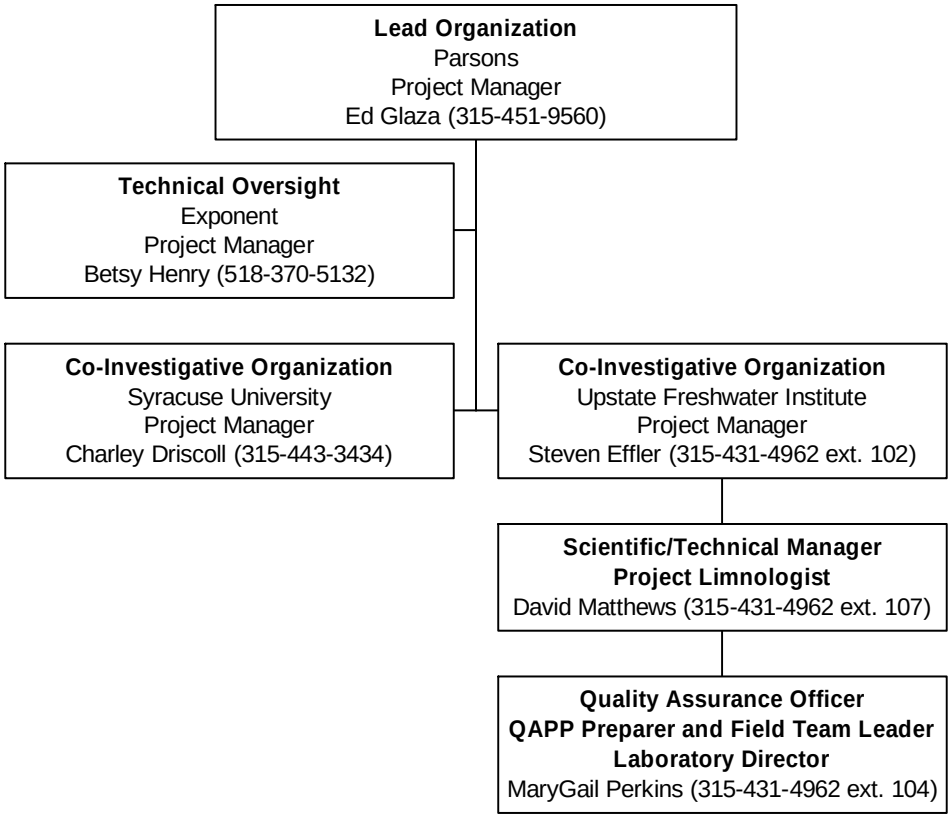
Organization: TestAmerica

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Mark Loeb	Project Manager	330-966-9387		
Dorothy Leeson	Quality Assurance Manager	330-497-9396		

Organization: Brooks Rand Labs

Project Personnel	Title	Telephone Number	Signature	Date QAPP Read
Michelle Briscoe	VP of Analytical Services, Laboratory Director	206-632-6206		
Jennifer Holmes	Client Services Manager, Project Manager	206-632-6206		
Frank McFarland	Quality Assurance Manager	206-632-6206		

Project Organizational Chart



Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Point of contact with data users	Lead Organization and Project Manager	Ed Glaza	315-451-9560	All materials and information about the project will be forwarded to the data users by Ed Glaza.
Manage all project phases	Lead Organization and Project Manager	Ed Glaza	315-451-9560	Ed Glaza will be the liaison with data users and SU, UFI, and Brooks Rand.
Manage all UFI project tasks	Co-Investigative Project Manager	Steven Effler	315-431-4962 ext. 102	Notify Ed Glaza of field-related problems by phone, email, or fax by COB the next business day.
QAPP changes in the field	Field Team Leader	MaryGail Perkins	315-431-4962 ext. 104	Notify Steven Effler by phone or email of changes to QAPP made in the field and the reasons within one business day.
Daily field progress reports	Field Team Leader	MaryGail Perkins	315-431-4962 ext. 104	Notify David Matthews of any problems or issues.

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Field and UFI analytical corrective actions	UFI Quality Assurance Officer/UFI Technical Director	MaryGail Perkins	315-431-4962 ext. 104	The need for corrective action for field and UFI analytical issues will be determined by MaryGail Perkins and David Matthews.
Release of UFI analytical data	UFI Quality Assurance Officer	MaryGail Perkins	315-431-4962 ext. 104	No UFI analytical data can be released until validation is completed and MaryGail Perkins has approved the release.
Reporting TestAmerica lab data quality issues	TestAmerica Project Manager	Mark Loeb	330-966-9387	Report data and supporting quality assurance information as specified in this QAPP.
Test America analytical corrective actions	TestAmerica Quality Assurance Manager	Dorothy Leeson	330-497-9396	The need for corrective action for TestAmerica analytical issues will be determined by Dorothy Leeson.
Release of TestAmerica analytical data	TestAmerica Project Manager	Mark Loeb	330-966-9387	No TestAmerica analytical data can be released until validation is completed and Mark Loeb has approved the release.
Reporting Brooks Rand lab data quality issues	Brooks Rand Quality Assurance Lead	Frank McFarland	206-632-6206	Notify Jennifer Holmes when problems occur, report data and supporting quality assurance information as specified in this QAPP.
Brooks Rand analytical corrective actions	Brooks Rand Quality Assurance Officer	Frank McFarland	206-632-6206	The need for corrective action for Brooks Rand analytical issues will be determined by Frank McFarland

Communication Drivers	Responsible Entity	Name	Phone Number	Procedure (Timing, Pathways, etc.)
Release of Brooks Rand analytical data	Brooks Rand Quality Assurance Officer	Frank McFarland	206-632-6206	No Brooks Rand analytical data can be released until validation is completed and Frank McFarland has approved the release.
QAPP Amendments	Lead Organization and Project Manager	Ed Glaza	315-451-9560	Any major changes to the QAPP must be approved by Ed Glaza before changes can be implemented.

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Steven Effler	UFI Project Manager	UFI	Overall responsibility for UFI activities. Provide approval of all necessary actions and adjustments for activities to accomplish project objectives. Provide management support of all project-related QA/QC activities.	Ph.D. Environmental Engineering; 30 years experience, 27 years Director of Research for UFI, 84 publications on Onondaga Lake
David Matthews	UFI Scientific/Technical Manager and Project Limnologist	UFI	Oversight of daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues, and oversight of field and laboratory progress; deliver data to project participants; organize and maintain project database. Authorize and document minor adjustments to the field/laboratory program in response to changing field conditions.	Ph.D. Environmental Engineering; 11 years experience on Onondaga Lake; 15 publications on Onondaga Lake
MaryGail Perkins	UFI Project Administrator, Quality Assurance Officer, and Field Manager	UFI	Coordinate and supervise field activities; ensure that field procedures are completed in accordance with the work plan and QAPP. Coordinate field and laboratory activities and notify Technical Manager of any problems or issues. Provide technical quality assurance assistance, develop and review QAPP, oversee quality assurance activities to ensure compliance with QAPP, review and submit quality assurance reports as required, supervise data validation. Maintain the official, approved QAPP.	M.S. Hydrogeology; 26 years experience on Onondaga Lake, 12 publications on Onondaga Lake

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
MaryGail Perkins	UFI Laboratory Director	UFI	Oversee all UFI laboratory personnel, activities, equipment, and records; track submittal and receipt of samples to the laboratory; retain all chain-of-custody records; and ensure that sample receipt and custody records are properly handled and data are reported within the specified turnaround times. Ensure that laboratory staff maintain and calibrate instruments as necessary, perform internal quality control measures and analytical methods as required, take appropriate corrective actions as necessary, notify QA/QC officer when problems occur, report data and supporting quality assurance information as specified in this QAPP.	M.S. Hydrogeology; 26 years experience on Onondaga Lake, 12 publications on Onondaga Lake
Charles Driscoll	SU Project Manager	SU	Overall responsibility for SU activities. Approve all necessary actions and adjustments for activities to accomplish project objectives. Provide management support of all project-related QA/QC activities.	Ph.D. Environmental Engineering; 27 years experience. Over 270 publications (authored or co-authored), PI of the LTER project at Hubbard Brook, CESE Director
Mark Loeb	TestAmerica – North Canton Project Manager	TestAmerica	Oversee daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues; oversee project specific laboratory progress; deliver data to project participants.	Bachelor's degree in physical sciences and 20 years experience with 8 years applied to project management.

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Dorothy Leeson	TestAmerica – North Canton Quality Assurance Manager	TestAmerica	The Quality Assurance Manager is responsible for developing and implementing the laboratory quality system. Responsibilities include providing Quality Systems training to all new personnel, maintaining a Laboratory Quality Manual (LQM), ensuring that the laboratory's quality system and LQM meet Requirements for both clients and regulatory officials. The QA Manager has the final authority to accept or reject data, and to stop work in progress in the event that procedures or practices compromise the validity and integrity of analytical data. The QA Manager is independent of laboratory operations.	Bachelor's degree in physical sciences and 18 years lab experience with 10 years of applied QA principles
Michelle Briscoe	Brooks Rand VP of Analytical Services, Laboratory Director	Brooks Rand	Oversee all Brooks Rand laboratory personnel, activities, equipment, and records; track submittal and receipt of samples to the laboratory; retain all chain–of-custody records; ensure that sample receipt and custody records are properly handled and data are reported within the specified turnaround times. Ensure that laboratory staff maintain and calibrate instruments as necessary, perform internal quality control measures and analytical methods as required, take appropriate corrective actions as necessary, notify QA/QC officer when problems occur, and report data and supporting quality assurance information as specified in this QAPP.	Bachelor's Degree in physical sciences with 24 hours of college chemistry credits, and 3 years experience in the environmental analytical lab business, including 1 year in supervisory position

Name	Title	Organizational Affiliation	Responsibilities	Education and Experience Qualifications
Jennifer Holmes	Brooks Rand Client Services Manager, Project Manager	Brooks Rand	Oversee daily project activities to ensure compliance with project objectives. Provide technical oversight and consultation on major technical and scientific issues; oversee field and laboratory progress; deliver data to project participants; organize and maintain project database. Authorize and document minor adjustments to the field/laboratory program in response to changing field conditions.	Bachelor's degree in physical sciences and 1 year experience in the environmental lab business
Frank McFarland	Brooks Rand Quality Assurance Manager	Brooks Rand	Provide technical quality assurance assistance, develop and review QAPP, oversee quality assurance activities to ensure compliance with QAPP, review and submit quality assurance reports as required, supervise data validation.	Bachelor's degree in physical sciences and 3 years lab experience with 1 year of applied QA principles

Project Function	Specialized Training – Title or Description of Course	Training Provider	Training Date	Personnel/Groups Receiving Training	Personnel Titles/ Organizational Affiliation	Location of Training Records/Certificates
Collection of water samples for mercury analysis	Instruction received on "clean hands-dirty hands" sampling protocol	Svetla Todorova	Initially April 2006, then annual refresher	BAW, MES, MTP, TP, DAM	UFI field staff	UFI

Project Name: Onondaga Lake Baseline Monitoring **Projected Date(s) of Sampling:** April–November 2008 **Project Managers: Ed Glaza, Parsons,** Charles Driscoll, SU, and Steven Effler, UFI	**Site Name:** Onondaga Lake **Site Location:** Onondaga Lake, Syracuse, NY

Date of Session: Numerous (see comments below)
Scoping Session Purpose: To discuss baseline monitoring needs

Name	Title	Affiliation	Phone #	E-mail Address	Project Role
Charles Driscoll	Project Manager	SU	315-443-3434	ctdrisco@ syr.edu	SU Project Manager
Steven Effler	Project Manager	UFI	315-431-4962 ext. 102	sweffler@ upstatefreshwater.org	UFI Project Manager
David Matthews	Scientific/Technical Manager	UFI	315-431-4962 ext. 107	damatthews@ upstatefreshwater.org	UFI Scientific/ Technical Manager
John McAuliffe	Project Manager	Honeywell	315-431-4443	John.mcauliffe@ honeywell.com	Overall Project Manager
Betsy Henry	Project Manager	Exponent	518-370-5132	henryb@ exponent.com	Technical support to Honeywell
Ed Glaza	Project Manager	Parsons	315-451-9560	edward.glaza@ parsons.com	Technical support to Honeywell
Tim Larson	Project Manager	NYSDEC	518-402-9767	tjlarson@ gw.dec.state.ny.us	NYSDEC Project Manager
Robert Montione	Scientist	Earth Tech	518-951-2226	robert.montione@ earthtech.com	Technical support to NYSDEC
Michael Spera	Senior Project Director	Earth Tech	212-798-8577	michael.spera@ earthtech.com	Technical support to NYSDEC

Comments/Decisions: The Baseline and Long-Term Monitoring Technical Work Group met on June 6 and October 26, 2007 and on January 7, 2008 to discuss baseline monitoring needs. Participants varied, but included representatives from Syracuse University, Upstate Freshwater Institute, Exponent, Parsons, NYSDEC, USEPA, EarthTech, and USFWS. Minutes of these meetings are on file. NYSDEC submitted comments on the work plan to Honeywell on March 28, 2008 and these comments were discussed on April 2, 2008.

Action Items: Parsons and SU/UFI to prepare/revise work plan.

Consensus Decisions: _____

Problem Definition and Background

The purpose and background for the remediation of the Onondaga Lake Bottom Subsite are summarized in the ROD (NYSDEC and USEPA, 2005) and presented in detail in the Feasibility Study Report (Parsons, 2004).

The overall goal of baseline monitoring is to document the condition of the lake prior to remedial action. This monitoring will permit evaluation of changes that result from remedial action and verification of remedy effectiveness in achieving the remedial action objectives and preliminary remedial goals. As described in the Baseline Monitoring Scoping Document (Parsons 2008), the Baseline Monitoring Program for Onondaga Lake has three program objectives:

- Establish a comprehensive description of baseline chemical conditions prior to remediation to assess remedy effectiveness and to facilitate remedy design;
- Provide additional data for future understanding of remedy effectiveness in achieving PRGs; and
- Provide habitat-related information.

Deep basin water monitoring is a component of water sampling, which is associated with the first objective. Zooplankton monitoring is a component of other biota sampling (i.e., biota other than fish), which is associated with the second objective.

Project Description

The deep basin water and zooplankton monitoring includes three components: water column, zooplankton, and gas. The water column component has three subcomponents, laboratory analyses of lake samples, profiles of total dissolved gas pressure (TDG), and spatially detailed monitoring with the ISUS rapid profiling instrument. The laboratory program includes selected features of the Upstate Freshwater Institute's (UFI's) long-term lake metabolism program, as well as a fully integrated mercury monitoring effort. The second component of the project consists of zooplankton sampling to assess mercury concentrations of the pelagic communities and their seasonal patterns in the lake. The gas monitoring component has a single element – the assessment of gas ebullition (gas bubble release from the sediment).

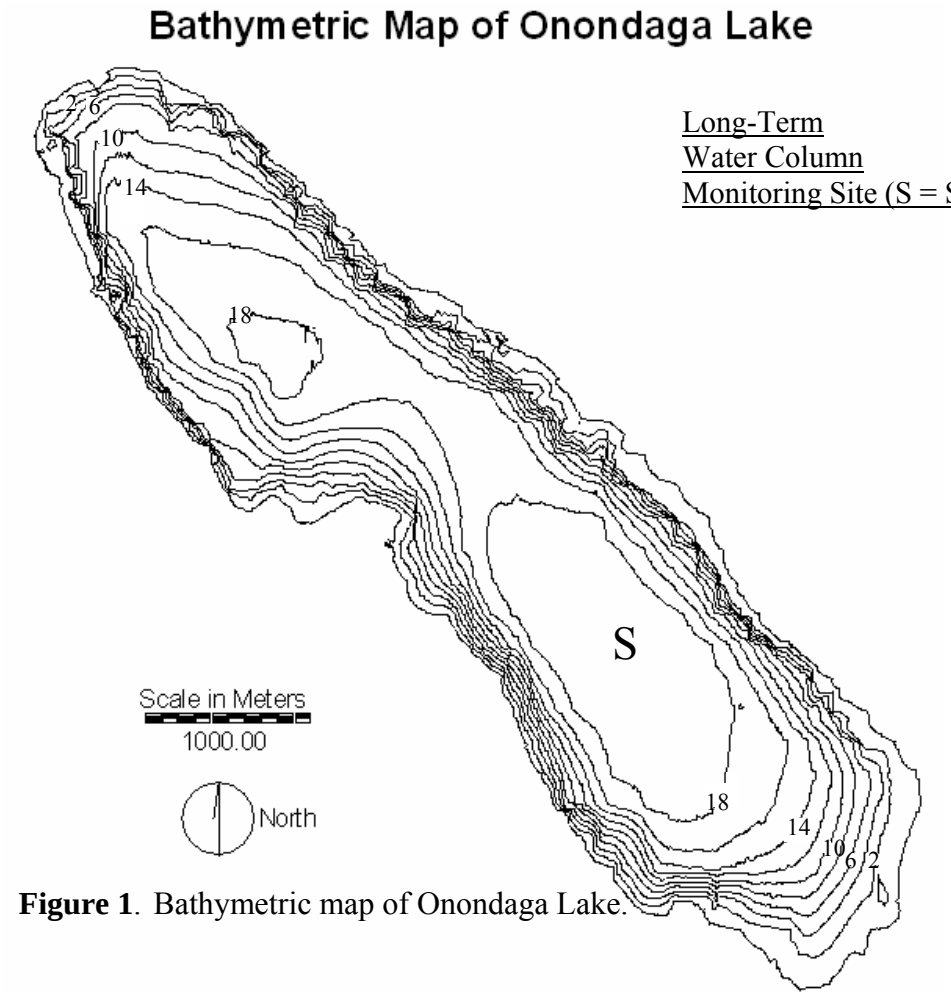


Figure 1. Bathymetric map of Onondaga Lake.

Who will use the data?

Honeywell, Parsons, NYSDEC, EPA, and other members of the Onondaga Lake Baseline and Long-Term Monitoring Technical Work Group will use the data.

What will the data be used for?

Deep basin water sampling supports three data uses as follows:

(1) provide basis to measure achievement of PRG3 (surface water quality standards),

(2) provide basis to measure success in controlling key processes (e.g., mercury methylation in the hypolimnion and mercury release from profundal sediment),

(3) provide information on the generation of methylmercury in the hypolimnion for use in the design of nitrate addition/oxygenation pilot tests and basis to measure results.

The primary data use for zooplankton sampling is to assess biological factors that may contribute to variability in fish mercury concentrations.

What type of data is needed? (target analytes, concentration levels, appropriateness of field screening, on-site analytical and/or off-site laboratory techniques, and the appropriateness of sampling techniques)

Water column monitoring includes samples collected for laboratory analysis and measurements made *in situ* for TDG and with the ISUS rapid profiling instrument. The target analytes for laboratory analysis are as follows:

- Chlorophyll a (EPA 445)
- NO_x and NO_2 (EPA 353.2)
- T-NH_3 (EPA 350.1)
- DOC and TIC (SM 18–20 5310C)
- Chloride (SM 18–20 4500 Cl^- C)
- Ferrous Iron (Heaney and Davidson, 1977)
- Sulfide (SM 18 4500 S E)
- Sulfide (SM 20 4500 S G)
- Dissolved CH_4 (Addess, 1990)
- Total mercury (EPA Method 1631E)

- Methylmercury (EPA Method 1630)

What type of data are needed? *(continued)*

The target analytes for *in situ* water monitoring are:

- Total dissolved gas (TDG)
- NO_3
- HS^-
- Temperature
- Specific conductance
- Transmissivity (c_{660}, beam attenuation coefficient at 660 nm)
- Turbidity (optical backscattering)
- Chlorophyll fluorescence
- Light penetration (photosynthetically active irradiance).

Zooplankton monitoring will measure total mercury and methylmercury concentrations in zooplankton. In addition, biomass and community composition will be evaluated. Gas ebullition monitoring will measure the volume of gas collected in inverted cones as described in the work plan.

Concentration levels (i.e., project action and quantitation limits, analytical and achievable laboratory method detection and quantitation limits) for the laboratory analytes are documented in Worksheet #15, field sampling techniques are referenced in Worksheet #21, and laboratory analytical techniques are referenced in Worksheet #23.

How "good" do the data need to be in order to support the environmental decision?

The data must support a long-term trend analysis for chemical concentrations in deep basin water and zooplankton and a long-term trend analysis for gas ebullition rate. The key analytes in terms of decision-making are total mercury, methylmercury, and nitrate. These analytes are Level IV data quality objectives as defined in the Pre-Design Investigation QAPP (Parsons 2005). Level IV data are generated using USEPA methods and enhanced by a rigorous QA program, supporting documentation, and data validation procedures described in Worksheet #36. All other analytes are Level III data quality objectives and will be validated according to EPA Level III protocol as described in Worksheet #36. Level III validation was performed for the 2006 and 2007 nitrate evaluation studies.

How much data are needed? (number of samples for each analytical group, matrix, and concentration)

See Worksheet #18.

Where, when, and how should the data be collected/generated?

Samples will be collected from Onondaga Lake from mid-April to mid-December (as feasible) using field sampling techniques summarized in Worksheet #21 and provided as attachments to the work plan. Water and zooplankton samples for laboratory analysis will be collected at depths and frequency specified in Worksheet #17. *In situ* water monitoring will be conducted on a weekly basis from mid-April to mid December (as feasible) at multiple depths along transects shown in the work plan.

Who will collect and generate the data?

UFI will collect the samples and analyze all analytes, except total mercury and methylmercury, which will be analyzed by TestAmerica (total mercury in water only) and Brooks Rand (total mercury in zooplankton, methylmercury in water and zooplankton).

How will the data be reported?

The data will be presented in the Data Summary and Usability Report referenced in the Work Plan.

How will the data be archived?

All field and UFI laboratory data are stored on the UFI server. Data are protected from corruption through routine data backups via computer and secure storage of data in hardcopy. All raw field and analytical data are stored in hardcopy form and, depending on format, on the UFI local area network (LAN). All data are managed and stored on the network system. Field and laboratory data are usually in the form of an Excel spreadsheet. Near-real-time data and some UFI laboratory data are stored in a database. The database is stored in a MySQL (v.4.1) server. The UFI server runs the Linux operating system on an AMD Athlon computer.

The laboratory has established procedures for identification, collection, indexing, access, filing, storage, maintenance and disposal of quality and technical records. Quality records are maintained by the Quality Assurance (QA) Manager in a database that is backed up as part of the regular network backup. Records are of two types; either electronic or hard copy paper formats depending on whether the record is computer or hand generated (some records may be in both formats). Technical records are maintained by the Records Manager.

All records are legible and stored and retained in such a way that they are secure and readily retrievable at the laboratory facility that provides a suitable environment to prevent damage or deterioration and to prevent loss**.** Records are maintained for a minimum of five years unless other wise specified by a client or regulatory requirement. For raw data and project records, record retention shall be calculated from the date the project report is issued. For other records, such as Controlled Documents, QA, or Administrative Records, the retention time is calculated from the date the record is formally retired.

Brooks Rand stores chain-of-custody forms and laboratory data in hard copy, and the electronic data are stored on the Brooks Rand server. Data are protected through daily backups via computer and secure storage of data in hardcopy. All hardcopy forms (COC, preparation logs, analytical bench sheets, etc.) are scanned and stored as electronic PDF files as well as in hardcopy form. The Brooks Rand server runs SuSE Linux

Professional (v. 9.1) on a Dell PowerEdge 700 computer. All hardcopy and electronic data are stored for a minimum of 7 years from the date of reporting.

Finally, all chemical data will be entered into the Onondaga Lake LocusFocus database by Parsons on behalf of Honeywell.

Analytes can be NELAC (National standards) certified, ELAP (NYSDOH standard) certified, or non-certified methods that follow a standard industry (EPA, ASTM, Standard Methods, etc) acceptable protocol. All NELAC certified methods are also ELAP certified methods. Not all ELAP certified methods are NELAC certified. Many traditional water quality parameters do not have NELAC or ELAP certified methods. The labs are certified for all NELAC/ELAP certifiable analytes listed here.

Matrix	Water
Analytical Group[1]	Chlorophyll a
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-1	L-8	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	NO_x
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-1	L-2	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value) for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]NELAC and ELAP certified method.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	NO_2
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-1	L-2	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]ELAP only certified method.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	T-NH_3
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
S-1	L-3	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]NELAC and ELAP certified method.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	DOC
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-1	L-4	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]There is no NELAC/ELAP certification available for DOC. UFI is NELAC and ELAP certified for TOC. DOC samples are filtered and run as a TOC.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	TIC
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-1	L-7	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Chloride
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-1	L-1	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Matrix spike and matrix spike duplicates	A
				Laboratory control samples	A
				Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]NELAC and ELAP certified method.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Ferrous iron
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-2	L-10	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value (based on monthly moving average with n≥10) for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses the accepted procedure Heaney and Davidson (1977). Heaney, S,I. and Davidson, W. 1977. The determination of ferrous iron in natural waters with 2, 2' bipyridyl. *Limnol. Oceanogr.* 22(4):753–759.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Sulfide Method 1[2]
Concentration Level	High

Sampling Procedure[3]	**Analytical Method/SOP**[4]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
S-2	L-5	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]All sulfide samples will be run using two sulfide methods (Method 1 - SM 18 4500 S^{2-} E and Method 2 - SM 20 4500 S^{2-} G) to assess comparability between the two methods over the observed concentration range. The SM 18 4500 S^{2-} E is UFI's historic long-term method. Method 2 is an NELAC and ELAP certified method, but Method 1 does not have a NELAC/ELAP certification available.
[2]Method 1 sulfide data will be used for comparison to historic analyses.
[3]Reference number from QAPP Worksheet #21.
[4]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Sulfide Method 2[2]
Concentration Level	Low

Sampling Procedure[3]	Analytical Method/SOP[4]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-2	L-6	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Accuracy/Bias	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Reference sample	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Method blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]All sulfide samples will be run using two sulfide methods (Method 1 - SM 20 4500 SE and Method 2 - SM 20 4500 S G) to assess comparability between the two methods over the observed concentration range. The SM 20 4500 S E is UFI's historic long-term method. Method 2 is an NELAC and ELAP certified method, but Method 1 does not have a NELAC/ELAP certification available.
[2]No measurement performance criteria are available for Method 1. Method 1 Sulfide data will be used for comparison to historic analyses.
[3]Reference number from QAPP Worksheet #21.
[4]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Dissolved methane
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
S-2 and S-5	L-9	Precision – Field	RSD 35%	Field triplicate samples	S&A
		Precision – Lab	RPD 10% for warning limits and 15% for control limits	Laboratory duplicate samples	A
		Contamination	Less than Achievable Laboratory Method Detection Limit	Method Instrument blanks	A
			Less than Achievable Laboratory Method Detection Limit	Field trip blanks (methane only)	S&A
		Sensitivity	Within 2 standard deviations of the mean value for warning limits and 3 for control limits	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data completeness check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses the accepted procedure of Addess (1990). Addess, J.M., 1990. Methane Cycling in Onondaga Lake, New York. M.S. Thesis, State University of New York, College of Environmental Science and Forestry. 111p.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Total mercury
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-3	L-17	Precision – Field	RSD 35%	Field duplicate samples	S&A
		Precision – Lab	RPD 24%	Laboratory duplicate samples	A
			77-123%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 75–125%	Initial calibration standards	A
			Control limit recovery 71-125%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 75-125%	Laboratory control samples	A
		Contamination	Less than reporting limit (0.4 ng/L)	Field, method, and instrument blanks	A
		Sensitivity	85-115% of expected value for ICV; 77-123% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]ELAP only certified method.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Methyl mercury
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-3	L-18	Precision – Field	RSD 35%	Field duplicate samples	S&A
		Precision – Lab	RPD 35%	Laboratory duplicate samples	A
			67-133%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 65-135%	Initial calibration standards	A
			Control limit recovery 65-135 %	Matrix spike and matrix spike duplicates	A
			Control limit recovery 70-130%	Laboratory control samples	A
		Contamination	Less than reporting limit (0.05 ng/L)	Field, method, and instrument blanks	A
		Sensitivity	80-120% of expected value for ICV; 67-133% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. Brooks Rand uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Zooplankton
Analytical Group[1]	Total mercury
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-4	L-19	Precision – Field	RSD 35%	Field duplicate samples	S&A
		Precision – Lab	RPD 30%	Laboratory duplicate samples	A
			77-123%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 75–125%	Initial calibration standards	A
			Control limit recovery 70-130%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 75-125%	Laboratory control samples	A
		Contamination	Less than reporting limit	Method and instrument blanks	A
		Sensitivity	85-115% of expected value for ICV; 77-123% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. Brooks Rand uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Zooplankton
Analytical Group[1]	Methyl mercury
Concentration Level	Low

Sampling Procedure[2]	Analytical Method/SOP[3]	Data Quality Indicators (DQIs)	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)
S-4	L-18	Precision – Field	RSD 35%	Field duplicate samples	S&A
		Precision – Lab	RPD 35%	Laboratory duplicate samples	A
			67-133%	Ongoing precision and recovery samples	A
		Accuracy/Bias	Five standards with the RSD ≤15% and low standard recovery 65–135%	Initial calibration standards	A
			Control limit recovery 65-135%	Matrix spike and matrix spike duplicates	A
			Control limit recovery 65-135%	Laboratory control samples	A
		Contamination	Less than reporting limit	Method and instrument blanks	A
		Sensitivity	80-120% of expected value for ICV; 67-133% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. Brooks Rand uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.

Matrix	Water
Analytical Group[1]	Nitrate
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	+/-0.05 umol/L	Field duplicate samples	A
		Accuracy/Bias	+/- 2 umol/L	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses the procedure described in Johnson and Coletti (2002).
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Bisulfide (HS^-)
Concentration Level	Low

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	+/-0.05 umol/L	Field duplicate samples	A
		Accuracy/Bias	+/- 2 umol/L	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses the procedure described in Johnson and Coletti (2002).
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Temperature
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	± 0.0003ºC	Field duplicate samples	A
		Accuracy/Bias	± 0.002ºC	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Specific conductance
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	± 0.1 µS/cm	Field duplicate samples	A
		Accuracy/Bias	± 3 µS/cm	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Transmissivity (beam attenuation coefficient at 660 nm)
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	± 0.1% transmission	Field duplicate samples	A
		Accuracy/Bias	± 0.1% transmission	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Turbidity (optical backscattering)
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	± 0.1 NTU	Field duplicate samples	A
		Accuracy/Bias	± 0.25 NTU	Control sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Chlorophyll fluorescence
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	± 0.1 µg/L	Field duplicate samples	A
		Accuracy/Bias	NA		
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Light penetration (photo-synthetically active irradiance)
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-15	Precision – Field	± 5% reading	Field duplicate samples	A
		Accuracy/Bias	± 5% reading	Check sample	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

Matrix	Water
Analytical Group[1]	Total dissolved gas
Concentration Level	Average

Sampling Procedure[2]	**Analytical Method/SOP**[3]	**Data Quality Indicators (DQIs)**	**Measurement Performance Criteria**[4]	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A) or both (S&A)**
NA	L-16	Precision – Field	± 1 mm Hg	Calibration and standardization	A
		Accuracy/Bias	± 6 mm Hg	Calibration and standardization	A
		Completeness	95% for all analyses	Data Completeness Check	S&A

[1]No NELAC/ELAP certification for this test is available. UFI uses an accepted procedure.
[2]Reference number from QAPP Worksheet #21.
[3]Reference number from QAPP Worksheet #23.
[4]Sensors are factory calibrated annually and maintained according to manufacturers instructions.

There are no plans to use secondary data as part of this study, although daily *in situ* robotic measurements from multiple depths, in Onondaga Lake will be collected and available for use as part of this program.

Secondary Data	Data Source (Originating Organization, Report Title, and Date)	Data Generator(s) (Originating Org., Data Types, Data Generation/Collection Dates)	How Data Will Be Used	Limitations on Data Use
Daily robotic measurements from multiple depths	UFI; available on www.ourlake.org	UFI; data includes dissolved oxygen, temperature, specific conductance, pH, fluorometric chlorophyll, and turbidity monitored on a daily basis	Seasonality of thermal stratification, oxygen depletion, plunging inflows, and phytoplankton biomass	No limitations

Sampling Tasks

1. Water Column Monitoring: The two components are water column sampling by boat using techniques summarized in Worksheet #21 and *in situ/in vivo* monitoring with the ISUS rapid robotic profiling instrumentation.
2. Zooplankton Monitoring: Sampling by boat using vertical tows with a zooplankton net (see Worksheet #21).
3. Monitoring of Ebullition: Assessment of gas ebullition with inverted cones.
4. The work plan documents the details of sample locations, depths, SOPs, and water sample collection.

Analysis Tasks

1. UFI will analyze water samples for parameters listed in Worksheet #11. In addition, UFI will conduct the zooplankton taxonomy determinations. Parameters for the *in situ* profiling are listed in Worksheet #11.
2. TestAmerica will analyze water for total mercury. Brooks Rand will analyze water for methylmercury and zooplankton samples for total mercury and methylmercury.

Quality Control Tasks

1. UFI field team leader will evaluate all samples and applicable field quality control samples for acceptability for transport/submission to the laboratory.
2. Implement SOPs for sample collection, packaging, transport, and storage prior to analysis. QC sample handling protocols are described on Worksheet #26.

Secondary Data

See Worksheet #13.

Documentation and Records

1. The QAPP is a UFI controlled document and is subject to all requirements of a controlled document as specified by NELAC.
2. Procedures, observations, and test results will be documented for all sample collection activities, laboratory analyses, and reporting. In addition to data reports provided by the laboratory, reports will be prepared that address data quality and usability and that provide tabulated laboratory and field data.
3. Field data and field profiling instrumentation-related sampling information will be recorded on pre-printed forms, which provide space for comments and suggestions, pertinent observations, and performance and maintenance indicators. Field records will be maintained during all stages of sample collection and preparation for transport to the laboratory.
4. Field records will include the following items:
   a. Field notebook to record daily sampling activities and conditions;
   b. Combined station/sample log to document station locations, depth, date, and time of collection; and
   c. Combined chain-of-custody/sample analysis request forms.

Laboratory Data Reports

1. UFI routinely reports environmental test results using a "simplified" format (NELAC, 2003). Additional detailed information and records related to sampling, testing, and QC results, as required by NELAC, are maintained by the laboratory and are considered a separate laboratory work request.
2. Material amendments to a test report after issue are made only in the form of a further document, or data transfer including the statement "Supplement to Test Report, report number __". Clients are notified promptly, in writing, of any event, such as the identification of defective measuring or test equipment that casts doubt on the validity of the results given in any test report or amendment to a report.

Data and Document Management Tasks

Records generated during sample collection and analyses document the validity and authenticity of the project data. The field and laboratory (electronic and hard-copy) data generated for this study will be retained at UFI's, TestAmerica's or Brooks Rand's facility (as appropriate) in the custody of the respective project manager. In addition, laboratory data will be entered into the Onondaga Lake LocusFocus database by Parsons on behalf of Honeywell. Field logs, sample records, and chain-of-custody records will be kept at UFI's facility for a period of five years.

Data Review Tasks

1. The laboratories will perform data reduction as described in each test method for this project and will submit sample results and QA/QC results.
2. The laboratory quality assurance officer and/or laboratory director are responsible for reviewing the laboratory data and QA/QC reports, and checking data reduction prior to submittal to Honeywell. The laboratory will correct any transcription or computational errors identified during this review.
3. Test results are certified to meet all requirements of the NELAC standards, or reasons are provided if they do not.

Assessment/Audit Tasks

1. Project oversight (field and laboratory) will consist of periodic inspection and audits of sampling and analytical techniques, as required by NELAC/ELAP (annual internal laboratory and field audit; external audit by NELAC/ELAP certified inspectors every two years). No additional field or laboratory audits are planned. Testing and calibration activities will also be reviewed. All audit and review findings and any corrective actions that arise from them will be documented. The laboratory director will ensure that corrective actions are carried out promptly. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, immediate corrective action will be taken, and any client whose work is affected will be notified immediately in writing.
2. The following reports may be completed if a deviation from the field sample matrix or QAPP is encountered, or to document an audit:
   a. Corrective action reports documenting any problems encountered during field activities and corrective actions taken;
   b. System and performance audit reports completed during the investigation and a summary of any changes made to documented procedures, and the rationale for the changes.
3. See Worksheets #31 and #32 for explanation of project assessments, assessment findings, and corrective action responses.

Matrix: Water
Analytical Group: Chlorophyll a
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Chlorophyll a	479-61-8	0.2 µg/L	0.5 µg/L	0.1 µg/L	0.2 µg/L	0.2 µg/L	0.5 µg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Nitrogen (NO_x and NO_2)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
NO_x	11104-93-1	NA	16 µg/L	1 µg/L	5 µg/L	5 µg/L	16 µg/L
NO_2	10102-44-0	NA	9 µg/L	1 µg/L	5 µg/L	3 µg/L	9 µg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Ammonia ($T\text{-}NH_3$)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
$T\text{-}NH_3$	7664-41-7	NA	41 µg/L	2 µg/L	NA	12 µg/L	41 µg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Carbon (DOC and TIC)
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
DOC	None	NA	0.9 mg/L	0.002 mg/L	NA	0.3 mg/L	0.9 mg/L
TIC	None	NA	1.8 mg/L	0.002 mg/L	NA	0.5 mg/L	1.8 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Chloride
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Chloride	16887-00-6	10 mg/L	NA	NA	100 mg/L	NA	100 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Ferrous iron
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Ferrous iron	15438-31-0	NA	0.006 mg/L	NA	0.028 mg/L	0.002 mg/L	0.006 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Sulfide
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Sulfide Method 1	H_2S 7783-06-4 S^{2-} 18496-25-8	NA	1 mg/L	NA	1 mg/L	0.5 mg/L	1 mg/L
Sulfide Method 2	H_2S 7783-06-4 S^{2-} 18496-25-8	NA	0.032 mg/L	NA	0.032 mg/L	0.016 mg/L	0.032 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Dissolved methane
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Dissolved methane	74-82-8	NA	0.5 mg/L	NA	NA	NA	0.5 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods; this information is not available for these specific parameters.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	0.7 ng/L	0.5 ng/L	0.2 ng/L	0.5 ng/L	0.12 ng/L	0.5 ng/L
Methyl mercury	22967-92-6	0.1 ng/L[3]	0.05 ng/L	0.02 ng/L	0.05 ng/L	0.020 ng/L	0.050 ng/L

[1]Analytical MDLs and QLs are those documented in validated methods. TestAmerica is analyzing total mercury; Brooks Rand is analyzing methylmercury.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method. TestAmerica is analyzing total mercury; Brooks Rand is analyzing methylmercury.
[3]This project action limit is draft.

Matrix: Zooplankton
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	NA		0.48 ng/g wet	1.20 ng/g wet	0.04 ng/g[3] wet	0.1 ng/g[3] wet
Methyl mercury	22967-92-6	NA		3.0 ng/g wet	9.0 ng/g wet	0.07 ng/g[4] wet	0.20 ng/g ng[4] wet

[1]Analytical MDLs and QLs are those documented in validated methods. In the case of methyl mercury, detection limits were established by Brooks Rand. Brooks Rand is analyzing both total mercury and methylmercury in zooplankton.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method. Brooks Rand is analyzing both total mercury and methylmercury in zooplankton.
[3]The MDL and QL concentrations are depending on amount of zooplankton collected. For an analysis of 1000 mg, the MDL is 0.04 ng/g wet. If a lower MDL is needed a larger sample amount can be used, or if only a small amount of sample is present (for example 10-20 daphnia), the sample will be digested, and the digested solution will be analyzed by EPA 1631E method to quantify the concentration.
[4]The MDL and QL concentrations are dependent on amount of zooplankton collected or the volume of digest used during analysis. For an analysis of 100 mg, the MDL is 3.0 ng/g wet.

Matrix: Water
Analytical Group: Nitrate
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Nitrate	14797-55-8	NA	0.007 mg/L	NA	0.007 mg/L	NA	0.007 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Matrix: Water
Analytical Group: Bisulfide
Concentration Level: Low

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Bisulfide (HS-)		NA	0.016 mg/L	NA	0.016 mg/L	NA	0.016 mg/L

[1]Analytical MDLs and QLs are those documented in validated methods.
[2]Achievable MDLs and QLs are limits that an individual laboratory can achieve when performing a specific analytical method.

Activities	Organization	Dates (MM/DD/YY)		Deliverable	Deliverable Due Date
		Anticipated Date(s) of Initiation	Anticipated Date of Completion		
Mobilization	UFI	March	April	NA	NA
Water column monitoring	UFI	mid-April	mid-November	NA	NA
Zooplankton sampling	UFI	mid-April	mid-November	NA	NA
In situ/in vivo monitoring	UFI	mid-April	mid-November	NA	NA
Scientific oversight	Exponent	continuous	continuous	NA	NA
Sample analysis	UFI/Brooks Rand	mid-April	December	Unvalidated data	Quarterly
Data Usability and Summary Report (DUSR)	Exponent	January following field season	June following field season	DUSR	June

Describe and provide a rationale for choosing the sampling approach (e.g., grid system, biased statistical approach)

The primary sample location for water sample collection and gas ebullition measurement is South Deep. Historical sampling by UFI and Onondaga County has shown that the water column of Onondaga Lake is well mixed horizontally and long-term monitoring at South Deep provides a historical record of water quality in the lake.

Similarly, zooplankton sampling will occur in the south basin as historical sampling by UFI and Onondaga County has shown communities and concentrations are comparable between north and south basins.

The ISUS gridding will evaluate horizontal homogeneity in the water column for numerous analytes by including measurements along a longitudinal and a lateral transect. Because one future use of ISUS is to monitor nitrate concentrations during a nitrate pilot study and because ISUS is a real-time and thus relatively inexpensive monitoring instrument, it is possible and desirable to understand variability on a smaller scale than sampling at South Deep alone.

Describe the sampling design and rationale in terms of what matrices will be sampled, what analytical groups will be analyzed and at what concentration levels, the sampling locations (including QC, critical, and background samples), the number of samples to be taken, and the sampling frequency (including seasonal considerations) [May refer to map or Worksheet #18 for details]:

See Worksheet #18 for matrices, analytical groups, concentration levels, sampling locations, number of samples, and sampling frequency. The sampling frequency and depths within each month are presented in the table below.

Month	Water Column		
	Frequency	Sampling Date	Depths (m)
April	bi-weekly	4/14, 4/28	2, 12, 19
May	bi-weekly	5/12, 5/26	2, 12, 19
June	bi-weekly	6/9, 6/23	2, 12, 19
July	bi-weekly	7/7, 7/21	2, 12, 16, 18, 19
August	weekly	8/4, 8/11, 8/18, 8/25	2, 12, 16, 18, 19
September	weekly	9/1, 9/8	2, 12, 16, 18, 19
		9/15, 9/22, 9/29	2, 12, 14, 16, 18, 19
October	weekly	10/6, 10/13	2, 12, 14, 16, 18, 19
		10/20, 10/27	2, 6, 12, 14, 16, 18, 19
November	weekly	11/3, 11/10, 11/17, 11/24	2, 6, 12, 14, 16, 18, 19
December	weekly	12/1, 12/8	2, 6, 12, 14, 19

Depths for water sampling were selected to provide a representative epilimnetic sample (2 m), a representative upper hypolimnetic sample (12 m), and a sample near the sediment-water interface (19 m). In addition, when the lake is stratified (July – October), samples will be collected at 16 m and 18 m to provide a gradient of concentrations from the sediment-water interface into the overlying water. Based on historical sampling, this region is where concentrations of mercury and electron acceptors change the most. In addition, 14 m water samples will be collected starting September 15, and 6 m water samples collected starting October 20. Sampling will continue into December for two weeks with water samples collected at 2, 6, 12, 14, and 19 m water depths on December 1 and 8, if field conditions allow samples to be collected on those dates. This plan will provide increased coverage during the critical fall turnover and post-turnover periods. For filtered total mercury, samples will be collected at 2 m (i.e., the epilimnetic sample) because the purpose of the analysis is to compare to surface water quality standards based on protection of human health via fish consumption. The 2 m water depth represents water to which fish are exposed before and after stratification (when the water column is well-mixed) and during stratification when fish are confined to the epiliminion because of reduced oxygen concentrations in the hypolimnion. In addition, dissolved mercury samples will be collected at 14 m depth starting on September 15 through the end of the sampling.

Sampling Location/ID Number	Matrix	Depth (units)	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)[1]	Sampling SOP Reference[2]	Rationale for Sampling Location
South Deep	Water	2, 12 m; See Worksheet #17 for dates	Chlorophyll a	Low	135 (54 env + 54 dups + 27 blanks)	S-1	See Worksheet #17
South Deep	Water	See Worksheet #17	NO_x and NO_2	Low	221 (140 env + 54 dups + 27 blanks)	S-1	
			$T\text{-}NH_3$	Low	221 (140 env + 54 dups + 27 blanks)		
			DOC and TIC	Low	221 (140 env + 54 dups + 27 blanks)		
			Chloride	Low	221 (140 env + 54 dups + 27 blanks)		
			Total mercury	Low	194 (140 env + 27 dups + 27 blanks)	S-3	
			Methyl mercury	Low	194 (140 env + 27 dups + 27 blanks)		
South Deep	Water	2 m biweekly, 14 m biweekly starting 9/15	Filtered total mercury	Low	43 (25 env + 18 dups)	S-3	
South Deep	Water	Anoxic depths; 12, 16, 18, 19 m (mid July – mid-November)	Ferrous iron	Low	91 (52 env + 26 dups + 13 blanks)	S-1 S-2	
			Dissolved methane	Low	91 (52 env + 26 dups + 13 blanks)		

Sampling Location/ID Number	Matrix	Depth (units)	Analytical Group	Concentration Level	Number of Samples (identify field duplicates)[1]	Sampling SOP Reference[2]	Rationale for Sampling Location
South Deep	Water	Anoxic depths; 1-m intervals (mid July – mid-November)	Sulfide method 1[2]	Low	169 (130 env + 26 dups + 13 blanks)	S-1 S-2	
			Sulfide method 2[2]	Low	169 (130 env + 26 dups + 13 blanks)		
South Deep	Zooplankton[4]	13 m vertical tow bi-weekly 4/14 – 10/13, weekly 10/20 – 12/8	Total mercury	Low	27 (25 composites + 2 dups)	S-4	
			Methyl mercury	Low	27 (25 composites + 2 dups)		

[1] Total does not equipment rinsate blanks for mercury analyses.
[2] From the Project Sampling SOP References table (Worksheet #21).
[3]Total number of samples will depend on the time of year and extent of anoxia. This estimate assumes 10 depths per sampling event.
[4]Analyses will also be run on large Daphnia if sufficient numbers are present.

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Water	Chlorophyll	Low	L-8	25 mL–4 L	Opaque plastic bottle (2 or 4 L)	Filter and freeze	21 days
Water	Nitrate/Nitrite as N (NO_x and NO_2)	Low	L-2	2 mL	Opaque plastic bottle (2 or 4 L)	Cool, 4°C	48 hours
Water	Ammonia as N (T-NH_3)	Low	L-3	2 mL	Opaque plastic bottle (2 or 4 L)	Cool, 4°C	48 hours
Water	Organic Carbon, Total/Total Dissolved as C (DOC)	Low	L-4	40 mL	Opaque plastic bottle (2 L)	Cool, 4°C may be preserved	28 days
Water	Carbon, Inorganic Dissolved and Total (TIC)	Low	L-7	40 mL	Glass sample tube (40 mL)	Cool, 4°C	48 hours
Water	Chloride	Low	L-1	250 mL	Opaque plastic bottle (500 mL)	Cool, 4°C	28 days
Water	Ferrous iron	Low	L-10	20 mL	Dark BOD bottle (300 mL)	Cool, 4°C	7 days
Water	Sulfide as S (Method 1)	Low	L-5	300 mL	BOD bottle (300 mL)	Cool, 4°C	7 days
Water	Sulfide as S (Method 2)	Low	L-6	150 mL	BOD bottle (300 mL)	Cool, 4°C	7 days
Water	Dissolved methane)	Low	L-9	20 mL	BOD bottle (300 mL)	Cool, 4°C	7 days
Water	Total mercury	Low	L-11	500 mL	Plastic[2], glass or Teflon bottle (500 mL or 1 L)	HCl, cool, 4°C	28 days (unpreserved), 90 days (preserved)

Matrix	Analytical Group	Concentration Level	Analytical and Preparation Method/SOP Reference[1]	Sample Volume	Containers (number, size, and type)	Preservation Requirements (chemical, temperature, light protected)	Maximum Holding Time (preparation/ analysis)
Water	Methyl mercury	Low	L-12	500 mL	Plastic[2] or Teflon bottle (500 mL or 1 L)	HCl, cool, 4°C	6 months (preserved)
Zooplankton	Total and methyl mercury	Low	L-12, L-13	1-5 g (preferably 2-10 g)	Plastic[2] or Teflon bottle (250 - 500 ml)	cool, 4°C, freeze upon receipt, or freeze dry	6 months (preserved)

[1]From the Analytical SOP References table (Worksheet #23).
[2]Plastic bottles for mercury samples are fluorinated high density polyethylene.

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS[3]	No. of Field Blanks[4]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Chlorophyll	Low	L-8	1 station, 2 depths, 27 sampling trips (54 samples)	Triplicate sets 27 (54 samples)		27			135
Water	Nitrate/Nitrite as N (NO_x)	Low	L-2	1 station, 3–7 depths, 27 sampling trips (140 samples)	Triplicate sets 26 (54 samples)		27			221
Water	Nitrate as N (NO_2)	Low	L-2	1 station, 3–7 depths, 27 sampling trips (140 samples)	Triplicate sets 27 (54 samples)		27			221
Water	Ammonia as N ($T\text{-}NH_3$)	Low	L-3	1 station, 3–7 depths, 27 sampling trips (140 samples)	Triplicate sets 27 (54 samples)		27			221
Water	Organic Carbon, Total/Total Dissolved as C (DOC)	Low	L-4	1 station, 3–7 depths, 27sampling trips (140 samples)	Triplicate sets 27 (54 samples)		27			221
Water	Carbon, Inorganic Dissolved and Total (TIC)	Low	L-7	1 station, 3–7 depths, 27 sampling trips (140 samples)	Triplicate sets 27 (54 samples)		27			221

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS[3]	No. of Field Blanks[4]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Chloride	Low	L-1	1 station, 3–7 depths, 27 sampling trips (140 samples)	Triplicate sets 27 (54 samples)		27			221
Water	Ferrous iron	Low	L-10	1 station, 4 depths, 13 sampling trips (52 samples)	Triplicate sets 13 (26 samples)		13			91
Water	Dissolved methane	Low	L-9	1 stations, 4 depths, 13 sampling trips (52 samples)	Triplicate sets 13 (26 samples)		13			91
Water	Sulfide as S (Method 1)	Low	L-5	1 station, ~10 depths, 13 sampling trips (130 samples)	Triplicate sets 13 (26 samples)		13			169[5]
Water	Sulfide as S (Method 2)	Low	L-6	1 station, ~10 depths, 13 sampling trips (130 samples)	Triplicate sets 13 (26 samples)		13			169[5]
Water	Total mercury	Low	L-11	1 station, 3–7 depths, 27 sampling trips (140 samples)	27		27	4		198
Water	Filtered mercury	Low	L-11	1 station, 1-2 depths, 27 sampling trips (27 samples)	27					54

Matrix	Analytical Group	Concen-tration Level	Analytical and Preparation SOP Reference[1]	No. of Sampling Locations[2]	No. of Field Duplicate Pairs	Inorganic No. of MS[3]	No. of Field Blanks[4]	No. of Equip. Blanks	No. of PT Samples	Total No. of Samples to Lab
Water	Methyl mercury	Low	L-12	1 station, 3–7 depths; 26 sampling trips (140 samples)	27		27	4		198
Zoo-plankton assembla-ges	Total and methyl mercury	Low	L-12, L-13,	1 station, 25 sampling trips (25 samples)	2					27
Zoo-plankton – Daphnia[6]	Total and methyl mercury	Low	L-12, L-13	1 station, up to 10 sampling trips (up to 10 samples)	1					10

[1]From the Analytical SOP References table (Worksheet #23).
[2]Samples collected at different depths at the same location are counted separately.
[3]Matrix spike and matrix spike duplicate samples will be prepared by the laboratory at a frequency of at least one pair per 20 samples.
[4]A field blank for non-mercury analyses is termed a "field trip blank" by the laboratory (UFI) and, as defined in the work plan, will consist of sample bottles that are filled in the laboratory, transported to the field and then back to the laboratory for analysis. A field blank for total mercury and methyl mercury will consist of mercury-free water (i.e., water containing mercury at concentrations below the minimum detection limit) placed in a clean sample bottle in the laboratory, transported to the field, and then poured into a second clean sample bottle for transport back to the laboratory.
[5]Total number of samples will depend on the time of year and extent of anoxia. This estimate assumes 10 depths per sampling event.
[6] *Daphnia* will be analyzed for total Hg and CH_3Hg if sufficient numbers are present to conduct laboratory analyses.

Reference Number	Title, Revision Date and/or Number[1]	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
S-1	UFI SOP 304 Water sample collection: submersible pump	UFI	Submersible pump with conduit, marine battery, collection bottles.	N	Includes descriptions and procedures for sampling with submersible pump
S-2	UFI SOP 306 Reduced species (H_2S, CH_4, and Fe^{2+}) sample collection	UFI	Submersible pump with conduit and a marine battery or a Kemmerer or Van Dorn, reduced species collection bottles, reagent cooler with bottles of zinc acetate solution and 6 N NaOH solution.	N	Includes descriptions and procedures for sampling and preservation of reduced species samples.
S-3	SU SOP AP # CESE-ENV-1669 Sampling stream and lake water for mercury at trace levels	SU	Peristaltic or submersible pump and precleaned fluoropolymer or styrene/ethylene/butylene/silicone (SEBS) tubing. A side arm filter apparatus is used for samples being analyzed for dissolved metals.	N	Includes descriptions and procedures for collecting low level mercury samples. NYSDEC (2007) approved discontinuing use of protective suits for surface water sampling by trained UFI and SU field personnel.

Reference Number	Title, Revision Date and/or Number[1]	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
S-4	SU SOP AP #CESE-ENV-310 Zooplankton sample collection and preservation and Secchi depth measurement field procedures	SU	A sampling net (diameter of 30 cm, length with cup 1m, and a mesh size of 64 µm) is slowly lowered to a depth.	N	Includes descriptions and procedures for sampling with mesh net. Note that zooplankton samples for this project are analyzed within 48 hours and are NOT preserved with AlkaSeltzer and ethanol.
S-5	UFI SOP 311 Gas cone deployment and collection	UFI	Gas cone (0.75 m diameter, concave polycarbonate plastic cone with stainless steel frame) with attached, inverted separatory funnel (500 ml or 1000 ml), cable or rope, marker buoy, tether rope, research (large white) marker buoy, cable or rope, and an anchor. For gas composition sampling, include a Pressure-Lok Series A Precision Analytical Syringe (Supelco brand).	N	Includes descriptions and procedures for collecting ebullient gas.

[1]All SOPs are available as attachments to Appendix B, the Quality Assurance Project Plan for the 2007 Nitrate Evaluation Study (UFI and SU, 2007).

References:

NYSDEC. 2007. Personal communication (letter from T.J. Larson, NYSDEC, to J.P. McAuliffe, Honeywell, dated December 7, 2007, regarding Onondaga Lake Bottom Subsite - Request to Discontinue Use of Protective Suits for Low-Level Mercury Sampling). NYSDEC, Albany, NY.

UFI and SU. 2007. Work Plan for Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake, 2007 Study. Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Syracuse, NY. May 2007. [Appendix B dated January 22, 2008.]

Field Equipment Calibration, Maintenance, Testing, and Inspection Table

Field Equipment	Calibration Activity	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference
Submersible pump and tubing	Check flow rate at beginning of field season	Rinse with tap water, flush with 10% HCl solution and then DI water. Drain and store in sealed container.		Check for physical damage and/or leaks	Weekly	Visual inspection	Repair as soon as possible (in field if possible or back at the lab)	B. Wagner	S-1[1]
ISUS profiler	Calibrated at factory, Perform routine DI water check in field before and after each use, DI water check done weekly in the lab to verify instrument is operating correctly	Rinse all sensors with DI water, gently wipe all sensors dry using optical lens paper	DI water checks	Check for physical damage, verify data looks correct and instrument is performing as per manufacturers instructions	DI water check with each use	Compare with laboratory ground-truth data, verify DI water checks are within ±2 μM	Repair as soon as possible (in field if possible or back at the lab)	A. Prestigiacomo	L-16[2]

[1] From the Project Sampling SOP References table (Worksheet #21).[2] From the Analytical SOP References table (Worksheet #23).

Reference Number	Title, Revision Date, and/or Number[1]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
L-1	UFI SOP 104 - Chloride, high range (SM 18–20 4500 Cl^- C)	Definitive	Chloride	Titration	UFI	N
L-2	UFI SOP 106.1 - Nitrate/Nitrite (as N) (U.S. EPA Method 353.2)	Definitive	NO_x and NO_2	Segmented Flow Analysis (SFA) system (OI Analytical Flow Solution IV) – Model 502	UFI	N
L-3	UFI SOP 105.1 - Ammonia (as N) (U.S. EPA Method 350.1)	Definitive	T-NH_3	Segmented Flow Analysis (SFA) system (OI Analytical Flow Solution IV) – Model 502	UFI	N
L-4	UFI SOP 110 - Organic carbon, total/total dissolved (as C) (SM 18–20 5310C)	Definitive	DOC	Phoenix 8000 Carbon analyzer	UFI	N
L-5	UFI SOP 112 - Sulfide (as S), high range (SM 18 4500 S^{2-} E)	Definitive	Sulfide	Titration	UFI	N
L-6	UFI SOP 212 - Sulfide (as S), high range (SM 20 4500 S^- G)	Definitive	Sulfide	Ion-selective electrode	UFI	N
L-7	UFI SOP 203 - Carbon, inorganic dissolved and total (SM 18-20 5310C)	Definitive	DIC	Phoenix 8000 Carbon analyzer	UFI	N
L-8	UFI SOP 216 - Chlorophyll (U.S. EPA 445)	Definitive	Chlorophyll	Model TD-700 Fluorometer	UFI	N
L-9	UFI SOP 217 - Dissolved gas: methane, carbon dioxide, nitrogen (Addess 1990)	Definitive	Dissolved methane	GOW-MAC gas chromatograph	UFI	N
L-10	UFI SOP 218 - Ferrous iron (Heaney and Davidson 1977)	Definitive	Ferrous iron	Spectrophotometer	UFI	N
L-15	UFI SOP UFI-ISUS/Optical frame	Definitive	Nitrate	Satlantic Inc., ISUS0095	UFI	N
		Definitive	Bisulfide	Satlantic Inc., ISUS0095	UFI	N

Reference Number	Title, Revision Date, and/or Number[1]	Definitive or Screening Data	Analytical Group	Instrument	Organization Performing Analysis	Modified for Project Work? (Y/N)
		Definitive	Temperature	SeaBird Elec, Inc., SBE 37-SI MicroCAT	UFI	N
		Definitive	Specific conductance	SeaBird Elec, Inc., SBE 37-SI MicroCAT	UFI	N
		Definitive	Transmissivity	WET Labs, C-Star	UFI	N
		Definitive	Turbidity	WET Labs, Eco Triplet-BB2 FL	UFI	N
		Definitive	Chlorophyll	WET Labs, Eco Triplet-BB2 FL	UFI	N
		Definitive	Light penetration	Biospherical Instruments, QSP-2150	UFI	N
L-16	UFI SOP Tensionometer In-Situ Inc. 300E	Definitive	Total dissolved gas	In-Situ Inc. Tensionometer 300E	UFI	N
L-17	SOP No. NC-MT-0001 (Revision No. 5.1) Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence, Methods 1631E and MCAWW 245.7	Definitive	Total mercury	Atomic Fluorescence Spectrophotometer	TestAmerica	N
L-18	SOP #BR-0011 Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630	Definitive	Methyl mercury	Brooks Rand Model III CVAFS	Brooks Rand	N
L-19	SOP #BR-0002 BRL Procedure for EPA Method 1631, Appendix: Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion, BrCl Oxidation, and Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)	Definitive	Total mercury	Brooks Rand Model III CVAFS	Brooks Rand	N

[1]All SOPs, except L-16 through L-19 are available as attachments to Appendix B, the Quality Assurance Project Plan for the 2007 Nitrate Evaluation Study (UFI and SU, 2008). L-16 through L-19 are provided in Attachment 1 to this QAPP.

Reference:

UFI and SU. 2007. Work Plan for Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake, 2007 Study. Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Syracuse, NY. May 2007. [Appendix B dated January 22, 2008.]

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
OI Analytical Flow Solution IV Model 502	See UFI SOP 106.1 See UFI SOP 105.1	Standards are placed at the start of every sample run.	The software calculates the standard curves and QC acceptance limits. The R^2 for the standards should be no less than 0.995.	Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.	Laboratory Staff	L-2 and L-3
		Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-4
Phoenix 8000 Carbon analyzer	See UFI SOP 110 See UFI SOP 203	Initial calibration after instrument set up. Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run..	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-4 and L-7

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Ion-selective electrode (sulfide)	See UFI SOP 212.1	Check electrode performance and calibrate with each use. Check electrode potential in a sulfide standard every 2 hours.	Change in potential should be within ±2 mV	Follow troubleshooting procedure in the electrode manual.	Laboratory Staff	L-6
Model TD-700 Fluorometer	See UFI SOP 216	Initial calibration after instrument set up. The calibration can be checked with each use with the solid standard. The instrument will need to be recalibrated if ranges are changed (low to high or visa versa) or if lamps or filters are changed.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.	Laboratory Staff	L-8

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
GOW-MAC gas chromatograph	See UFI SOP 217	Initial calibration after instrument set up. Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run. NOTE: If curve is not run daily, highest standard must be run as a continuing calibration verification sample (CCV).	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-9
Spectrophotometer	See UFI SOP 218	Initial calibration after instrument set up. Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a minimum of 10 values	Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-10
CVAFS	See Test America SOP No. NC-MT-0001 (Revision No. 5.1) Preparation and Analysis of Mercury	Initial Calibration - Daily prior to sample analysis	6 standards with the RSD $\leq$15%, or R2 $\geq$ 0.995 Low Std. Recovery 75–125%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	L-17

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
	in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence, Methods 1631E and MCAWW 245.7	Initial Calibration Verification - Immediately after Initial calibration	85-115% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		
		Continuing Calibration Verification - After every ten samples and at the end of the run	77-123 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCV must be reanalyzed		
Brooks Rand Model III CVAFS	See Brooks Rand SOP #BR-0011	Initial calibration after instrument set up	5 standards with the RSD $\leq$15%, Low Std. or R2 $\geq$ 0.995 Recovery 63-135%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	L-18
		ICV Immediately after Initial calibration	80-120% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		
Brooks Rand Model III CVAFS *(continued)*	Brooks Rand SOP #BR-0011 *(continued)*	CCV after every ten samples and at the end of the run	67-133 % of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCV must be reanalyzed	Laboratory Staff	L-18

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Brooks Rand Model III CVAFS	Brooks Rand SOP #BR-0002	Daily prior to sample analysis	5 standards with the RSD ≤15%, or R2 ≥ 0.995 Low Std. Recovery 75–125%	1. Reanalyze standards 2. Remake and reanalyze standards 3. Change all peristaltic pump tubes	Laboratory Staff	L-19
		ICV Immediately after Initial calibration	85-115% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration		
		CCV after every ten samples and at the end of the run	77-123% of expected value	1. Reanalyze 2. If criteria are still not met, repeat initial calibration 3. All samples analyzed after the last passing CCV must be reanalyzed		
Satlantic Inc., ISUS0095	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	DI water check, ±2 μM	Perform new DI water calibration; if that fails send back to manufacturer for recalibration	T. Prestigiacomo	L-15
SeaBird Elec, Inc., SBE 37-SI MicroCAT	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent with ground-truth and other laboratory parameters	Annual recalibration	T. Prestigiacomo	L-15
WET Labs, C-Star	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent with ground-truth and other laboratory parameters	Annual recalibration	T. Prestigiacomo	L-15

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
WET Labs, Eco Triplet-BB2 FL	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent with values expected for this parameter	Annual recalibration	T. Prestigiacomo	L-15
Biospherical Instruments, QSP-2150	See UFI SOP UFI-ISUS/Optical frame profiling and maintenance	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent values expected for this parameter	Annual recalibration	T. Prestigiacomo	L-15
In-Situ Inc. Tensionometer 300E	See UFI SOP - Tensionometer In-Situ Inc. 300E	Factory calibrated and maintained according to manufacturers instructions	Ensure data are consistent values expected for this parameter. Conduct manufacturers recommended performance checks.	Annual recalibration	T. Prestigiacomo	L-16

[1]From the Analytical SOP References table (Worksheet #23).

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
OI Analytical Flow Solution IV – Model 502 Nitrogen Analyzer	Tubing and reagents routinely changed, system lines cleaned	Semi-annual PT samples	Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-2 and L-3
Phoenix 8000 Carbon Analyzer	Check connections, clean lines, change tubing, reagents and halogen scrubber	Semi-annual PT samples	Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-4
Ion Selective Electrode (Sulfide)	Maintain internal solution levels	Annual PT samples from independent supplier	Visual inspection of electrode with each use	As required by manufacturer or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-6
TD-700 Fluorometer	Check lamps	Standardize with liquid chlorophyll standards every 3 months	Visual inspection of hardware with each use	As required to maintain instrument in proper working order	Standards have < 5% RSD	Re-run standards, investigate and document any potential problems	Laboratory staff	L-8

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
GOW-MAC GC	Keep lines clear, check/ change septum as needed	Compare current recoveries to previous/ historic recoveries	Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Reproducible standards and a low blank	Re-run standards, investigate and document any potential problems	Laboratory staff	L-9
Spectrophotometer	Change bulb as needed, annual inspection by manufacturer		Visual inspection of hardware with each use	As required by NELAC or to maintain instrument in proper working order	Calibration curve should have a R2 ≥ 0.995	Remake standards, investigate and document any potential problems	Laboratory staff	L-10
Leeman Labs Hydra AF gold plus, CVAFS	Routine inspections, check intensity of Hg lamp, inspect liquid/gas separator and Nafion Dryer	Change liquid/gas separator and Nafion Dryer	Check argon flow, pump tubing, drain, and soda lime drying tube	Daily except check intensity of Hg lamp semiannually and inspect/change liquid/gas separator and Nafion Dryer as needed		Change Hg lamp and/or liquid/gas separator and Nafion Dryer	Analyst	L-17
Brooks-Rand Model III CVAFS	Check ethylation agent and analytical system	Analyze primer and blank	Visual check shape of peak and response	At start of an analysis run	Calibration curve should have a %RSD ≤15 % or R2 ≥ 0.995	Re-calibrate, compare against 2nd source, and OPR	Analyst	L-18, L-19

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Satlantic Inc., ISUS0095	Rinse with deioinized water and gently wipe sensor dry with optical lens paper	Pre-cast and post-cast deionized water checks for the nitrate sensor are required each day the unit is deployed.	Visual inspection of hardware with each use	Daily	Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences and presence of data points outside parameter detection range values.	Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (i.e., instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.		L-15
SeaBird Elec, Inc., SBE 37-SI MicroCAT WET Labs, C-Star WET Labs, Eco Triplet-BB2 FL	Rinse with deioinized water and gently wipe sensor dry with optical		Visual inspection of hardware with each use	Daily	Assessment of results is done at UFI facilities (post collection). Acceptance	Identify data that fail QA/QC, record throughout data transfer to client. Analyze		L-15

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
Biospherical Instruments, QSP-2150	lens paper				criteria for quality control include consideration of field notation concerning interferences and presence of data points outside parameter detection range values.	cause of unacceptable data (i.e., instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.		
In-Situ Inc. Tensionometer 300E	Cleaning with clean water	Calibrate and standardize as recommended by manufacturer	Visual inspection	Prior to use	As per manufacturer – listed in SOP.	Return instrument to manufacturer for repair and recalibration if deemed necessary.	Field staff	L-16

[1]Specify the appropriate reference letter or number from the Analytical SOP References table (Worksheet #23).

SAMPLE COLLECTION, PACKAGING, AND SHIPMENT
Sample Collection (Personnel/Organization): MaryGail Perkins, UFI,
Sample Packaging (Personnel/Organization): MaryGail Perkins, UFI,
Coordination of Shipment (Personnel/Organization): MaryGail Perkins, UFI,
Type of Shipment/Carrier: Samples delivered in person by field sampling team to UFI laboratory; Samples for mercury analysis shipped on ice by overnight shipment to TestAmerica and Brooks Rand
SAMPLE RECEIPT AND ANALYSIS
Sample Receipt (Personnel/Organization): Laboratory staff (UFI, TestAmerica, Brooks Rand)
Sample Custody and Storage (Personnel/Organization): Laboratory staff (UFI, TestAmerica, Brooks Rand)
Sample Preparation (Personnel/Organization): Laboratory staff (UFI, TestAmerica, Brooks Rand)
Sample Determinative Analysis (Personnel/Organization): Laboratory staff (UFI, TestAmerica, Brooks Rand)
SAMPLE ARCHIVING
Field Sample Storage (No. of days from sample collection): See Worksheet #19
Sample Extract/Digestate Storage (No. of days from extraction/digestion): See Worksheet #19
Biological Sample Storage (No. of days from sample collection): See Worksheet #19
SAMPLE DISPOSAL
Personnel/Organization: Laboratory staff (UFI, TestAmerica, Brooks Rand)
Number of Days from Analysis: 60 days

Field Sample Custody Procedures (sample collection, packaging, shipment, and delivery to laboratory):

Standard procedures for sample collection and shipping will be followed to ensure that samples are preserved and stored as required (Worksheet #19). All field measurements and sample collection activities will follow approved standard operating procedures as noted in UFI's "*Environmental Sample Collection Quality and Field Methods Manual*" and SU's SOPs. The general procedure is as follows:

- Water samples will be collected by UFI personnel for the purpose of determining chemical concentrations in the water column. All mercury samples will be collected using a continuous flow sampling device. The sampling device will consist of Teflon-lined tubing connected to a non-metallic submersible pump, consistent with EPA Method 1669 and SU's field sampling SOP.
- Appropriate field notes will be taken throughout the sampling process, and sample locations, depths, and types will be checked/verified against the field sampling matrix (FSM) in the project work plan.
- Samples will be kept on ice and stored in the dark while in the field.
- Any sample-handling difficulties that are encountered in the field will be described in the field log.
- The samples will be delivered to the appropriate laboratory (UFI or Brooks Rand) with a fully documented chain-of-custody form.
- Field personnel are responsible for making sure all documentation has been completed and turned over to the laboratory and/or other support personnel.
- The field log will be reviewed and sample integrity verified as part of the data validation procedures.

Laboratory Sample Custody Procedures (receipt of samples, archiving, disposal):

On receipt, laboratory personnel will check samples, and the cooler temperature will be determined. The temperature and condition of the samples will be recorded at the laboratory, and any problems will be described in the narrative for the data report. The field log and narrative will be reviewed during the quality assurance review, and data will be flagged if the sample integrity was compromised. Data may be rejected as unusable if severe handling problems are encountered.

Sample Identification Procedures:

The laboratory will log in the samples, verify the sample containers/labels against the chain of custody, and assign a unique sample identification number to each sample, which will be attached to that sample throughout the life of the sample. Laboratory personnel are responsible for verifying that all required documentation has been completed by field personnel. Laboratory records related to sample handling and analysis are maintained through all stages of the analytical process. All laboratory processes, activities, and SOPs comply with NELAC standards and are fully documented in the UFI document "Environmental Testing Laboratory Quality Assurance Manual" and the Brooks Rand Comprehensive Quality Assurance Plan.

Chain-of-custody Procedures:

A continuous record of the possession and proper handling of samples must be documented, so that sample custody and handling are traceable from the time of sample collection until the analytical data have been validated and accepted for use.

Matrix	Water
Analytical Group	Chlorophyll a
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-8
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheets #17 and 18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per batch	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit

Matrix	Water
Analytical Group	NO_x
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-2
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10–15 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Laboratory control samples (LCS)	1 per sample run	Control limit recover 82 – 115 µg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 65 – 127 µg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	NO_2
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-2
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10–15 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Laboratory control samples (LCS)	1 per sample run	Control limit recover 83.5 – 107.5 µg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 87.5 – 108.5 µg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	$T\text{-}NH_3$
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-3
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10–15 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Laboratory control samples (LCS)	1 per sample run	Control limit recovery 51 – 143 µg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recovery 66 – 121µg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	DOC
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-4
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples or one per run	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration verification (ICV/CCV)	1st CCV at the beginning of a run and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Laboratory control samples (LCS)	1 per sample batch	Control limit recovery 78.6 – 138.2 mg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 58.7 – 134.9 mg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	TIC
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-7
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	Every sample batch	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples following CCV	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st sample and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Chloride
Concentration Level	Low
Sampling SOP	S-1
Analytical Method/ SOP Reference	L-1
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 per sample run	Control limit recover 78 – 130 mg/L	Reanalyze and/or report LCS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)
Matrix spike sample (MS)	1 every 20 samples or 1 per batch if less than 20 samples	Control limit recover 59.8 – 145.4 mg/L	Reanalyze and/or report MS as failed	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Ferrous iron
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-10
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheets #17 and 18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample run, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	Every sample batch	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples, following CCV	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	No more than 15% greater than the limit of quantification or method reporting limit
Initial and continuing calibration verification (ICV/CCV)	1st sample in a run and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Sulfide (Method 1)
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-5
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #17 and 18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%

Matrix	Water
Analytical Group	NO_2
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-6
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheets #17 and 18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Reference	Every sample run	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	Reanalyze, up to one time, remake and reanalyze standards and reference until it passes	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial and continuing calibration blanks (ICB/CCB)	1st CCB in a run and every 10 samples following the CCV	Less than Level of Detection	Reanalyze and/or report data as associated with failed ICB, repeat calibration and analysis if necessary	Laboratory staff	Contamination	Warning Limit = LOD; Control Limit = LOQ
Initial and continuing calibration verification (ICV/CCV)	1st sample, one per sample run and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Dissolved methane
Concentration Level	Low
Sampling SOP	S-1 and S-2
Analytical Method/ SOP Reference	L-9
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	UFI
No. of Sample Locations	See Worksheets #17 and 18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field triplicate	Every sample batch	RSD 35%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 35%
Laboratory duplicate	1 every 10 samples or one per sample batch, if fewer than 10 samples	RPD within 10% for warning limits, 15% for control limits	Reanalyze and/or report a failed duplicate.	Laboratory staff	Precision - Lab	RPD within 10% for warning limits, 15% for control limits
Initial and continuing calibration verification (ICV/CCV)	1st sample and every 10 samples afterwards, and the last sample of any run. Note: If curve is not run daily, highest standard must be run as a CCV.	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	ICV: Reanalyze, up to one time, remake and reanalyze standards and ICV until it passes CCV: Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary	Laboratory staff	Accuracy/Bias	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value • Mean value: based on a monthly moving average (with a minimum of 10 values)

Matrix	Water
Analytical Group	Total Mercury
Concentration Level	Ultra Low
Sampling SOP	S-4
Analytical Method/ SOP Reference	L-17
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	TestAmerica
No. of Sample Locations	See Worksheet #17.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RPD 20%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.		Precision - Field	RPD 20%
Equipment rinsate blank (Sampling equipment)	4 per sampling season		• Reanalyze. • If criteria are still not met, repeat initial calibration.	Lab	Contamination	< MRL
Initial Calibration Verification (ICV/QCS)	Beginning of every analytical sequence	80-120%	If initial is out, terminate analysis; correct the problem; recalibrate or reprep with calibration curve.	Lab	Precision - Lab	80-120% of expected value for ICV.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	One per sample preparation batch of up to 20 samples. Note: additional prep blanks(s) required if additional BrCl needed in some sample(s).	The result must be within +/- RL.	• Redigest and reanalyze samples. • Sample results greater than 20x the blank concentration are acceptable.	Lab	Contamination	The result must be within +/- the RL
Initial Calibration Blank (ICB)	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL (0.5 ng/L for aqueous, 1.25 ng/L for solid)	• Terminate analysis; correct the problem; recalibrate or reprep with calibration curve.	Lab	Contamination	The result must be within +/- the RL
Initial calibration	Daily prior to sample analysis/as per method	6 standards with the RSD $\leq$15%, Low Std One standard must be at the reporting limit.	• Correct the problem and reanalyze standards • Remake and reanalyze standards	Lab	Accuracy/Bias	6 standards with the RSD $\leq$15%
Continuing calibration verification samples (CCV/OPR)	After every 10 samples and at the end of each run	77-123% of expected value for CCV samples	• Terminate analysis, correct the problem • Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve.	Lab	Accuracy/Bias	77-123% of expected value for CCV samples
Laboratory control samples (LCS)	One per sample preparation batch of up to 20 samples	75-125% of expected value for aqueous samples	• Terminate analysis, correct the problem. • If recovery is high and the analyte is not detected, document excursion only. • Redigest and reanalyze all samples associated with the LCS.	Lab	Accuracy/Bias	Recovery within appropriate control limits (75–125%)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike and matrix spike duplicate samples (MS/MSD)	2 sets per sample preparation batch of up to 20 samples. If insufficient volume has been provided a Duplicate Laboratory Control Sample may be prepared and analyzed.	Recovery (71–125%) and RPD (<24%)	• If Recovery is not within QC limits, the LCS must be in control. • If the RPD is >24 %, document the excursion.	Lab	Accuracy/Bias	Flag the data, no flag required if the sample level is > 4Xthe spike added.

Matrix	Water
Analytical Group	Methyl Mercury
Concentration Level	Ultra Low
Sampling SOP	S-4
Analytical Method/ SOP Reference	L-18
Sampler's Name	B. Wagner
Field Sampling Organization	UFI
Analytical Organization	Brooks Rand
No. of Sample Locations	See Worksheet #18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	1 per sampling event	RSD 35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision – Field	RSD 35%
Equipment rinsate blank (Sampling equipment)	4 per sampling season	< MRL	• Reanalyze for verification • Notify client	Frank McFarland	Contamination	< MRL
Laboratory duplicate	1 every 10 samples	RPD 35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision – Lab	RPD 35%

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Initial precision and recovery (IPR)	Set of four analyses	IPR within s (31%) and X (69–131%)	• Reanalyze	Frank McFarland	Initial method implementation and Precision – Lab	IPR within s (31%) and X (69–131%)
Ethylation Blank	Immediately after initial calibration,	Less than reporting limit	• Reanalyze • If criteria are still not met, repeat initial calibration • Change air bubble tubing	Frank McFarland		
Method blank	3 with every batch of samples	Average less than 2x MDL; StDev less than 2/3rds MDL	• Reanalyze for verification • If criteria are still not met, calculate batch specific MDL using standard deviation of the method blanks • If samples are non-detects using elevated detection limits, then redistill the affected samples and reanalyze at client's request	Frank McFarland	Contamination	Average less than 2x MDL; StDev less than 2/3rds MDL
Instrument blank	Immediately after initial calibration and after every CCV	Less than reporting limit	• Reanalyze until passes • If criteria are still not met, repeat initial calibration • All samples analyzed on affected quipment must be reanalyzed •	Frank McFarland	Contamination	Less than reporting limit
Initial calibration	Calibrate prior to sample analysis/as per method	5 standards with the RSD ≤15%, Low Std. Recovery 65-135%	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Frank McFarland	Accuracy/Bias	5 standards with the RSD ≤15%, Low Std. Recovery 65–135%
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	80-120% of expected value for ICV; 67-133% of expected value for CCV samples	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Frank McFarland	Accuracy/Bias	80-120% of expected value for ICV; 67-133% of expected value for CCV samples

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Laboratory control samples (LCS)	1 with every batch of samples	Recovery within appropriate control limits (70-130%) or as specified in QAPP.	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Frank McFarland	Accuracy/Bias	Recovery within appropriate control limits (70–130%)
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	Recovery (65-130%) and RPD (35%) or as specified in QAPP	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recovery is within QC limit, and RPD criterion is not met, reanalyze.	Frank McFarland	Accuracy/Bias	Recovery 65–135%
Method Detection Limit (MDL) Minimum reportable Limit (MRL)	Daily prior to sample analysis	0.02 ng/L 0.05 ng/L	• Reanalyze • If criteria are still not met, reprep blank and all associated samples • If concentration is high and the analyte is not detected, document excursion	Frank McFarland	Accuracy/Bias	0.02 ng/L 0.05 ng/L

Matrix	Zooplankton
Analytical Group	Total and methyl mercury
Concentration Level	Low
Sampling SOP	S-4
Analytical Method/ SOP Reference	L-18, L-19
Sampler's Name	UFI
Field Sampling Organization	B. Wagner
Analytical Organization	Brooks Rand
No. of Sample Locations	See Worksheet #18.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Field duplicate	2 per sampling season	RPD 35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision - Field	RPD 35%
Laboratory duplicate	1 every 10 samples	Total mercury RPD < 30%; Methyl mercury RPD < 35%	• If < 5x MRL or is non-detect, the MS/MSD will be used for precision. • If MS/MSD does not meet precision criteria requirements, sample will be reanalyzed.	Frank McFarland	Precision - Lab	Total mercury RPD < 30%; Methyl mercury RPD < 35%
Ongoing Precision and Recover (OPR)	1 at the beginning and end of every batch	77-123% (THg) 67-133% (MeHg)	• If initial is out, reanalyze. • If closing is out, reanalyze, if still out, review last CCV that was run and follow CCV criteria.	Frank McFarland	Precision - Lab	77-123% (THg) 67-133% (MeHg)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Method blank	3 per every batch of sample	Average less than 2x MDL; StDev less than 2/3rds MDL	• Reanalyze for verification • If criteria are still not met, calculate batch specific MDL using standard deviation of the method blanks	Frank McFarland	Contamination	Average less than 2x MDL; StDev less than 2/3rds MDL
Instrument blank	Immediately after initial calibration and after every CCV	Less than reporting limit	• Reanalyze until passes • If criteria are still not met, repeat initial calibration • All samples analyzed on affected equipment must be reanalyzed •	Frank McFarland	Contamination	Less than reporting limit
Initial calibration	Calibrate prior to sample analysis/as per method	5 standards with the RSD ≤15%, Low Std. Recovery 75–125%(THg) 69-135% (MeHg)	• Reanalyze standards • Remake and reanalyze standards • Change all peristaltic pump tubes	Frank McFarland	Accuracy/Bias	5 standards with the RSD ≤15%, Low Std. Recovery 75–125%(THg) 69-135% (MeHg)
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	85-115% for T Hg and 80-120% for MeHg for ICV; 77-123% for T Hg and 67-133% for MeHg for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Frank McFarland	Accuracy/Bias	85-115% for T Hg and 80-120% for MeHg for ICV; 77-123% for T Hg and 67-133% for MeHg for CCV
Quality control sample (QCS)	Immediately after initial calibration	75-125% (THg) 65-135% (MeHg)	• Reanalyze • Remake and reanalyze ICV • If criteria are still not met, repeat initial calibration	Frank McFarland	Accuracy/Bias	75-125% (THg) 65-135% (MeHg)
Laboratory control samples (LCS)	1 with every batch of samples	75-125% (THg) 65-135% (MeHg)	• Reanalyze • If criteria are still not met, reprep LCS and all associated sample. • If recovery is high and the analyte is not detected, document excursion only	Frank McFarland	Accuracy/Bias	75-125% (THg) 65-135% (MeHg)

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 10 samples or 4 every 20 samples, which ever is higher frequency	70-130% (THg) 65-135% (MeHg)	• If Recovery is not within QC limits, and an RPD criterion is met document excursion. • If recover y is within QC limit, and RPD criterion is not met, reanalyze.	Frank McFarland	Accuracy/Bias	70-130% (THg) 65-135% (MeHg)

Matrix	Water
Analytical Group	ISUS rapid profiling sensors: nitrate, bisulfide, temperature, specific conductance, transmissivity, chlorophyll, and light penetration
Concentration Level	Nitrate and bisulfide–Low Other parameters–N/A
Sampling SOP	N/A
Analytical Method/ SOP Reference	L-15
Sampler's Name	UFI
Field Sampling Organization	B. Wagner
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #11.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
NO_3 instrument validation	~ 25 samples	N/A	DI water checks; DI water recalibration if regular DI check exceeds ± 0.007 mg/L	T. Prestigiacomo	N/A	Acceptable DI water checks (± 0.007 mg/L)
HS^- instrument validation	~ 25 samples	N/A	DI water checks; DI water recalibration if regular DI check exceeds ± 0.016 mg/L	T. Prestigiacomo	N/A	Acceptable DI water checks (± 0.016 mg/L)

Matrix	Water
Analytical Group	Total dissolved gas
Concentration Level	N/A
Sampling SOP	N/A
Analytical Method/ SOP Reference	L-16
Sampler's Name	UFI
Field Sampling Organization	B. Wagner
Analytical Organization	UFI
No. of Sample Locations	See Worksheet #11.

QC Sample:	Frequency/Number	Method/SOP QC Acceptance Limits	Corrective Action	Person(s) Responsible for Corrective Action	Data Quality Indicator (DQI)	Measurement Performance Criteria
N/A	N/A	See UFI SOP Tensionometer In-Situ Inc. 300E	Recalibration or return to manufacturer if necessary	T. Prestigiacomo	N/A	See UFI SOP Tensionometer In-Situ Inc. 300E

Sample Collection Documents and Records	On-site Analysis Documents and Records	Off-site Analysis Documents and Records	Data Assessment Documents and Records	Other
Field notes Chain-of-custody records Corrective action forms		Sample receipt, custody, and tracking records Standard traceability logs Equipment calibration logs Sample preparation logs Run logs Equipment maintenance, testing, and inspection logs Corrective action forms Reported field sample results Reported results for standards, QC checks, and QC samples Instrument printouts (raw data) for field samples, standards, QC checks, and QC samples Sample disposal records Telephone logs Raw data (stored on CD or DVD)	Field sampling audit checklists Field analysis audit checklists Fixed laboratory audit checklists Data usability and summary report Corrective action forms	

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP[1]	Data Package Turnaround Time[2]	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	Chlorophyll	Low	South Deep	L-8	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Nitrate/Nitrite as N (NO_x)	Low	South Deep	L-2	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Nitrate as N (NO_2)	Low	South Deep	L-2	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Ammonia as N ($T\text{-}NH_3$)	Low	South Deep	L-3	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Organic Carbon, Total/Total Dissolved as C (DOC)	Low	South Deep	L-4	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP[1]	Data Package Turnaround Time[2]	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	Carbon, Inorganic Dissolved and Total (DIC)	Low	South Deep	L-7	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Chloride	Low	South Deep	L-1	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Ferrous iron	Low	South Deep	L-10	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Sulfide as S (Method 1)	Low	South Deep	L-5	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Sulfide as S (Method 2)	Low	South Deep	L-6	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP[1]	Data Package Turnaround Time[2]	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	Dissolved methane	Low	South Deep	L-9	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Total mercury	Low	South Deep	L-17	28 days	TestAmerica 4101 Shuffel St. NW North Canton, OH 44720 Mark Loeb 330-497-9396	N/A
Water	Methyl mercury	Low	South Deep	L-18	28 days	TestAmerica 4101 Shuffel St. NW North Canton, OH 44720 Mark Loeb 330-497-9396	N/A
Zooplankton	Total and methyl mercury	Low	South Deep	L-19 and L-18	28 days	TestAmerica 4101 Shuffel St. NW North Canton, OH 44720 Mark Loeb 330-497-9396	N/A

Matrix	Analytical Group	Concen-tration Level	Sample Locations/ ID Numbers	Analytical SOP[1]	Data Package Turnaround Time[2]	Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)	Backup Laboratory/ Organization (Name and Address, Contact Person and Telephone Number)
Water	ISUS rapid profiling sensors: nitrate, bisulfide, temperature, specific conductance, transmissivity, chlorophyll, and light penetration	Nitrate and bisulfide– Low Others– N/A	South Deep, North Deep, and ISUS gridding stations	L-15	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Water	Total dissolved gas	N/A	South Deep	L-16	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A

[1]Reference number from QAPP Worksheet #23.
[2] Turnaround times for Brooks Rand analyses (total mercury and methylmercury analysese in zooplankton, methylmercury analyses in water) begin when samples come off hold (i.e., if samples are held until the 5-sample minimum sample delivery group is met).

Assessment Type	Frequency	Internal or External	Organization Performing Assessment	Person(s) Responsible for Performing Assessment (Title and Organizational Affiliation)	Person(s) Responsible for Responding to Assessment Findings (Title and Organizational Affiliation)	Person(s) Responsible for Identifying and Implementing Corrective Actions (CA) (Title and Organizational Affiliation)	Person(s) Responsible for Monitoring Effectiveness of CA (Title and Organizational Affiliation)
Field sampling technical systems audit	2 times (at ~3 month intervals) during the field sampling season	Internal	UFI	David Matthews Technical Director, UFI	MaryGail Perkins, Field Team Leader, UFI	MaryGail Perkins Field Team Leader, UFI and Bruce Wagner Field staff, UFI	Bruce Wagner Field staff, UFI

Assessment Type	Nature of Deficiencies Documentation	Individual(s) Notified of Findings (Name, Title, Organization)	Timeframe of Notification	Nature of Corrective Action Response Documentation	Individual(s) Receiving Corrective Action Response (Name, Title, Org.)	Timeframe for Response
Field sampling Technical Systems Audit (TSA)	Verbal communication or written audit report	MaryGail Perkins Field Team Leader, UFI Steven Effler, Project Manager, UFI Charles Driscoll, Project Manager, SU, Ed Glaza, Project Manager, Parsons	48 hours	Written document (electronic or hardcopy)	David Matthews, Technical Director, UFI Steven Effler, Project Manager, UFI Charles Driscoll, Project Manager, SU, Ed Glaza, Project Manager, Parsons	48 hours

Project oversight (field and laboratory) will consist of periodic inspection and audits of sampling and analytical techniques, as required by NELAC/ELAP (annual internal laboratory and field audit; external audit by NELAC/ELAP certified inspectors every two years). No additional field or laboratory audits are planned. Testing and calibration activities will also be reviewed. All audit and review findings and any corrective actions that arise from them will be documented. The laboratory director will ensure that corrective actions are carried out promptly. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, immediate corrective action will be taken, and any client whose work is affected will be notified immediately in writing.

Type of Report	Frequency (daily, weekly monthly, quarterly, annually, etc.)	Projected Delivery Date(s)	Person(s) Responsible for Report Preparation (Title and Organizational Affiliation)	Report Recipient(s) (Title and Organizational Affiliation)
Field sampling technical systems audit report	2 times (at ~3 month intervals) during the field sampling season	Deficiencies reported within 48 hours of audit and Corrective Action Response within 48 hours of audit report receipt	David Matthews, Technical Director, UFI	MaryGail Perkins, Field Team Leader, UFI Steven Effler, Project Manager, UFI Charles Driscoll, Project Manager, SU
Data usability and summary report	Annually	June following field season	Linda Cook, Exponent and/or Lorraine Weber, Parsons	Tim Larson, NYSDEC

Verification Input	Description	Internal/ External	Responsible for Verification (Name, Organization)
Chain-of-custody forms	Chain-of-custody forms will be reviewed internally upon their completion and verified against the packed sample coolers they represent. A copy of the chain-of-custody forms will be attached to the data report.	I	Laboratory Staff at UFI, TestAmerica, and Brooks Rand
Field notes	Field notes will be reviewed internally and placed in the site file. A copy of the field notes will be attached to the final report.	I	Laboratory Staff at UFI, TestAmerica, and Brooks Rand
Laboratory data	All laboratory data packages will be verified internally by the laboratory performing the work for completeness and technical accuracy prior to submittal. All received data packages will be verified externally according to the data validation procedures specified in Worksheet #36.	I, E	Laboratory Staff at UFI, TestAmerica, and Brooks Rand (I) and Exponent and/or Parsons (E)

Each laboratory's QA officer will perform a verification of chemical data. The laboratory will be responsible for the review and verification of all work sheets and data packages, manual entry or transcription of data, and any professional judgments made by an analyst during sample preparation, analysis, and calculation, and reporting of the final concentrations. The laboratory will also be responsible for reviewing quality control results to determine whether data are of usable quality or reanalysis is required. Any nonconformance issues identified during the laboratory's quality assurance checks will be corrected and noted by the laboratory. Close contact will be maintained between the Laboratory Director, the QA Officer, and the Scientific/Technical Manager, so that any quality issues can be resolved in a timely manner. Any data quality deviations will be discussed in the laboratory data narrative, including the direction or magnitude of any bias to the data, if possible.

Responsibilities for verification of data and sampling activities

Project Personnel	Verification Activity
Compliance	
UFI Field Manager/ UFI QA Officer	Assign appropriate staff to perform the work and ensure that all field personnel are familiar with the field SOPs Verify that the proper sampling protocols, including sample preservation, handling, and storage are performed during field work Track the samples sent to the laboratories; verify that the chain-of-custody forms are filled out correctly and that samples were received in good condition at the appropriate laboratory Verify that the appropriate number of field blanks and sample duplicates/triplicates are collected Conduct field data collection audit to ensure that the proper field procedures are followed
UFI, TestAmerica, and Brooks Rand QA Officers	Verify that the laboratory instruments are calibrated, and quality control samples are analyzed (e.g., blanks, duplicates, MS/MSD, LCS) Verify that the laboratory conducted proper calibration and quality control sample procedures (i.e., the laboratory followed the contract scope of work) Confirm that the analytical data meet specified detection limits in analytical SOPs
Correctness	
	Inspect and ensure that the field and analytical equipment are calibrated and properly functioning in accordance with field instrument user manuals and laboratory QA manuals
UFI, TestAmerica, and Brooks Rand QA Officers Scientific/Technical Manager	Review data reduction process, examine the raw data to verify that the correct calculations of sample results were reported by the laboratory or transferred from field logs, examine the raw data for any anomalies, and verify that there are no transcription or reduction errors
Consistency (Comparability)	
UFI QA Officer	Ensure that proper data-handling procedures were followed (e.g., the SOPs and contract scope of work are followed consistently throughout the project); recheck any handwritten data in field logs for transcription errors Review data transfer procedures and make all efforts to minimize data problems
Completeness	
UFI Field Manager	Verify proper documentation of chain-of-custody and sample handling/transfer procedures, document any problems encountered during sample collection, identify any problems with damaged samples, and confirm with laboratory that all samples have been received
UFI Field Manager UFI QA Officer	Ensure that an accurate record was maintained during sample collection and analysis
UFI, TestAmerica, and Brooks Rand Laboratory Personnel and QA Officers	Document that general quality control measures were conducted (e.g., instrument calibration, routine monitoring of analytical performance, calibration verification) Ensure that a unique sample number was assigned to each sample Document deviations from scope of work (e.g., analytical procedures), document any corrective actions taken if QC checks identify a problem, ensure that the appropriate analytical method was used.

Note: LCS - laboratory control sample
MS/MSD - matrix spike/matrix spike duplicate
QA/QC - quality assurance and quality control
SOP - standard operating procedure

Step IIa/IIb	Validation Input	Description	Responsible for Validation (Name, Organization)
IIa	SOPs	Ensure that all sampling and analytical SOPs were followed.	MaryGail Perkins at UFI, Dorothy Leeson at TestAmerica, and Frank McFarland at Brooks Rand
IIa	Documentation of Method QC Results	Establish that all method required QC samples were run and met required limits.	Laboratory Staff at UFI, TestAmerica, and Brooks Rand
IIb	Documentation of QAPP QC Sample Results	Establish that all QAPP required QC samples were run and met required limits	Laboratory Staff at UFI, TestAmerica, and Brooks Rand
IIb	Project Quantitation Limits	Establish that all samples results met the project quantitation limits specified in the QAPP	Laboratory Staff at UFI, TestAmerica, and Brooks Rand
IIa	Raw Data	Review 100% of raw data to confirm manual laboratory calculations and review 10% review of raw data to confirm automated laboratory calculations	Laboratory Staff at UFI, TestAmerica, and Brooks Rand

Step IIa/IIb	Matrix	Analytical Group	Concentration Level	Validation Criteria	Data Validator (title and organizational affiliation)
IIa	Aqueous	All Analyses	Low	QAPP Worksheets #12, #15, and #28	Exponent and/or Parsons

Data verification and assessment will be completed by Exponent and/or Parsons. EPA has not prepared national functional guidelines for any of the project-specific analytes included in this program (i.e., low-level total mercury, methyl mercury, and the conventional parameters). Therefore, chemical data for these analytes will be verified and assessed following the "evaluation procedures" specified in National Functional Guidelines (e.g., assessment of holding times, accuracy, and precision data). For these data, method-specific quality control requirements and laboratory-established control limits (as presented in the QAPP), as they are applicable to the analytical methods being used, will be used to determine whether data require qualification.

Consistent with the Pre-Design Investigation QAPP (Parsons 2005), the first phase of the data review process is contract compliance screening (CCS) and involves review of sample data deliverables for completeness. The PDI QAPP describes this process as follows:

> "Completeness is evaluated by ensuring that all required data deliverables are received in a legible format with all required information. The CCS process also includes a review of the chain-of-custody forms, case narratives, and reporting limits. Sample resubmission requests, documentation of nonconformances with respect to data deliverable completeness, and corrective actions often are initiated during the CCS review. The results of the CCS process are incorporated into the data validation process."

The second phase of data review is data validation. As discussed in Worksheet #11, EPA Level III validation protocol will be applied to all analytes except total mercury, methylmercury, and nitrate. These three analytes will be validated according to EPA Level IV validation protocol. The PDI QAPP describes Level III validation as follows:

> The EPA Level III validation protocol….includes a review of summary information to determine adherence to analytical holding times; results from analysis of field duplicates, method blanks, field blanks, surrogate spikes, MS/MSDs, LCSs, and sample temperatures during shipping and storage. Data qualifiers are applied to analytical results during the data validation process based on adherence to method protocols and laboratory-specific QA/QC limits.

For Level III validation, instrument calibrations, calculations, and transcriptions will not be checked because the laboratories will be responsible for 100-percent verification of these results and procedures. For total mercury, methylmercury, and nitrate (i.e., the Level IV data quality objectives), ten percent of the data will

undergo a Level IV validation, which incorporates the Level III validation protocol and adds calculation checks from the raw data of reported and summarized sample data and QC results.

Data qualifiers will be applied to the results according to procedures described in the EPA Contract Laboratory Program national functional guidelines for inorganic data review (U.S. EPA 2004), as applicable, with modifications as appropriate to accommodate method-specific quality control requirements or when specific MQOs and DQIs established for this project (e.g., control limits for bias and precision) are not achieved.

Algorithms to Assess Quality Control Results
Data verification includes checking that quality control procedures were included at the required frequencies and that the quality control results meet control limits defined in the method descriptions. The equations provided below will be used to determine whether measurement targets for project requirements were met for each quality control procedure.

Duplicate and Triplicate Analyses — Precision for duplicate chemical analyses will be calculated as the relative percent difference (RPD), expressed as an absolute value, between the duplicate samples. Replicate precision will only be assessed for sample results greater than 5 times the method detection limit due to increased variability at low concentrations. When replicate results are less than 5 times the method detection limit the absolute difference of the results will be evaluated. The formula that will be used to assess precision for both laboratory and field duplicate samples is as follows:

$$\text{RPD} = \left| \frac{D_1 - D_2}{(D_1 + D_2)/2} \right| \times 100$$

where:

D1 = sample value, and

D2 = duplicate sample value.

The percent relative standard deviation of triplicate sample data points will be calculated to evaluate replicate precision. The formula for relative standard deviation is as follows:

$$\%RSD = \frac{100 \times s}{\bar{x}}$$

where:

s = standard deviation, and

$\bar{x}$ = mean sample value.

Matrix Spike Recoveries — Spiked samples provide an indication of the bias of the analytical system. The recovery of MSs will be calculated as the ratio of the recovered spike concentration to the known spiked quantity:

$$\%R = \frac{A - B}{C} \times 100$$

where:

A = the analyte concentration determined experimentally from the spiked sample,

B = the background level determined by a separate analysis of the unspiked sample, and

C = the amount of the spike added.

Completeness — Completeness will be calculated for each sample type by dividing the number of valid measurements (all measurements except rejected data) actually obtained by the number of valid measurements that were planned:

$$\%\text{Completeness} = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100$$

To be considered complete, the data sets must also contain all quality control check analyses that verify the precision and accuracy of the results.

Sensitivity — The detection limit of the sample preparation and analysis process is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte is greater than zero" (40 CFR 136B); it is the concentration at which qualitative, not quantitative, identification can be made.

Best professional judgment is used to adjust the limit of detection upward in cases where high instrument precision (i.e., low variability) results in a calculated limit of detection and equivalent instrument response that are less than the absolute sensitivity of the analytical instrument. The actual reporting limit for environmental samples is generally higher than the instrument detection limit, because the sample matrix tends to contribute to fluctuations in the instrument's background signal. Although reporting limits have been established (Worksheet #15 series), achievement of these reporting limits is based on the analysis of samples without matrix interferences. In the event that matrix interferences are encountered (on a sample-specific basis), laboratory personnel will determine whether elevated *reporting limits* are required. Whether to report elevated reporting limits will be determined based on the experience of the laboratory with samples of matrix similar to those collected for this study and on the response of each instrument to samples for this study. The MRLs will be verified during data validation.

Blanks Actions – The data will be assessed in accordance with the general guidance specified by the Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (USEPA, 2004) since the quality control associated with these analyses are similar to the inorganic methods. With the exception of mercury, there are no published data validation procedures for these analytical methods. For this study the data validator will try to limit the negation of results due to blank action levels (U qualified) based on the judgment that imprecise low concentration results are more useful in the analysis for this study then negated results. Sample results will be compared to the associated instrument, method, and field blank results to assess the potential for contamination. Sample results less than 5 times the associated blank concentration will be qualified as estimated and potentially biased high (J+).

Reference:

Parsons. 2005. Onondaga Lake Pre-Design Investigation Quality Assurance Project Plan, Syracuse, New York. Prepared for Honeywell, Morristown, NJ. Parsons, Liverpool, NY.

USEPA. 2004. USEPA Contract Laboratory Program national functional guidelines for inorganic data review. EPA/540-R-04-004. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC.

Summarize the usability assessment process and all procedures, including interim steps and any statistics, equations, and computer algorithms that will be used: See Worksheet #36 and associated text.
Describe the evaluative procedures used to assess overall measurement error associated with the project: See Worksheet #36 and associated text.
Identify the personnel responsible for performing the usability assessment: See Worksheet #36 and associated text.

Describe the documentation that will be generated during usability assessment and how usability assessment results will be presented so that they identify trends, relationships (correlations), and anomalies:

The data quality and usability report will be prepared by Exponent and/or Parsons on behalf of Honeywell. The report will meet the requirements for a NYSDEC data usability and summary report (DUSR) as described in Appendix B of the 2002 Draft Voluntary Cleanup Guide (NYSDEC Division of Environmental Remediation, Albany, NY). The report will summarize the results of the data validation and data quality review and will describe any significant quality assurance problems that were encountered. The report will include the following items:

- Project Objectives and Background
- Description of sample collection methods (including a description of deviations from planned sampling activities that may have occurred and the impact, if any, on the project and quality objectives) and shipping, including chain-of-custody and holding-time documentation
- Description of analytical methods (including a description of deviations in laboratory procedures that may have occurred and the impact, if any, on the project and quality objectives) and detection limits
- Summary of Data Verification performed by the laboratory and a description of any deviations from the work plan and quality assurance project plan
- Summary of Data Validation performed by Exponent and/or Parsons with appendix tables detailing the validation findings
- General overview and test-specific summaries of data usability
- Tables detailing 1) target analyte list, methods, and method detection and reporting limits; 2) listing of study analytes and projected and actual analyses, 3) verification activities and responsible project personnel, 4) analytical components and associated appendix tables, 5) sample analysis summary count by event date, and 6) data usability summary by parameter.
- Appendices containing the data validation summary tables, analytical result summary tables, analytical result graphs, analytical quality control results, and chain-of-custody documents.

ATTACHMENT 1

Standard Operating Procedures

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization
L-16	UFI SOP Tensionometer In-Situ Inc. 300E	UFI
L-17	SOP No. NC-MT-0001 (Revision No. 5.1) Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence, Methods 1631E and MCAWW 245.7	Test America
L-18	SOP #BR-0011 Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630	Brooks Rand
L-19	SOP #BR-0002 BRL Procedure for EPA Method 1631, Appendix: Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion, BrCl Oxidation, and Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)	Brooks Rand

ATTACHMENT 1

Standard Operating Procedure
L-16
UFI SOP Tensionometer In-Situ Inc. 300E

1) **Test method:**
Tensionometer – In-Situ Inc. 300E

2) **Applicable matrix or matrices:** salt and fresh surface waters, <53 m depth

3) **Detection limit:** ΔP differential gas pressure, measurement range is ±750 mm Hg, resolution is ±1 mm Hg, accuracy is ±6 mm Hg.

4) **Scope and application:** *In situ* measurement of differential gas pressure (ΔP), which is defined as the difference between the atmospheric pressure at the surface of the water and the sum of all the partial pressures of the gases, including water vapor, dissolved in the water. ΔP is used primarily for determination of supersaturated water, as supersaturated conditions can have deleterious effects on fish. ΔP can also be reported as percent saturation (see 16. Calculations).

5) **Summary of test method:** The tensionometer probe consists of a pressure transducer, conditioning electronics, and a membrane cartridge. The membrane cartridge consists of a sensing membrane – approximately 1.5 m of a very small bore silicon tubing. One end of the tube is sealed; the other end is connected to the pressure transducer, which converts the internal tube pressure to an electrical signal. The tube is permeable to all gases, including water vapor. When the probe is immersed in water, gases effuse through the tubing wall until the gas pressure inside the tube is equal to the gas pressure outside the tube. This condition is called equilibrium and when reached, the tensionometer will display the total dissolved gas pressure in the water, commonly referred to as differential gas pressure (ΔP).

6) **Definitions:** none

7) **Interferences:** In relatively shallow supersaturated water gas bubbles can form on the silicon tubing, which can cause false low estimates of ΔP. This problem can be avoided by agitating the probe. Dirt, oil, or algae buildup on the membrane will slow response time. Response time is slower in colder waters.

8) Safety: Standard field safety procedures should be applied. Keep work area clean and clutter free. The submersible cable should be stowed in an organized fashion and not left in a location where it could become a tripping hazard.

9) Equipment and supplies: Appropriate field sheets, connection cables, and tensionometer display. A spare probe is stored in the travel case in case of probe failure.

10) Reagents and standards: none.

11) Reference Solution: none.

12) Sample collection, preservation, shipment and storage: No water samples collected.

13) Quality Control: Agitate probe to avoid bubble formation on silicon tubing (see # 7).

14) Calibration and standardization: To check calibration and operation:

1. with the power ON, rotate the zero control fully clockwise (CW) and note the reading, including the sign.
2. rotate the zero control fully counterclockwise (CCW) and again note the reading, including the sign.
3. derive the span: span = CW-CCW. The CW and CCW readings will vary as a function of barometric pressure, but the span should be within ±2 mm Hg of 250. Factory recalibration is necessary when span values vary from 250 mm Hg by more than ±6 mm Hg.
4. adjust the zero control to obtain a 000 reading. The value should remain stable within ±1 mm Hg. Zeroing has the effect of nulling the barometric pressure. This should be adjusted when the probe is out of water and has equilibrated with the atmosphere. Accuracy is dependent on how well the probe has equilibrated.
5. as an additional check, exhale over the tubing. This will cause a brief positive 2 or 3 mm Hg increase in pressure because of the increase in temperature of the gas inside the tube. If the membrane is wet when you blow across the tubing it will evaporate the water and lower the temperature inside the tubing. In this case a drop of 2 or 3 mm Hg will result.

15) Procedure:

1. attach probe to meter
2. place instrument in vicinity of measurement and allow it to come to ambient barometric pressure (20-25 minutes)
3. turn instrument on and observe reading
4. wait a few minutes for the reading to stabilize
5. turn zero knob completely counterclockwise
6. calculate barometric pressure by adding reading to number posted on side of meter (e.g., display reads -45, posted number is 800, 800 + (-45) = 755 mm Hg
7. adjust zero knob until display shows '000'
8. place probe into water. If colder than ambient air, reading will change suddenly as gas inside membrane contracts
9. if supersaturation is suspected and probe is near surface (<1 m), agitate probe to dislodge bubbles on tubing
10. observe reading
11. if reading continues in a negative direction, water is undersaturated. If reading continues in a positive direction, water is supersaturated.
12. allow time for display to stabilize. This may take 5 minutes or more if water is cold
13. when stable (<2 mm Hg change per minute), record reading on field sheet
14. lower probe to next depth and repeat from step 12

2. Maintenance

1. store the probe out of direct sunlight and protect it from excessive moisture. **Do not store the probe in a sealed plastic bag**
2. if the probe has been used in dirty, brackish, or otherwise contaminated water, be sure to rinse the probe in clean water after use, and clean the membrane. **Do not let contaminants dry on the probe surface**
3. refer to operation and maintenance manual for further details

16) Calculations: total differential gas pressure (ΔP) can be used to calculate (1) total gas pressure as percent saturation, (2) percent saturation of O_2, (3) percent saturation of N_2, (4) differential partial pressure of O_2 (ΔO_2), and (5) differential partial pressure of N_2 (ΔN_2). See appendix of operation and maintenance manual for calculation details

17) Method performance: see #3 above

18) Pollution prevention: This procedure has no discernible negative impact on the environment.

19) Data assessment and acceptance criteria for quality control measures: Assessment of results is done at UFI facilities (post collection). Acceptance criteria for quality control include consideration of field notation concerning interferences and presence of data points outside parameter detection range values.

20) Corrective actions for out-of-control or unacceptable data: Identify data that fail QA/QC, record throughout data transfer to client. Analyze cause of unacceptable data (*i.e.*, instrument error or interferences). Return instrument to manufacturer for repair and recalibration if deemed necessary.

21) Contingencies for handling out of control or unacceptable data: calibration and standardization procedures listed above (#14) ensure that data are within specification

22) Waste management: This procedure generates no hazardous waste.

23) References:

In-Situ Inc.
221 East Lincoln Ave.
Fort Collins, CO 80524 USA
Phone: (970) 498-1500
Fax: (970) 498-1598
www.in-situ.com

ATTACHMENT 1

Standard Operating Procedure
L-17

SOP No. NC-MT-0001 (Revision No. 5.1) Preparation and Analysis of Mercury in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence, Methods 1631E and MCAWW 245.7

Controlled Copy
Copy No. _____

Implementation Date: 8/12/07

SOP No. NC-MT-0001
Revision No. 5.1
Revision Date: 07/29/07
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TESTAMERICA NORTH CANTON STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS AND SOLID SAMPLES BY COLD VAPOR ATOMIC FLUORESCENCE, METHODS 1631E AND MCAWW 245.7

(SUPERSEDES: REVISION 5, REVISION DATE 01/17/05)

Approved by: Roger K. Scott — Technical Specialist — 8/7/07 Date

Approved by: Dorothy J. Reeson — Quality Assurance Manager — 8/12/07 Date

Approved by: _____ — Environmental, Health and Safety Coordinator — 8/8/07 Date

Approved by: _____ — Laboratory Director — 8/8/07 Date

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LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS) using Method 1631E and MCAWW Method 245.7.

1.2. The associated LIMs method codes are PR (Method 1631E) and D5 (Method 245.7). The sample preparation code for all methods is D4 (BrCl Oxidation).

1.3. CVAFS analysis provides for the determination of total mercury (organic and inorganic). The oxidant, bromine monochloride has been found to give quantitative recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.4. Method1631E (hereafter abbreviated to Method 1631 in this SOP) is applicable to the preparation and analysis of mercury in ground water, surface water, effluents and other aqueous samples. Appendix A to Method 1631 is applicable to the preparation and analysis of mercury in sediments, soils, biological media and other solid samples.All matrices require sample preparation prior to analysis.

1.5. Method 245.7 is applicable to the determination of mercury in drinking, surface and saline waters and domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.6. The TestAmerica North Canton reporting limit for mercury in aqueous matrices is 0.5 ng/L by Method 1631, and 5 ng/L by Method 245.7. The reporting limit for mercury by Method 1631 in solid matrices is 1.0 ug/kg.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solids and aqueous solutions. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor and fluorescence at 253.7 nm. For aqueous samples, a representative portion of the sample is digested and oxidized in bromine monochloride. For solid samples, 1 gram of sample is digested with cold aqua regia, diluted, and further oxidized with bromine monochloride Excess free halogens in the digestate are then reduced with hydroxylamine hydrochloride. The mercury (+2) is reduced to its elemental state with stannous chloride and purged from solution with argon in a gas / liquid separator. For Method 1631, the mercury vapor is collected on a gold trap and then thermally desorbed to the detector. For Method 245.7, the mercury vapor is transported directly from the gas /

liquid separator to the detector. The mercury vapor passes through a cell positioned in the light path of an atomic fluorescence spectrophotometer. Fluorescence is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample fluorescence to the calibration curve (fluorescence vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane and are oxidized by bromine monochloride. (Sample is preserved after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion and oxidation.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Gold, silver and iodide are known interferences. At mercury a concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent.

4.2. The use of a brominating digestion coupled with atomic fluorescence detection overcomes many of the chloride, sulfide and molecular absorbance interferences. No interferences have been noted for sulfide concentrations below 24 mg/L.

4.3. Water vapor may collect in the gold traps (Method 1631), and subsequently condense in the fluorescence cell upon desorption, giving a false peak due to scattering of the excitation radiation. Condensation can be avoided by predrying the gold trap and by discarding those traps that tend to absorb large quantities of water.

4.4. The fluorescent intensity is strongly dependent upon the presence of molecular species in the carrier gas that can cause *quenching* of the excited atoms.

4.5. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. The analytical instrument and sample / standards preparation area should be protected from mercury vapor or particulates in the laboratory air. Samples, standards and

blanks should only be opened in a clean area. Gloves must be powder free and should be checked for mercury contamination. Do not use powdered nitrile gloves as they have been shown to have either low level mercury contamination or interferences. Only clean gloves should touch the instrument and other equipment used to process blanks, standards and samples.

4.6. Samples known to contain mercury concentrations greater than 200 ng/L should be diluted prior to bringing them into the clean work area dedicated to processing low level mercury samples.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Bromine Monochloride	Corrosive Poison Oxidizer	0.1 (Br) ppm TWA	May be fatal if inhaled. Causes severe eye and skin burns. Causes damage to the following organs: Lungs, mucous membranes, respiratory tract, skin, central nervous system, eyes, lens or cornea.
Potassium Bromate	Oxidizer	0.1 Mg/M3 TWA	Irritates respiratory tract. May causecoughing and shortness of breath. Causes irritation to the skin. May cause redness, itching, and pain. In the presence of liquids, it is slowly absorbed in toxic amounts. Prolonged exposure may cause burns. Causes irritation to eyes with redness, pain. May cause eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as a carbon filter.

5.4. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Exposure to hazardous chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation, where possible. All samples with stickers that read "Caution/Use Hood!" **must** be opened in the hood. Contact the EH&S Coordinator if this is not possible. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica North Canton associate. The situation must be reported **immediately** to the EH&S Coordinator and to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders are located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAFS apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Atomic Fluorescence Spectrophotometer equipped with:

6.1.1. Fluorescence Cell with quartz ends. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.1.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL).

6.1.3. Peristaltic pump.

6.1.4. Flowmeter.

6.1.5. Recorder or Printer.

6.1.6. Gas /Liquid separator:

6.1.7. Drying devices: Nafion Dryer (used for all methods), soda lime trap (Method 1631).

6.1.8. Gold traps (2): quartz tube containing gold coated sand.

6.2. Sample bottles, 40 mL borosilicate glass VOC vials, QEC or equivalent, < 0.5 ng/L contamination when used for Method 1631 samples. In actual practice, should contribute less than 0.1 ng/L to facilitate meeting method blank criteria. Unless tested by the manufacturer for cleanliness and accuracy, 12 vials from each lot must be gravimetrically tested at the 40 mL point. Cleanliness is assessed by adding 0.2 mL BrCl (Section 7.15). Store the test vials at room temperature for at least 12 hours and analyze as samples. All vial results must be less than the reporting limit.

6.3. Argon gas supply, high purity, or equivalent. A gold trap may be used in-line to further purify the argon.

6.4. Calibrated automatic pipettes.

6.5. Disposable cups or tubes, low mercury content.

6.6. Starch / iodine paper.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a US Filter PureLab Plus deionized water system or equivalent. Reagent water must be free of mercury and interferences as demonstrated through the analysis of reagent and method blanks.

7.2. Stock (10 mg/L) mercury standards (in 5-10% HNO_3) are purchased. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 µg/L): Fill a 100 mL volumetric flask about half full with reagent water. Add 0.5 mL of BrCl solution (Section 7.15). Add 0.10 mL of the stock mercury standard (Section 7.2) and dilute to 100 mL with reagent water. The intermediate mercury standard should be replaced every 9 months.

7.4. Working mercury standard (1 µg/L): Fill a 40 mL vial about half full with reagent water.

Add 0.2 mL of BrCl solution (Section 7.15). Add 4.0 mL of the intermediate mercury standard (Section 7.3) and dilute to 40 mL with reagent water. The working mercury standard should be replaced every 3 months.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (Section 7.4) by transferring 0, 0.02, 0.04, 0.08, 0.2, 0.4, and 1.0 mL of a mercury standard into 40 mL vials and diluting to volume with reagent water; for Method 1631 use the working standard (Section 7.4), for 245.7 use the intermediate standard (Section 7.3). BrCl (Section 7.15) and $NH_2OH \bullet HCl$ (Section 7.13) reagent solutions are also added.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, some automated mercury systems may not require 40 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (QCS) must be made from a different manufacturer or lot than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed with all reagents that are used for sample preparation.

7.8. Hydrochloric acid (HCl), concentrated, trace metal grade and ultra trace mercury grade.

Note: Ultra trace mercury HCl (when commercially available) should be used to prepare the bromine monochloride solution. Trace metal grade HCl may be used to prepare the stannous chloride and 2% HCl rinse solutions provided that these solutions are purged with argon prior to use.

7.9. Autosampler rinse solution (2%): 400 mL trace metal grade HC1 diluted to 20 L reagent water. Purge overnight with argon.

7.10. Stannous chloride solution concentrate: Add 500 g of $SnCl_2 \bullet 2H_2O$ to 2.4 L trace metals concentrated hydrochloric acid. Allow the $SnCl_2 \bullet 2H_2O$ to completely dissolve. ACS Reagent grade suitable for mercury determination (< 1 ppb) recommended.

7.11. Stannous chloride working solution: Fill a 2.5 L glass bottle (HCl leached) with 2.25 L of reagent water. Add sufficient stannous chloride concentrate (Section 7.10) to bring the total volume to 2.5 L. This produces a reductant solution that is 10% HCl and 2%

$SnCl_2 \bullet 2H_2O$. Purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.8).

7.12. Hydroxylamine hydrochloride solution: Dissolve 300 g of $NH_2OH \bullet HCl$ in reagent water. Dilute to 1 L. Add 1 mL of stannous chloride solution working solution and purge with argon (0.5 L/min) for at least 24 hours. Analyze a reagent blank made with this solution prior to analysis of samples (Section 9.8).

7.13. Potassium bromide: KBr, reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg(0) contamination.

7.14. Potassium bromate: $KBrO_3$, reagent grade, low mercury content is desirable. This dry reagent may be baked at 250°C for at least 8 hours to volatilize trace Hg(0) contamination.

7.15. Bromine monochloride preservative/oxidizing solution: In a ventilation hood, add 5.4 g KBr to 500 mL of ultra trace (low mercury) HCl. Allow the salt to dissolve. Slowly add 7.6 g $KBrO_3$. Halogen fumes will be emitted during this step. Adequate ventilation is essential to protect analyst safety. Analyze a reagent blank with this solution prior to analysis of samples (Section 9.8)

7.16. Nitric acid, concentrated, trace metal grade.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Preservation and Holding Time

8.1.1. Holding time from time of collection to the time of preservation is extended to 28 days when the oxidation step is performed in the sample bottle used for collection. Preservation/oxidation is verified by the persistence of the yellow color of the BrCl. Additional BrCl must be added if the preservative/oxidizer is consumed. Record any additional BrCl used (see Section 11.1.5). Samples to be analyzed for dissolved Hg must be filtered within 48 hours of collection, then preserved as above. Once preserved, holding time is 90 days from sample collection to analysis.

8.1.2. Solid sample holding time for Hg is one year from collection. The holding time for digested and preserved solid samples is 90 days from sample preparation

8.2. Collection and Storage

8.2.1. The clean hands/dirty hands procedure should be followed for collection. Samples are stored in a mercury clean area.

8.2.2. Solid samples may be stored in fluoropolymer or borosilicate glass or polyethylene bags.

9. QUALITY CONTROL

9.1. Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.2. Initial Demonstration of Capability

9.3. Prior to the analysis of any analyte using Method 1631 or Method 245.7, the following requirements must be met.

9.3.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below both the TestAmerica North Canton reporting limit. In addition the MDL for Method 1631 must be ≤ 0.2 ng/L.

9.3.2. Initial Demonstration Study (initial precision and recovery study)- This requires the analysis of four QC check samples. The QC check sample is a well-characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.3.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.3.3. Carryover determination – Analyte system blanks immediately after calibration solutions containing successively larger concentrations of Hg – from this test determine the amount of Hg that will carry >0.5 ng/L of Hg into a succeeding system blank. When a sample one half or more of this determined amount is analyzed then a system blank must be analyzed to demonstrate cleanliness at the RL. Samples with detectable Hg analyzed after the high sample but before the system blank must be reanalyzed.

9.4. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must

contain a method blank, a LCS and a matrix spike/matrix spike duplicate (2 MS/MSD pairs if the batch has more than 10 samples). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.5. Sample Count - Laboratory generated QC samples (Method Blanks, LCS, and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.6. Method Blank (MB): One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit. The sample result must be a minimum of 20 times higher than the blank contamination level.

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exceptions noted above).

- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.7. If a sample requires additional BrCl beyond the normal amount (Section 11.1.5) an additional preparation blank should be prepared with the same amount of BrCl. The result of this prep blank will be added to the narrative of the associated sample if the result is ≥ the reporting limit. This prep blank does not have any specific acceptance criteria, but it should be proportional to the amount of BrCl used.

9.8. System / subtraction / reagent blank: The reagent blank consisting of all reagents used to prepare samples and standards will be used for background subtraction and system cleanliness monitoring. Three reagent blanks are prepared and analyzed with the daily initial calibration curve (ICal) . Apply the average calibration factor from the ICal to the average

raw response from these 3 reagent blanks. The calculated mercury concentration must be less than the reporting limit. The average raw response from these 3 calibration blanks will be subtracted from all raw response data from all other data prior to calculating concentration factor (for cal standards) or concentrations. Subsequent bubbler / reagent blanks are run as ICB and CCB in conjunction with the ICV (QCS) and CCV (OPR). These IC and CC blanks are used to monitor the cleanliness of the instrument and are calculated in the same manner as samples and are not used for background subtraction purposes. The absolute value of the calculated mercury concentration must be less than the reporting limit.

9.9. Laboratory Control Sample (LCS): One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. If the LCS is outside established control limits the system is out of control and corrective action must occur.

- In the instance where the LCS recovery is greater than the maximum and the sample results are < RL, the data may be reported with qualifiers**. Such action must be addressed in the case narrative.**

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.10. Matrix Spike/Matrix Spike Duplicate (MS/MSD): One MS/MSD pair must be processed for each 10 samples in preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Method 1631 requires that each matrix be spiked at a 10% frequency. Some regulatory agencies interpret each discharge or sampling point as a separate matrix. It is the client's responsibility to determine which sample(s) is to be matrix spiked each time samples are submitted for analysis. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, control limits of 71 - 125 % recovery and 24% RPD for 1631 aqueous, 70-130% recovery and 30% RPD for 1631 solid, and 76 – 111% recovery and 18% RPD for 245.7 must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results, which fall outside the control limits, must be addressed in the narrative.

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.11. Initial Calibration Verification (ICV/ICB) (QCS – quality control sample): Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 20% of the true value for that solution . An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.3.5) for required run sequence). If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the ICV, ICB, CCV, and CCB with the calibration curve.

9.12. Continuing Calibration Verification (CCV/CCB) (on-going precision and recovery - OPR): Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV concentration must be at 5 ng/L for 1631. The CCV result must fall within 77-123% of the true value for that solution for 1631. A CCB is analyzed immediately following each CCV. (See Section 11.3.5 for required run sequence). The CCB (system/reagent blank) must fall within +/- the reporting limit (RL) from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs.

- In the instance where the CCV or CCB is greater than the maximum and the sample

results are < RL, the data may be reported. Such action must be addressed in the case narrative.

9.13. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences, which cause a baseline shift. Refer to Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1 except that the oxidation time need does not need to be a minimum of 12 hours and can be used immediately since the mercury is already in an oxidized state in the standard.

10.2. Due to the differences in calibration ranges separate calibration and calibration verification standards must be prepared for Methods 1631 and 245.7. See Section 7.5 and Table 1.

10.3. Calibration may be performed daily (every 24 hours), but is required only when indicated by instrument and preparation QC problems. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer (Table III). Allow the instrument to become thermally stable before beginning calibration (approximately 1-2 hours of warm-up is required if the lamp has been turned off). The most stable results are obtained if the lamp is left on full time. Refer to the CVAFS instrument manual for detailed setup and operation protocols.

10.5. Run 3 deionized water blanks to ensure that the instrument, reductant solution and rinse solutions are adequately clean.

10.6. Calibrate the instrument according to instrument manufacturer's instructions, using 6 standards and 3 calibration blanks. One standard must be at the TestAmerica North Canton reporting limit. Analyze standards in ascending order beginning with the blanks. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.7. The calibration factors must have less than 15% RSD or the instrument shall be stopped and recalibrated prior to running samples. Sample results can not be reported from a curve with

an unacceptable RSD. Also, the low standard must calculate back within ±25% of the true value.

10.8. Refer to Sections 9.11 and 9.12 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Aqueous Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed with the digestion reagents used for the field samples.

11.1.2. Open the outer sample bag, carefully dump the inner bag containing the sample bottles onto a clean bench top in the low level mercury area with a minimum of handling. Immediately discard the outer sample bag. Change gloves between each sample or work with another analyst using the clean hands-dirty hands technique.

11.1.3. Change gloves and open the remaining inner bag, remove the sample vials, label and place in the low level mercury prep area.

11.1.4. Remove ~2.7 mL from each sample vial. This will leave 40 mL in the bottle. Confirm by checking the meniscus and the 40mL calibration point. Set the cap back on the original vial. Repeat this process for all 40 mL vial aliquots of the sample. Transfer 1 mL of sample from a separate unpreserved "10X dilution" labeled tube and add 9 mL of reagent water. Reseal the original sample vial caps if it will be greater than 3 minutes before the next step of performed (Section 11.1.5)

Note: Typically two sample vials and one screening vial will be prepared per sample (six sample vials for client requested MS/MSD samples).

11.1.5. Temporarily lift the cap and add 0.20 mL of BrCl (Section 7.15) to the 40 mL sample vial, reseal and mix. If the yellow tint from the BrCl disappears add an additional aliquot of BrCl. This iterative process may be repeated until a maximum of 2 mL has been added. Record the amount of BrCl used on the bench sheet. If the 2 mL maximum was reached and the yellow BrCl color still does not persist consult supervisor to determine if sample dilution prior to preservation / oxidation is appropriate. At least one method preparation blank must be prepared for each different volume of BrCl added.

11.1.6. Add 0.05 mL BrCl to the dilution tube(s) from Section 11.1.4. Confirm the 10X

dilution tube has adequate BrCl. Add more as needed.

11.1.7. Store the sample vials at room temperature for at least 12 hours. If the yellow BrCl color disappears during the storage period, the oxidizer has been consumed. Add additional BrCl until the yellow color persists. Do not exceed a total of 2 mL. Consult laboratory Technical Director or supervisor if yellow color does not persist after 2 mL addition of BrCl. Record the total volume of BrCl added on the benchsheet. Starch / iodine paper may be used to detect excess halogens (i.e. BrCl) in colored samples where the yellow color of the BrCl can not be seen.

Note: To speed or improve oxidation, especially for samples with high organic content or known interferences, the vials may be heated at approximately 50°C. For samples requiring greater than 0.2 ml of BrCl, this can lessen preparation time.

Note: The 12 hour oxidation time is not required for the sample aliquots in the screening tubes.

11.1.8. Prepare method blank and LCS vials using the same reagents as used for the samples.

11.2. Solid sample Preparation:

11.2.1 Homogenize the sample then weigh 1 g into a 40 mL VOA vial. The VOA vial must come from a lot that has been pre-screened for Hg contamination (Sec. 6.2).

11.2.1.1 For the method blank, add approximately 1 mL of reagent water in lieu of 1 g of solid sample.

11.2.1.2 For the LCS, add 1.0 mL of the 10 ug/L intermediate mercury standard (Sec. 7.3) in lieu of 1 g of solid sample.

11.2.1.3 For the MS/MSD, add 1.0 mL of the 10 ug/L intermediate mercury standard (Sec. 7.3) in addition to the 1 g of solid sample.

11.2.2 In a fume hood, add 8 ml of concentrated HCl, swirl, and add 2 mL concentrated HNO_3 to the sample in the 40 mL vial. Cap and allow the sample to digest for at least 4 hours.

11.2.3 Add 1 ml of BrCl (Sec. 7.15) to the digestate, then dilute with reagent water (Sec. 7.15) to the 40 mL calibration point. Shake, then allow to settle until supernatant is

clear. Centrifuge or filter if necessary.

11.2.4 For screening, transfer 0.1 mL of the supernatant into a "5X dilution" 10 ml culture tube and dilute to 10 mL with reagent water. For analysis, transfer 2 mL of the supernatant into a pre-screened VOA vial and dilute to the 40 mL calibration point with reagent water, then cap and shake. The "5X dilution" aliquot may be analyzed as specified in Sec. 11.3. The 40 mL VOA vial sample is ready for analysis and may be analyzed as specified in Sec. 11.4. Based on sample matrix and/or historical results, a greater dilution may be required.

11.3. Sample screening

11.3.1. Add 0.05 mL of hydroxylamine solution (Section 7.12) and analyze the 5X screening aliquot of the sample using a single point calibration (10 ng/L) and Method 245.7.

11.3.2. If the sample response exceeds that of the 10 ng/L standard (i.e. sample concentration > 2000 ng/L), then low level analysis by either 245.7 or 1631 is not technically appropriate. Remove all vials associated with this sample from the low level prep and storage areas immediately. Consult supervisor.

11.3.3. If the estimated concentration is greater than 200 ng/L, consult supervisor about analysis by 245.7. If approved, calculate the appropriate dilution and proceed with 245.7 analysis. Alternately, prepare an appropriately large dilution of the sample before bringing it into the low level preparation area. Direct low level analysis by 1631 is not technically appropriate due to the likelihood of contamination.

11.3.4. If the sample response (Note: this is a 5X dilution) exceeds that of the 5 ng/L standard then the sample concentration is beyond the normal calibration range of Method 1631. Either analyze the sample 245.7 (if allowed by the client) or prepare the appropriate dilution for 1631 analysis.

11.3.5. If the 5X dilution screen response is non-detect at 5 ng/L then the sample may be analyzed without dilution by either 245.7, or Method 1631 depending on the reporting limit needed by the client unless matrix interferences warrant dilution.

11.4. Sample Analysis

11.4.1. When ready to begin analysis, add 0.10 mL of hydroxylamine hydrochloride solution (Section 7.12) to the samples to reduce the excess BrCl (the BrCl has been reduced when no yellow color remains). Cap and shake. Add the

hydroxylamine solution in 0.10 mL increments until the BrCl is completely reduced. Record the total volume used on the benchsheet.

Note: Spiking is done before the addition of the hydroxylamine hydrochloride reagent.

11.4.2. With instrument control parameters set to appropriate values (See Table III), load samples into autosampler. Use 40 mL vials for Method 1631 and 14 mL or 40 mL tubes for 245.7.

11.4.3. Start autosampler sequence.

11.4.4. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.4.5. The following analytical sequence must be used:

Instrument Calibration
ICV (QCS)
ICB
CCV (OPR)
CCB
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 3 and Table II (Appendix A) for the appropriate quality control criteria.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

Note: Instrument calibration need not be performed if the run QC parameters indicate that the system is in control.

11.5. To facilitate the early identification of QC failures and samples requiring rerun it is strongly

recommended that sample data are reviewed periodically throughout the run.

11.6. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.7. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by the QA Manager. The Non-Conformance Memo shall be filed in the project file.

11.8. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1.Calibration Factors are calculated according to the equation:

$$CF(x) = \left(\frac{Area(x) - Area(b)}{Conc(x)} \right)$$

Where:

CF(x) = calibration factor of standard (x)
area(x) = area of standard (x)
conc(x) = concentration of standard (x)
area(b) = average area of 3 calibration blanks

12.2. ICV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(ICV)}{True(ICV)} \right)$$

12.3. CCV percent recoveries are calculated according to the equation:

$$\%R = 100 \left(\frac{Found(CCV)}{True(CCV)} \right)$$

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%\ R\ = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.6. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.7. The final concentration for an aqueous sample is calculated as follows:

$$ng/L = \text{C x D}$$

Where:

C = Concentration (ng/L) from instrument readout
D = Instrument dilution factor

12.8. The final concentration for a solid sample is calculated as follows:

$$ug/kg = C \times D \times W \times P$$

Where:

C = Concentration (ng/L) from instrument readout

D = Instrument dilution factor

W = Weight/volume factor = 0.040, when 1 g of sample is digested and diluted to 40 mL.

P = Preparation factor = 20, when 2 mL of digestate is diluted to 40 mL.

12.9. Appropriate factors must be applied to sample values if dilutions are performed.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.3.

13.2. Method performance is determined by the analysis of method blanks and laboratory control samples. The method blanks must meet the criteria in Section 9.6. The laboratory control sample should recover within 25% of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and

Pollution Prevention."

15.2.Waste Streams Produced by the Method

15.2.1. The following waste streams are produced when this method is carried out.

15.2.1.1. **Acid Waste- Aqueous waste generated by the analysis.** Samples vials are collected and taken to the waste storage building. The vials are crushed and the liquid waste and glass are separated. The liquid waste is neutralized and released to the POTW. The glass is disposed of in the trash.

16. REFERENCES

16.1. References

16.1.1. Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry, U.S. EPA, August 2002.

16.1.2. Appendix to Method 1631, Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation, U.S. EPA, January 2001.

16.1.3. Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, U.S.EPA, January 2000.

16.1.4. Corporate Quality Management Plan (QMP), current version.

16.1.5. TestAmerica Laboratory Quality Manual (LQM), current version.

16.1.6. TestAmerica Corporate Safety Manual, M-E-0001 and TestAmerica North Canton Facility Addendum and Contingency Plan, current version.

16.2.Associated SOPs and Policies, latest version

16.2.1. QA Policy, QA-003

16.2.2. Glassware Washing, NC-QA-0014

16.2.3. Statistical Evaluation of Data and Development of Control Charts, NC-QA-0018

16.2.4. Method Detection Limits and Instrument Detection Limits, S-Q-003 and NC-QA-

0021

16.2.5. Supplemental Practices for DoD Project Work, NC-QA-0016

16.2.6. Standards and Reagents, NC-QA-0017

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method.

17.1.1 Section 9.1.7 of the method requires three method blanks per analytical batch. The section also describes an analytical sequence that includes a CCV (OPR) only at the beginning and end of the sequence, and that includes no CCBs (system blanks) after calibration. This SOP requires only one method blank per preparation batch, but requires additional stability and cleanliness checks through the analysis of a CCV/CCB pair at the beginning, end and after every ten analyses during an analytical run.

17.1.2 Section 9.2.1 of the method recommends that an MDL be determined whenever a new operator begins work. At this laboratory, a new operator receives proper, documented training and must prove competence through an initial demonstration of performance that includes the successful analysis of (4) LCSs (See Section 9.3.2).

17.1.3 Conventional MS/MSD techniques and criteria have been maintained in contrast to Section 9.3.4 of the method (See Section 17.1.2.1 of this SOP).

17.1.4 Section 9.4.3.1 of the method requires reagent blank concentrations to be <0.2 ng/L. In this laboratory, reagent blanks are analyzed as system calibration blanks and are held to the system blank criteria of <0.5 ng/L (See Section 9.8 of this SOP).

17.1.5 Section 9.4.5.1 of the method recommends that field blank analysis immediately before analyzing samples from the batch. Field blanks are analyzed as normal samples in this laboratory with no particular run order requirement.

17.1.6 Section 9.4.7 of this method recommends that 5% of the bottles in a lot be monitored. Bottle cleanliness in this laboratory is verified by the initial analysis of 5% of the bottles from three boxes of a lot of 40 mL sample vials, and then monitored through the routine analyses of system blanks (calibration blanks).

17.1.7 The volume descriptions for the equation in Section 12.3.2 of the method includes

subtraction of the volume of reagent used in the standards and the samples. Since the volume of reagents used in samples and standards is typically the same (or differs insignificantly in rare cases), this subtraction is not included in the determination of Hg concentration in this laboratory.

17.2 Performance Based Modifications from Method 245.7.

17.2.1 The preservative / oxidizer solution (Section 7.15) from Method 1631B has been used in place of the bromate/bromide oxidizer solution (Section 7.7.4 in method).

17.2.2 The autosampler is rinsed with 2% HCI solution as recommended by the manufacturer rather than deionized water (Section 11.3.2 in method).

17.3 Other Interpretations and Differences from Method 245.7.

17.3.1 Reagent blank acceptance criteria is an absolute value less than the reporting limit (Section 9.8) rather than MDL (Section 9.2.1.3 in method)

17.3.2 Conventional fixed concentration matrix spiking has been used in this SOP (Section 9.10) rather than the variable concentration spiking described in the method (Section 9.5 in method). Also, batch acceptability is determined by method blank and LCS criteria and not MS/MSD recovery and RPD.

17.3.3 All standards are prepared using the same reagents as the samples rather than only in reagent water (Section 10.1.1.2 in method). (See Section 10.1)

17.3.4 The digested sample is used for dilution since no undigested sample (Section 11.3.4 in method) is available as the BrCl solution both preserves and oxidizes the sample. Also, this form of the sample should be more homogeneous for total mercury analysis.

17.4 Interpretations and Differences from Method 1631 Appendix A

17.4.1 In the method, after digestion with aqua regia is complete, the digestate is diluted with 0.07 N BrCl for elemental carbon-containing samples. In this SOP, all samples are diluted reagent water to which 1 mL of 0.2 N BrCl has been added. This presents a BrCl concentration in the diluted digestate comparable to the concentration achieved using the method technique. Also, since it is added to all digestates (not only those known to contain elemental carbon), the analyzed digestate will always contain some BrCl, and thereby be more comparable to the calibration standards.

17.5 Documentation and Record Management

17.5.1 The following documentation comprises a complete CVAFS raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

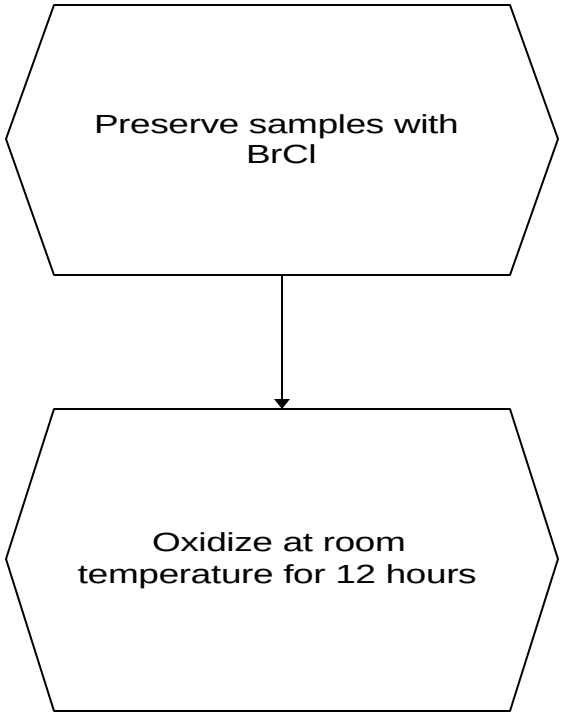
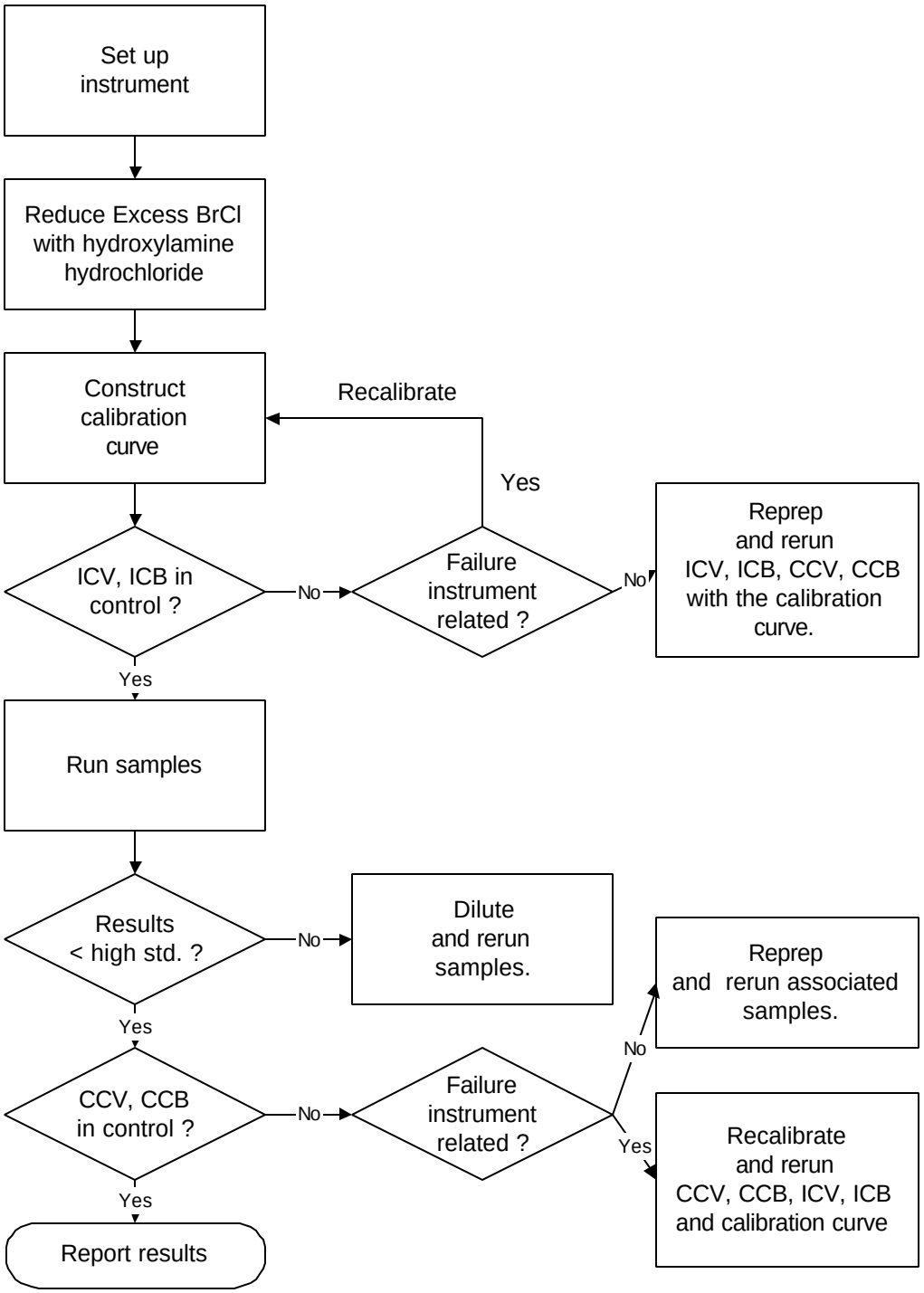


Figure 2. CVAF Mercury Analysis



APPENDIX A

TABLES

TABLE I
MERCURY REPORTING LIMITS, CALIBRATION STANDARD, QC STANDARD, AND SPIKING LEVELS (ng/L)

	1631E				245.7	
	Conc ng/L	**mL Std (Sec.7.4)**	**Conc ug/kg Solid**	**mL Std (Sec.7.3) Solid**		**mL Std (Sec.7.3)**
Standard Water RL	0.5				5	
Standard Solid RL			1.0		NA	
Std 1 (in triplicate)	0	0			0	0
Std 2	0.5	20			5	20
Std 3	1	40			10	40
Std 4	2	80			20	80
Std 5	5	200			50	200
Std 6	10	400			100	400
Std 7	25	1000			250	1000
ICV (QCS)	5	200 (Sec 7.6)			10	40 (Sec 7.6)
CCV (OPR)	5	200			10	40
LCS	5	200	10	1000		
MS/MSD	5	200	10	1000	10	40

TABLE II
SUMMARY OF QUALITY CONTROL REQUIREMENTS

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA 1631	ACCEPTANCE CRITERIA 245.7	CORRECTIVE ACTION
ICV (QCS)	Beginning of every analytical sequence.	80-120 % recovery	80-120 % recovery	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve. (see Section 9.11)
ICB	Beginning of every analytical run, immediately following the ICV	The result must be within +/- RL (0.5 ng/L for aqueous, 1.25 ng/L for solid)	The result must be within +/- RL (5 ng/L)	Terminate analysis; Correct the problem; Recalibrate or reprep with calibration curve (see Section 9.11)
CCV (OPR)	Every 10 samples and at the end of the run	77-123 % recovery	76-111 % recovery	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep with calibration curve (Note exceptions in Section 9.12)
CCB	Immediately following each CCV	The result must be within +/- RL (0.5 ng/Lfor aqueous, 1.25 ng/L for solid)	The result must be within +/- RL (5 ng/L)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep with calibration curve (Note exceptions in Section 9.12)
Method Blank	One per sample preparation batch of up to 20 samples. Note: additional prep blank(s) required if additional BrCl needed in some sample(s)	The result must be within +/- RL Sample results greater than 20x the blank concentration are acceptable.	The result must be within +/- RL (5 ng/L)	Redigest and reanalyze samples Note exceptions under criteria section See Section 9.6 for additional requirements.

TABLE II

SUMMARY OF QUALITY CONTROL REQUIREMENTS (Cont'd)

QC PARAMETER	FREQUENCY *	ACCEPTANCE CRITERIA 1631	ACCEPTANCE CRITERIA 245.7	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	75-125 % recovery	75-125 % recovery	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (Note exception under Section 9.9)
Matrix Spike	Two per sample preparation batch of up to 20 samples.	71-125 % recovery for aqueous, 70-130% recovery for solid. If the MS/MSD is out for an analyte, it must be in control in the LCS	76-111 % recovery. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added (see Section 9.10)
Matrix Spike Duplicate	See Matrix Spike	Same as Matrix Spike RPD ≤ 24% for aqueous, ≤30% for solid	76-111 %; RPD ≤ 18% (see MS)	See Corrective Action for Matrix Spike

*See Section 11.3.5 for exact run sequence to be followed

TABLE III
SUMMARY OF INSTRUMENT PARAMETERS
(LEEMAN LABS HYDRA AF GOLD +)

Instrument Parameter	**1631**	**245.7**
Argon flow (L/min)	0.5	0.4
Pump flow (mL/min)	10	10
Rinse (sec)	60	120
Uptake (sec)	240	35
Sample volume (mL)	40	11
Integration (sec)	0.70 (70 sec total)	35 sec total
Method	CVAFS with trap	CVAFS
Furnace 1 temp (°C)	450	
Furnace 2 temp (°C)	450	
Dry Time (sec)	5	
Desorption Time (sec)	70	
Stabilize Time (sec)	10	

APPENDIX B

EXAMPLE
TESTAMERICA NORTH CANTON Hg DATA REVIEW CHECKLIST

Example

TestAmerica North Canton Hg Data Review Checklist

Run/Project Information

Run Date: _____ Analyst:_____ Instrument:_____
Prep Batches Run:_____
Circle Methods used: 1631E : NC-MT-0001 Rev 4 **245.7 :** NC-MT-0001 Rev 4
245.7 screen : NC-MT-0001 Rev 4

Review Items

A. Calibration/Instrument Run QC	Yes	No	N/A	2ndLevel
1. Instrument calibrated per manufacturer's instructions and at SOP specified levels (including 3 initial calibration blanks)?				
2. ICV/CCV analyzed at appropriate frequency and within control limits?				
3. ICB/CCB analyzed at appropriate frequency and within +/- RL?				
B. Sample Results				
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?				
2. All reported results bracketed by in control QC?				
3. Sample analyses done within holding time?				
C. Preparation/Matrix QC				
1. Samples preserved within holding time at lab?				
2. LCS done per prep batch and within QC limits?				
3. Method blank done per prep batch and < RL?				
4. MS run at required frequency (1 per 10 samples) and within limits?				
5. MSD or DU run at required frequency (1 per 10 samples) and RPD within SOP limits?				
D. Other				
1. Are all nonconformances documented appropriately?				
2. Current MDL data on file?				
3. Calculations and Transcriptions checked for error?				
4. All client/ project specific requirements met?				
5. Date of analysis verified as correct?				

Analyst: _____ Date:_____
Comments:
_____
_____

2nd Level Reviewer : _____ Date:_____
_____
_____

Standard and Reagent Numbers

ICal/CCV _____ **ICV _____**

BrCl _____ NH2OH HCl _____ SnCl2 _____

APPENDIX C

MSA GUIDANCE

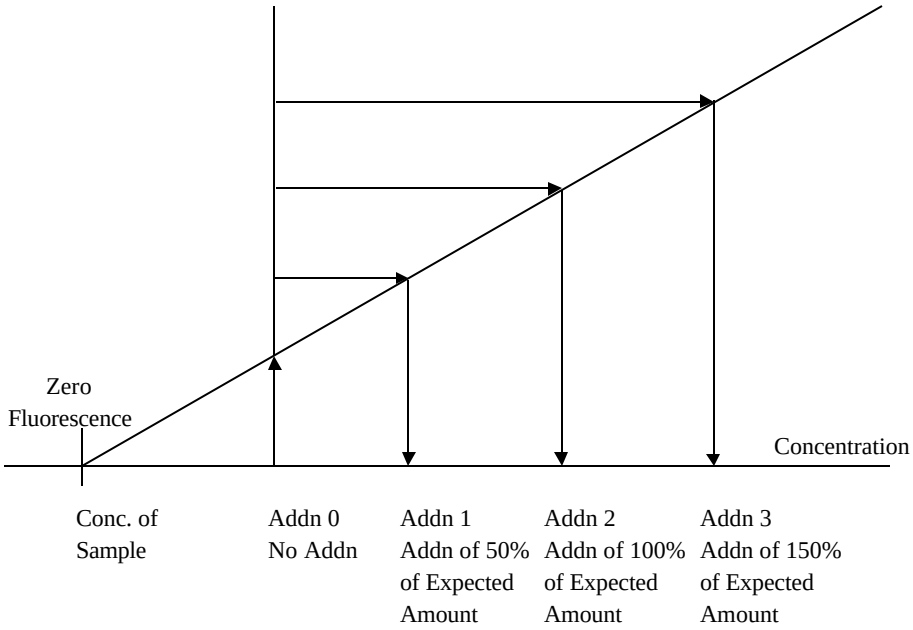
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the fluorescence (or response) of each solution is determined and a linear regression performed. On the vertical axis the fluorescence (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero fluorescence , the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

TROUBLESHOOTING GUIDE

APPENDIX D

TROUBLESHOOTING GUIDE

Problem	Possible Cause
Poor or No Fluorescence or Sensitivity Check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Empty sample cup Incorrectly made standards Gas leak EDL power supply set on "Continuous"
Erratic Readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL Won't Light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal fluorescence or concentration	Incorrect standard used Incorrect dilution performed Dirty cell

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 hydrochloric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered Gloves must not be used in the mercury laboratory since the powder contains mercury, as well as other metallic analytes. Only powder free gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and discard.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman Labs Hydra AF gold plus) (1)

Daily	Semi-annually	As Needed
Check argon flow	Check Hg lamp intensity	Change Hg lamp
Check pump tubing		Change liquid/gas separator
Check drain		Change Nafion dryer
Check soda lime drying tube		

APPENDIX G

INSTRUMENT SET UP

Hg Analysis (Leeman Labs Hydra AF gold plus)

TO SET UP INSTRUMENT FOR ANALYSIS

1. WinHG Rack File editor

2. New Rack file

    A. Enter sample workorder # into corresponding "Sample name" (limit 8 chars, no spaces)

    B. Enter client ID into "Extended ID"

    C. Save file with Date/letter name (e.g. 0324a) (limit 8 characters, no spaces)

3. WinHg Database

    A. Select most recent calibration of appropriate method (1631 or 245.7)

    B. Save Protocol As, method / current date (e.g. 16310324) (limit 8 characters, no spaces)

    C. Clear calibration data from new protocol

    D. Apply (i.e. Save changes)

    E. Upload protocol to Runner

3. WinHg Runner

    A. Sample tab

    B. Select appropriate rack file(s), click auto sample

ATTACHMENT 1

Standard Operating Procedure
L-18

SOP #BR-0011 Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

Summary of SOP #BR-0011

Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630

Brooks Rand LLC

Written 5/26/05

Determination of Methyl Mercury by Aqueous Phase Ethylation, Trapping Pre-Collection, Isothermal GC Separation, and CVAFS Detection: BRL Procedure for EPA Method 1630

1.0 SCOPE AND APPLICATION

Method BR-0011 is the performance based procedure followed at Brooks Rand LLC (BRL) as EPA Draft Method 1630. Unless specifically stated otherwise in this document, all apparatus, materials, reagents, standards and procedures as stated in EPA Method 1630 are used at BRL.

NOTE: EPA Draft Method 1630 is for the determination of methyl mercury only in filtered and unfiltered aqueous samples. BRL Method BR-0011 is additionally for the determination of methyl mercury in sediment and biota. BRL has developed specific sample preparation methods for these matrices. With the exception of the maximum volumes analyzed, the procedures followed for the analysis of sediment and biota preparations are identical to the procedures followed for aqueous preparations.

2.0 SUMMARY OF METHOD

2.1. Prior to instrumental analysis, aqueous samples are prepared by distillation according to the procedure discussed in EPA Draft Method 1630, section 11. Sediment samples are prepared by dichloromethane (DCM) extraction. Biota samples are prepared by alkaline digestion.

2.2. Mono-methylmercury (MMHg) is determined by a modification to EPA Draft Method 1630. The MMHg is first ethylated with sodium tetraethylborate ($NaBEt_4$) and collected by purging with nitrogen onto a quartz tube filled with either Carbotrap™ or Tenax. The ethyl mercury derivatives are then thermally desorbed and transferred to a GC column held in an oven, which separates the species chromatographically by mass. The ethylated Hg compounds are pyrolized to Hg^o, then quantified by a cold vapor atomic fluorescence spectrophotometer (CVAFS). This method can be applied for the determination of MMHg in a variety of sample matrices and has been demonstrated as being very sensitive, precise, and accurate. Very good results were obtained for the determination of MMHg in standard and certified reference materials and numerous intercalibration samples (Liang, Bloom, and Horvat 1994).

3.0 INTERFERENCES

3.1. If properly applied, the distillation procedure will remove most to all significant interferences. EPA Method 1630 dictates that fresh water samples must be preserved with between 0.3% to 0.5% (v/v) 11.6 M HCl and that salt water samples must be preserved with between 0.1% to 0.2% (v/v) 9 M sulfuric acid (H_2SO_4).

3.2. Refer to EPA Method 1630, Section 4.0 for a detailed account of possible contamination and interference to the analysis, and how these are avoided or minimized at BRL.

4.0 APPARATUS AND MATERIALS USED AT BRL

4.1. Refer to EPA Method 1630, Section 6.0 for a list of materials used in the method employed at BRL.

4.2. Specific equipment used at BRL is listed below. Any modifications to EPA Method 1630 are described and explained.

4.2.1. Atomic fluorescence spectrophotometer (BRL part #AF-03): CVAFS systems are built by BRL (BRL Model III). Refer to the "Brooks Rand, LLC Model III Operations Manual" for instrument operating instructions.

4.2.2. Recorder: BRL uses direct data acquisition with the BRL Guru™ integration software instead of a chart recorder or integrator as described in EPA Method 1631E, section 6.6. The BRL Model III comes complete with the Guru™ integrating software. Refer to the "Brooks Rand LLC Model III Operations Manual" for Guru™ software/integrator operating instructions. Guru™ software requires an IBM compatible computer (minimum requirements are a Pentium II® processor running at 400 MHz, a CD-ROM Drive, 128 MB RAM, and 50 MB free space on the hard-drive) and runs MS Windows® 98 or higher. Use of this integration software is faster, eliminates the expense of chart recorders and/or integrators, allows for storage of data in diskette form, and eliminates possible transcription errors.

4.2.3. Reaction and purge vessels (BRL part #AF-32).

4.2.4. Trapping column (BRL part #AF-21).

4.2.5. Isothermal gas chromatography system: Consisting of GC column (BRL part #AF-34), GC oven (BRL part #AF-33), pyrolitic column (BRL part #AF-35), and temperature controller for GC oven (BRL part #AF-36).

5.0 STANDARDS AND REAGENTS

5.1. Refer to EPA Method 1630, Section 7.0 for a list of standards and reagents employed at BRL.

5.2. Water: 18 megohm ultra-pure deionized water starting from a pre-purified (distilled, R.O., etc.) source.

5.3. MMHg Standard solutions

5.4. Sodium tetraethylborate ($NaBEt_4$) solution.

5.5. Sodium acetate buffer.

5.6. Methanolic potassium hydroxide solution.

5.7.Helium and nitrogen.

5.8. 20% potassium chloride (KCl) / 0.2% L-Cysteine solution.

5.9. 9 M sulfuric acid (H_2SO_4).

5.10. 0.05% hydroxylamine hydrochloride ($NH_2OH \cdot HCl$).

5.11. Potassium bromide/sulfuric acid solution(KBr/H_2SO_4).

5.12. 1 M copper sulfate solution ($CuSO_4$).

5.13. DCM (HPLC Grade).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1. Refer to EPA Method 1630, Section 8.0 and EPA Method 1669 (*Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels*) for a detailed description of sample collection, preservation, and storage methods.

7.0 SAMPLE PREPARATION

7.1. Refer to EPA Method 1630, Section 11.0 for a detailed description of the preparation of aqueous samples. Depending on the purposes and definitions of investigations of mercury biogeochemistry cycling, samples are prepared in the following methods prior to analysis.

7.2. Preparation of aqueous samples for MMHg analysis.

The following two isolation methods, distillation and solvent extraction, have been used in our labs for the determination of MMHg in aqueous samples. Good agreement was obtained in the comparison of the two methods for most water samples studied: For organic rich and/or high level sulfide containing samples, the distillation showed some advantages over the solvent extraction method with higher recoveries (85 ± 4%, Horvat, Bloom, and Liang, 1993). In addition, extraction consumes large quantities of organic solvent, which can result in environmental contamination. Therefore, distillation is the preferred preparation method for aqueous samples at BRL.

7.2.1. Distillation:

Reagents: 20% KCl in 0.2% L-Cysteine, 9 M H_2SO_4

Distillation devices: Vials and caps for distillation and distillate collection are made of fluoropolymer obtained by Savillex Corporation, USA. Instead of fluoropolymer, a glass distillation still may also be used (Horvat and Stoeppler, 1988).

Distillation procedures: An aliquot of water sample is transferred into a fluoropolymer vial. Add KCl, L-Cysteine, and H_2SO_4. Start the distillation.

The distillate is collected in a fluoropolymer vial containing DDW.

7.2.2. Solvent extraction

Reagents: 30% KCl (saturated) and DCM.

Extraction procedure: An extraction procedure described by Bloom (1989) is used. Weigh an appropriate volume of the sample into a fluoropolymer bottle. Add KCl and swirl the bottle to mix. Add DCM. Shake the bottle for a set period of time with a mechanical shaker to reach distribution equilibrium of MMHg between aqueous and solvent phases, then allow the two phases to separate. Remove the upper phase. Add DDW to the bottle and place it uncapped on a hotplate until all of the DCM has boiled away. After all visible solvent has evaporated, purge the samples N_2 to remove any residual solvent.

7.3. Preparation of biological materials and sediments for MMHg.

7.3.1. Alkaline digestion for biological materials: Weigh the appropriate amount of sample into a fluoropolymer vial. Add KOH in methanol and cap the vial. Digest the samples in an oven. After digestion, dilute to volume with methanol prior to analysis.

7.3.2. Distillation for sediments: Sediment samples should be distilled directly by weighing an appropriate amount into a fluoropolymer vial and adding DDW. Distill as per the procedure mentioned above.

7.3.3. Solvent extraction for sediments: Sediment samples may be extracted to avoid the potential for artifact formation of MMHg during distillation. Sediment samples are weighed into a clean glass vial with a Teflon® lined screw cap. KBr, H_2SO_4, and $CuSO_4$ are added to the sample, which is then allowed to leach for a set amount of time. After leaching, DCM is added. The sample is shaken by hand for a set amount of time and then centrifuged to assist in the separation of the aqueous layer from the organic layer. The sample is then passed through phase separating filter paper so that only the organic layer is collected. The

organic layer is collected directly in to a Teflon® bottle. DIW is added to the bottle. The sample is then heated until the DCM layer has evaporated off. The sample is then diluted with DIW.

7.4. Holding times for sample preparations.

7.4.1. Distillations: Water and sediment distillates are stable for up to 48 hours if stored at room temperature and in the dark.

7.4.2. Extractions: Water and sediment extractions are stable for up to 48 hours if stored at room temperature in the dark.

7.4.3. Digestions: Biological digestates are more stable than distillates and may be stored up to seven days prior to analysis.

8.0 INSTRUMENT CALIBRATION AND SAMPLE ANALYSIS

8.1. Refer to EPA Method 1630, Sections 10.0, 11.0, and 12.0 for a detailed description of the analysis of samples and the calculation of results.

8.2. Instrument Calibration: BRL follows EPA method 1630, Section 10.0 for the instrument calibration with the same exceptions as for sample analysis.

8.3. Instrumental Analysis: BRL has adopted the following modifications.

For samples, add appropriate sample volumes plus DDW as necessary for a final bubbler volume of 50 to 75 mL. Allow the mixture to react without purging for 15 minutes.

Purge with N_2 for 15 minutes. Then the valve is switched to pass dry gas over the column for 5 minutes. Biota samples should be allowed to react without purging for 20 minutes, purged with N_2 for 15 minutes, and allowed to dry for 5 minutes.

9.0 CALCULATIONS

BRL uses the following formulas for the calculation of monomethyl mercury in a given sample.

9.1. Mean Calibration Coefficient:

A calibration coefficient (CF) is calculated for each standard used in the calibration as follows:

$$CF = CS_{pgMMHg} / (CS_{PH} - EB_{PH})$$

Where CS_{pgMMHg} is the calibration standard measured in picograms of methyl mercury, CS_{PH} is the peak height obtained during the analysis of the standard, and EB_{PH} is the

mean peak height obtained during the analyses of all of the ethylation blanks. The mean calibration coefficient (CF_{avg}) is then calculated for all of the standards used in the calibration.

9.2. Measured methyl mercury in the sample preparation:

The amount of methyl mercury present in the analyzed volume of the sample preparation is calculated using the equation:

$$MMHg_{measured\ pg} = (A_{PH} - EB_{PH}) \cdot CF_{avg}$$

Where A_{PH} is the peak height obtained during the analysis of the sample preparation.

9.3. Total methyl mercury in the sample preparation:

The total amount of methyl mercury present in the sample preparation is calculated using the equation:

$$MMHg_{total\ pg} = [(MMHg_{measured\ pg}) / V_A] \cdot V_D$$

Where V_D is the final dilution volume of the sample preparation in mL and V_A is the volume analyzed of the sample preparation in mL.

9.4. Concentration of methyl mercury in the sample:

The final concentration of methyl mercury in the sample is calculated using the equation:

$$MMHg_{conc} = (MMHg_{total\ pg} - MB_{total\ pg}) / V_o$$

Where $MB_{total\ pg}$ is the average total picograms of methyl mercury present in the method blanks and V_o is either the volume of the prepared sample measured in mL (aqueous samples) or the weight of the prepared sample measured in mg (solid samples). Therefore, the final concentration of methyl mercury in the sample is reported in units of ng/L for aqueous samples and in units of ng/g for solid samples.

NOTE: The total picograms of mercury present in each method blank is calculated using the same formula used to calculate the total picograms of methyl mercury in the sample preparation.

9.5. Empirically derived correction factor

BRL routinely recovery corrects results for distilled samples, as per EPA Draft Method 1630, to account for the fact that the distillation procedure is not 100% efficient in recovering methyl mercury. Results are multiplied by an empirically derived correction factor that is based on the average recovery of the appropriate quality control sample (Laboratory Fortified Blanks for aqueous distillates and the certified reference material

(CRM) BCR 580 (Marine Sediment) for sediment distillates). If an appropriate QCS sample is not available, the correction factor is based on the average recovery of the spikes made to samples with a similar matrix to the sample of concern.

The correction factor is calculated using the following equation:

$$F = 100 / R$$

Where F is the empirically derived correction factor and R is the running mean of the recoveries of the last 30 quality control samples or matrix spikes. The empirically derived correction factor is updated quarterly or any time that there is a significant change in performance.

BRL does not use the IPR and OPR samples to calculate the correction factor since, unlike the client samples and quality control samples, these samples are not distilled.

10.0 QUALITY CONTROL

10.1. Refer to EPA Method 1630, Section 9.0 for a detailed description of the quality control procedures employed at BRL for this method.

10.2. All quality control data should be maintained and available for easy reference and/or inspection.

10.3. Each analyst must perform an initial demonstration of capability (IDOC) for the analysis of methyl mercury prior to the analysis of any client samples. The IDOC consists of an initial precision and recovery (IPR) study following the procedure in EPA Draft Method 1630, Section 9.2.2. The acceptance criteria and run sequence for the IDOC can be found in Table 3 in Section 12 of this SOP.

10.4. Calibration data must be composed of a minimum of 1 ethylation blank (BRL analyzes 4 ethylation blanks prior to analyzing the calibration standards) and a minimum of 5, preferably 6, standards. Such a calibration should be run daily, prior to analysis, or whenever stock standards have been remade, conditions have changed, or initial calibration check (ICV) or ongoing precision and recovery (OPR) do not yield acceptable recoveries.

10.5. The OPR solution prepared by spiking the ethylation vessel with 25 pg methyl mercury using the calibration standard and followed by an ethylation blank must be analyzed following calibration, after the analysis of every 10 client samples, and at the end of the analysis of each analytical batch. Additionally, BRL analyzes an independent calibration check (ICV) solution obtained from a source independent from that used to obtain the calibration standard and prepared by spiking the ethylation vessel with 500 pg methyl mercury prior to the analysis of each analytical batch. The criterion for the recovery of the OPR solution is 67-133% and the recovery criterion for the recovery of

the ICV solution is 80-120%. All ethylation blanks must contain no more than 2.0 pg methyl mercury.

10.6. Matrix spike/matrix spike duplicate (MS/MSD) analysis should be performed once per every 10 client samples or once per batch, whichever is greater. A matrix spike sample is defined as an aliquot of homogenized sample that has a known amount of analyte added to it. The matrix spike sample is then processed through the entire preparation and analytical procedure. Bias is then determined by calculating the percent recovery of the known amount using the following formula:

Percent Recovery = 100 * (spiked sample result (conc.) - sample result (conc.)) / (amount spiked)

The criterion for spike recovery is determined by control charts and is different for each matrix type. The specific matrix spike recovery criteria for each matrix type and preparation procedure can be found in Tables 5 and 6 in Section 12 of this SOP.

The relative percent difference between the MS and the MSD is calculated using the following formula:

$$RPD = 200 \cdot (\left| MS\text{-}MSD \right|) / (MS + MSD)$$

The RPD for the MS/MSD pair must meet the criterion for each of the matrix types found in Tables 5 and 6 in Section 12 of this SOP.

10.7. Method duplicates are prepared and analyzed upon client request. For solid matrices method duplicates should be performed in conjunction with the MS/MSD samples and whenever the heterogeneity of a sample is deemed great enough that it may cause problems with the analysis of the sample. The relative percent difference (RPD) between duplicate samples is calculated using the same formula as used to calculate the RPD between the MS and MSD samples. The specific RPD criteria for each matrix type and preparation procedure can be found in Tables 5 and 6 in Section 12 of this SOP. If the acceptance criterion for duplicate analysis is not met for either samples or matrix spike samples, then the system performance is unacceptable. Associated samples must be qualified or the problem must be corrected and the samples reanalyzed.

10.8. Field duplicates are analyzed at the client's discretion. The acceptance criterion for field duplicate analysis is the same as that used for method duplicate analysis. The client must be notified immediately anytime that the acceptance criterion for field duplicates is not met.

10.9. Four method blanks (MB) should be prepared and analyzed with each batch. Method blanks are prepared using reagent water. HCl is not added to the method blanks since excess chloride is already provided by the KCl added to all samples prior to distillation. All method blank results must meet the acceptance criteria set forth in Tables 5 and 6 of Section 12.

10.10. Laboratory fortified blanks (LFB) are prepared and analyzed with each batch at a frequency of once per every 10 client samples or once per batch, whichever is greater. LFBs are prepared by spiking a method blank sample with the calibration standard at a concentration of approximately 2.0 ng/L. The LFB is then distilling as per an aqueous sample. The acceptance criterion for the recovery of the LFB (recovery corrected) is identical to the acceptance criterion for the recovery of OPR samples.

10.11. Appropriate certified reference materials (CRM) for MMHg are prepared for all batches containing tissue or sediment samples. It is BRL policy to prepare two CRMs with every solid batch. The two CRM samples may be duplicate aliquots of a single CRM or two entirely different CRMs if different matrix types are analyzed together. Criteria for CRM recoveries are determined by control charts. If control charts are not available then CRM results should be within 35% of the certified value (following recovery correction) for the analysis to be considered valid. CRM accuracy results not meeting this criterion shall be reprepared and reanalyzed or qualified at the discretion of the Laboratory Director. Currently, there are not any water based CRMs available.

11.0 REFERENCES

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Horvat, M.; May, K.; Stoeppler, M.; and Byrne, A.R. (1988) *Appl. Organomet. Chem.* 2: 515.

EPA Draft Method 1630 (January 2001) "Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS."

EPA Method 1669 (April 1995) "Sampling Ambient Water for Trace Metals At EPA Water Quality Criteria Levels."

12. TABLES

Table 1 Current Method Detection Limits and Minimum Levels Determined at BRL for the Analysis of Methyl Mercury Using EPA Method 1630

Matrix	Preparation Method	Method Detection Limit (MDL)[1]	Minimum Level (ML)
Water	Distillation	0.02 ng/L	0.045 ng/L
Sediment/Sludge	Distillation[2]	0.022 ng/g	0.06 ng/g
Sediment/Sludge	Extraction	0.01 ng/g	0.025 ng/g
Biota	Digestion	3.0 ng/g	9.0 ng/L

NOTES:
1. MDL as determined by the procedure 40 CFR Part 136, Appendix B. MDL and ML reported here for distillations are for recovery corrected results.
2. Brooks Rand no longer routinely performs distillations on sediment/sludge samples. This preparation method is reserved for sediments that are particularly high in organics and would not yield acceptable recoveries if prepared by extraction. The listed MDL/ML for this preparation method are not current, but are achievable based on past results.

Table 2 Summary of Control Chart Data Ending February 2005 (Last 30 Data Points) for the Analysis of Methyl Mercury Using EPA Method 1630

QA Sample	Matrix	Mean[1] Recovery (%)	Warning Limit (%) Mean ± 2 StDev	Control Limit (%) Mean ± 3 StDev
ICV	ALL	101.4	83.4-119.3	74.4-128.3
OPR	ALL	97.2	75.3-119.2	65.3-130.2
Matrix Spikes	Water	96.6	73.4-119.8	61.8-131.4
Matrix Spikes[2]	Sed/Sludge	86.5	65.5-107.6	54.9-118.1
Matrix Spikes[3]	Sed/Sludge	92.4	70.7-114.1	59.8-124.9
Matrix Spike	Biota	100.0	71.5-128.6	57.2-142.9
LFB	Water	100.6	80.6-120.5	70.6-130.5
CRM[2,4]	Sed/Sludge	100.5	77.0-123.9	65.3-135.7
CRM[3,4]	Sed/Sludge	98.7	76.7-120.6	65.7-131.6
CRM[5]	Biota	99.9	76.1-123.7	64.3-135.5
QA Sample	**Matrix**	**Mean RPD**	**Warning Limit (%) Mean ± 2 StDev**	**Control Limit (%) Mean ± 3 StDev**
Duplicates[6]	Water	7.8	20.8	27.3
Duplicates[2,6]	Sed/Sludge	8.9	22.7	29.6
Duplicates[3,6]	Sed/Sludge	9.5	24.7	32.2
Duplicates[6]	Biota	10.7	28.3	37.0

NOTES:
1. Recoveries for distillations (water and applicable sediment samples) have been recovery corrected using an empirically derived correction factor.
2. Control limits for distilled sediment samples. Last data point from 7/3/03.
3. Control limits for sediments prepared by DCM extraction.
4. BCR-580 (Marine Sediment) is the CRM used for sediments.
5. DORM-2 (Dogfish Muscle) is the CRM used for most biota samples.
6. Duplicates criteria is for both duplicates of the native sample and duplicates of the matrix spike.

Table 3 Quality Control Acceptance Criteria and General Analytical Run Sequence for the Initial Demonstration of Capability for the Analysis of Methyl Mercury

Run	Run Name	Section Name	Analyze	Requirements
1	Ethylation Blank	Calibration	Ethylation Blank	Each ≤ 2 pg
2	Ethylation Blank		Ethylation Blank	
3	Ethylation Blank		Ethylation Blank	
4	Ethylation Blank		Ethylation Blank	
5	2 pg std	Calibration[2]	2 pg std	RSD of Avg. CF ≤ 15% Recovery of Low Standard 65-135%
6	10 pg std		10 pg std	
7	50 pg std		50 pg std	
8	250 pg std		100 pg std	
9	500 pg std		250 pg std	
10	1000 pg std[1]		1000 pg std	
11	ICV	Independent Calibration Verification	500 pg	Recovery 80-120%
12	OPR std (25pg)	Ongoing Precision and Recovery	25 pg	Recovery 67-133%
13	Ethylation Blank	Contamination Check	Ethylation Blank	≤ 2 pg
14	Method Blank	Contamination Check	Method Blank	Mean < 2 x Target MDL StDev < 2/3rd of Target MDL
15	Method Blank		Method Blank	
16	Method Blank		Method Blank	
17	IPR std (25pg)	Initial Precision and Recovery	25 pg	Ave. recovery 69-131%, RSD ≤ 31%
18	IPR std (25pg)		25 pg	
19	IPR std (25pg)		25 pg	
20	IPR std (25pg)		25 pg	
21	MDL sample	Method Detection Limit[3,4]	Appropriate matrix spiked at a level of 1 – 5 times the expected MDL	Calculated MDL no greater than 5 times the spike level and RSD > 10%
22	MDL sample			
23	MDL sample			
24	MDL sample			
25	MDL sample			
26	MDL sample			
27	MDL sample			
28	OPR std (25pg)	Ongoing Precision and Recovery	25 pg	Recovery 67-133%
29	Ethylation Blank	Contamination Check	Ethylation Blank	≤ 2 pg

NOTES:
1. 1000 pg standard typically analyzed only when analyzing solid sample preparations.
2. All standards and samples are corrected for mean ethylation blank.
3. All samples are corrected for mean method blank.
4. Distilled samples are recovery corrected prior to calculating the MDL.

Table 4 Quality Control Acceptance Criteria and General Analytical Run Sequence for the Analysis of Methyl Mercury

RUN	Analyze	Description	Requirements
1 2 3 4	Ethylation Blank (EB) Ethylation Blank (EB) Ethylation Blank (EB) Ethylation Blank (EB)	Contamination Check	≤ 2.0 pg
5 6 7 8 9 10	2 pg std 10 pg std 50 pg std 250 pg std 500 pg std 1000 pg std	Calibration Curve[1]	RSD of Avg. CF ≤ 15% Recovery of Low Standard 65-135%
11	ICV (independent calib. verific.) (500 pg)	Precision and Recovery	80 – 120% recovery
12	OPR std (25 pg)	Ongoing Precision and Recovery	67 – 133% recovery
13	Ethylation Blank	Contamination Check	≤ 2.0 pg
14 15 16	Method Blank 1 (MB-1) Method Blank 2 (MB-2) Method Blank 3 (MB-3)	Contamination Check	Refer to specific water and solid criteria found in Tables 5 and 6.
17	Known Blanks	Trip, Field, or Equipment Blanks	Result < ML or < 1/5th associated sample results
18	LFB or CRM	Precision and Recovery	Rec = 67 – 133%[3] for aqueous, Rec = 65 – 135% for sediment samples and biota samples
19 20	Sample 01[2] Sample 01MD	Native Sample Duplicate Sample	RPD ≤ 35% or ±PQL for aqueous samples and ±2xPQL for solids if results are ≤5xPQL
21 22	Sample 01MS Sample 01MSD	Matrix Spike Matrix Spike Duplicate	Rec = 65 – 135%[3] for aqueous; Rec = 65 – 135% for sediment and biota samples; RPD ≤ 35%
23 through 31	Sample 02 through Sample 10	Client Sample	
32	OPR std (25 pg)	Ongoing Precision and Recovery	67 – 133% recovery
33	Ethylation Blank	Contamination Check	≤ 2.0 pg
34 35	Sample 11 Sample 11MD	Native Sample Duplicate Sample	RPD ≤ 35% or ±PQL for aqueous samples and ±2xPQL for solids if results are ≤5xPQL
36 37	Sample 11MS Sample 11MSD	Matrix Spike Matrix Spike Duplicate	Rec = 65 – 135%[3] for aqueous; Rec = 65 – 135% for sediment and biota samples; RPD ≤ 35%
38 through 46	Sample 12 through Sample 20	Client Sample	
47	OPR std (25 pg)	Ongoing Precision and Recovery	67 – 133% recovery
48	Ethylation Blank	Contamination Check	≤ 2.0 pg

NOTES:

1. The calibration curve may be adjusted depending on the expected range of samples (i.e. seds and biota 10pg-5000pg)
2. Any known field or equipment blanks should not be spiked and should be analyzed prior to other samples. The acceptance criterion for these samples is a result < the ML.
3. Recovery corrected.

Table 5 Quality Control Acceptance Criteria and Corrective Action Guidelines for the Analysis of Methyl Mercury in Aqueous Samples by Distillation.

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Ethylation Blank	Contamination from bubblers	4 per batch; following each OPR	≤ 2 pg	Clean and test bubblers until criteria met prior to any analysis
Calibration Standards	Acceptability of the Calibration Curve	Daily, prior to analysis of samples or whenever the OPR fails	RSD of response factors ≤ 15%; Recovery of Low Standard = 65 – 135%	Reanalyze suspect calibration standard. If criteria still not met, then remake standards and recalibrate the instrument
Independent Cal. Ver. (ICV) Ongoing precision and recovery (OPR)	Accuracy	Following Cal.; Beginning and end and 1 per 10 sample preparations	ICV Rec. = 80-120% OPR Rec. = 67-133%	Correct problem (recalibrate, remake standard, etc.) and reanalyze ICV/OPR. If criteria met, reanalyze samples backwards until 2 consecutive results with RPD ≤ 20%
Carryover Check Ethylation Blank	Contamination due to carryover in the bubbler/trap	Following any unusually high result. Currently ≥ 2x the high standard	≤ 2 pg	Clean and continue to test bubbler/trap combo until criteria met prior to further use. Reanalyze samples that were analyzed in same bubbler/trap following high result
Method Blank	Contamination from reagents, lab ware, etc.	3 per batch	Avg ≤ 0.045 ng/L StDev ≤ 0.015 ng/L or < 1/10th of associated samples	Correct problem. All samples associated with a contaminated method blank must be reanalyzed.
Laboratory Fortified Blank (LFB)	Accuracy	1 per batch	Recovery = 67 – 133%*	Reanalyze remaining volume. Correct problem prior to continuing analysis
Matrix Spike/Spike Duplicate	Accuracy and Precision within a given matrix	1 per 10 client samples	Recovery = 65 – 135%*; RPD ≤ 35%	If **recoveries** similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicates	Precision	Per client request	RPD ≤ 35% or ± PQL if sample < 5x PQL	Correct problem and reanalyze all associated samples.

* Recovery Criteria for Matrix Spikes and LFB samples are based on recovery corrected results.

Table 6 Quality Control Acceptance Criteria and Corrective Action Guidelines for the Analysis of Methyl Mercury in Solid Samples by Distillation, Extraction, and Digestion.

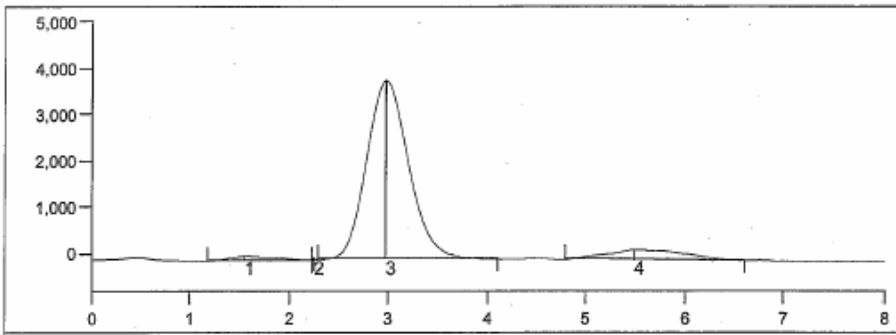
QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Ethylation Blank	Contamination from bubblers	4 per batch; following each OPR	≤ 2 pg	Clean and test bubblers until criteria met prior to any analysis
Calibration Standards	Acceptability of the Calibration Curve	Daily, prior to analysis of samples or whenever the OPR fails	RSD of response factors ≤ 15%; Recovery of Low Standard = 65 – 135%	Reanalyze suspect calibration standard. If criteria still not met, then remake standards and recalibrate the instrument
Independent Cal. Ver. (ICV) Ongoing precision and recovery (OPR)	Accuracy	Following Cal.; Beginning and end and 1 per 10 sample preparations	ICV Rec. = 80-120% OPR Rec. = 67-133%	Correct problem (recalibrate, remake standard, etc.) and reanalyze ICV/OPR. If criteria met, reanalyze samples backwards until 2 consecutive results with RPD ≤ 20%
Carryover Check Ethylation Blank	Contamination due to carryover in the bubbler/trap	Following any unusually high result. Currently ≥ 2x the high standard	≤ 2 pg	Clean and continue to test bubbler/trap combo until criteria met prior to further use. Reanalyze samples that were analyzed in same bubbler/trap following high result
Method Blank	Contamination from reagents, lab ware, etc.	3 per batch	Avg ≤ 2 x MDL StD ≤ 2/3rd MDL or < 1/10th of associated samples	Correct problem. All samples associated with a contaminated method blank must be reanalyzed.
Certified Reference Material (CRM)	Accuracy	1 per batch	Soil Rec=65-135%* Biota Rec=65-135%	Correct problem prior to continuing analysis
Matrix Spike/Spike Duplicate	Accuracy and Precision within a given matrix	1 per 10 client samples	Soil Rec=65-135%*; RPD ≤ 35% Biota Rec=65-135%; RPD ≤ 35%	If **recoveries** similar but fail recovery criteria, an interference is present in the sample and the result must be qualified. If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicate	Precision within a given matrix	In association with MS/MSD	RPD ≤ 35% or ± 2x PQL if sample < 5x PQL	If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.

* Recovery Criteria for Distilled Matrix Spikes and CRM samples are based on recovery corrected results.

Batch Number: 05-0060
Method Number: BR-0011

Project Number(s): FMI001,DWQ002
Instrument ID: BR-08

Date Analyzed: 2/2/05
Analyst Name: JPM

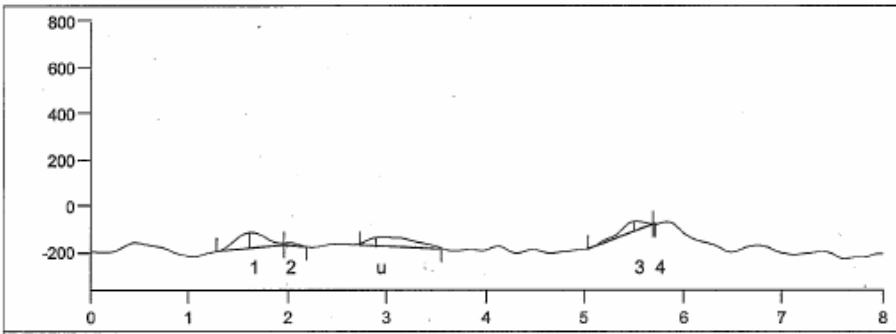


Date:	2/2/05
Time:	6:07 PM

Peak	rt	Height
1	1.56	95
2	2.26	1
3	2.97	3,879
4	5.49	222

Run	Run Type	Name/ID	M B	Peak	Peak Height	Analyzed Result	Final Result	QA Results	Criteria	Notes
7	OPR	OPR 25 pg		3	3,879	27.4		110	67-133	accept

Notes:



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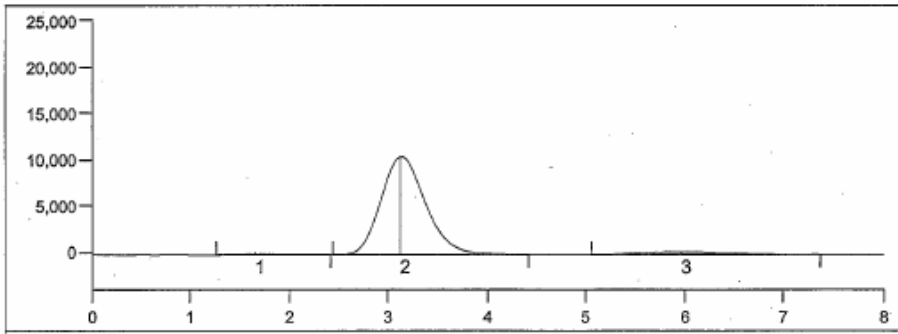
Time:	6:15 PM

Peak	rt	Height
1	1.62	65
2	1.99	2
3	5.51	44
4	5.72	1
u	2.90	31

Run	Run Type	Name/ID	M B	Peak	Peak Height	Analyzed Result	Final Result	QA Results	Criteria	Notes
8	CCB	Ethylation blank		u	31	0.222		0.222	< 2	accept

Notes:



Date:	2/2/05
Time:	8:19 PM

Peak	rt	Height
1	1.65	175
2	3.13	10,718
3	5.97	419

Run	Run Type	Name/ID	M B	Peak	Peak Height	Analyzed Result	Final Result	QA Results	Criteria	Notes
21	MSD	05BR0214-6	MBA	2	10,718	76.3	2.03	99.1	65-135	accept

Notes:

ATTACHMENT 1

Standard Operating Procedure
L-19

SOP #BR-0002 BRL Procedure for EPA Method 1631, Appendix: Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion, BrCl Oxidation, and Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

Summary of SOP #BR-0002

BRL Procedure for EPA Method 1631, Appendix: Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion, BrCl Oxidation, and Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

Brooks Rand Labs

Revision 009
Revised 05/25/06

Reviewed _____
_____
_____
_____

VP of Analytical Services	Date
QA Manager	Date
Scientist (if applicable)	Date

BRL Procedure for EPA Method 1631, Appendix: Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion, BrCl Oxidation, and Cold Vapor Atomic Fluorescence Spectrophotometry (CVAFS)

1.0 SCOPE AND APPLICATION

1.1 Method BR-0002 is modification of Appendix to EPA Method 1631 and is based on peer-reviewed, published articles for the determination of total mercury in a wide range of biological and geological matrices. All samples must be subject to an appropriate digestion step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid samples must be acid digested to break down the sample matrix and oxidized to convert all mercury species to mercuric ions.

2.2 Method BR-0002 is a cold vapor atomic fluorescence technique, based upon the fluorescence of 253.7 nm radiation by excited elemental mercury (Hg^0) atoms in an inert gas stream. Mercuric ions in the oxidized sample are reduced to Hg^0 using stannous chloride ($SnCl_2$), and then purged onto gold amalgamation traps using nitrogen gas as a means of preconcentration. Mercury vapor is thermally desorbed into the fluorescence cell. Fluorescence intensity is measured as a function of total mercury collected, which is converted to concentration by the size of the aliquot purged.

2.3 The actual detection limits for this method will be dependent upon the specific techniques used to prepare the samples. Current detection limits as determined by Brooks Rand LLC (BRL) are found in Table 1 of this document.

3.0 INTERFERENCES

3.1 The potential exists for destruction of the gold traps (and consequently, low recoveries) if free halogens are purged onto them.

3.2 Water vapor may collect in the gold traps, and be released into the fluorescence cell where it condenses, giving a false peak due to scattering of the excitation radiation.

3.3 As always with atomic fluorescence, the fluorescent intensity is strongly dependent upon the inertness of the carrier gas.

4.0 APPARATUS AND MATERIALS

4.1 Atomic fluorescence spectrophotometer (BRL part #AF-03): To achieve the low detection levels a very sensitive CVAFS detector is required. Such systems are built at BRL (BRL Model III) based on the principles discussed in the literature. Refer to the "Brooks Rand, LLC Model III Operation Manual" for instrument operating instructions.

4.2 Flow meter/needle valve (BRL part #AF-60): Capable of controlling and measuring gas flow to the purge vessel at 200-500 mL·min^{-1}.

4.3 Fluoropolymer adapters (BRL part #s AF-80 through AF-84) and tubing

4.4 Acid-fume and moisture pre-trap

4.5 Cold vapor generator (BRL part #AF-31)

4.6 Gold wire traps or gold-coated sand traps (BRL part #AF-19 or AF-20): Used for trapping gaseous Hg^0.

4.7 Recorder: The BRL Model III comes complete with Guru® integrating software. Refer to the "Brooks Rand, LLC Model III Operation Manual" for Guru® software/integrator operating instructions. Guru® software requires an IBM compatible computer (Pentium® II, 400MHz, 128MB RAM minimum) and running MS Windows® 98SE/ME/NT4/NT2000/XP.

4.8 Pipettors: Pneumatic fixed volume and variable pipettors in the range of 10 µL to 5.0 mL.

4.9 Refluxing digestion flask

4.10 Cold digestion vials

4.11 Nichrome wire coil (BRL part #AF-40) with plug (BRL part #AF-41): Used for heating the gold trap to thermally desorb the mercury.

5.0 REAGENTS

Document standard or reagent preparation in the appropriate logbook located in the Mercury Analysis Laboratory. Record the standard or reagent type, identification number, preparation date, lot number, expiration date, and analyst name in the appropriate standard or reagent preparation logbook. Record the standard or reagent type, identification number, preparation date, and expiration date on the container.

5.1 Water: 18 megohm ultrapure deionized water (ASTM type I) originating from a pre-purified source.

5.2 Nitric acid (HNO_3): Trace-metal reagent grade pre-analyzed, low mercury (<5.0 ng·L^{-1} Hg) concentrated nitric acid.

5.3 Sulfuric acid (H_2SO_4): Trace-metal reagent grade pre-analyzed, low mercury (<5.0 ng·L^{-1} Hg) concentrated sulfuric acid.

5.4 Hydrochloric acid (HCl): Trace-metal reagent grade pre-analyzed, low mercury (<5.0 ng·L^{-1} Hg) concentrated hydrochloric acid.

5.5 Stannous chloride

5.6 Bromine monochloride (BrCl)

5.7 Hydroxylamine hydrochloride (NH_2OH·HCl)

5.8 Stock mercury standard: A commercially available 1000 mg·L^{-1} mercury atomic absorption standard that is traceable to NIST is used. Alternatively, $HgCl_2$ may be dissolved in water and BrCl, and brought to volume.

5.9 Intermediate mercury standard solution: This solution contains 1.00 µg·mL^{-1} Hg.

5.10 Mercury working standards: The intermediate mercury standard solution is diluted with ultrapure deionized water and BrCl, to make a 10.0 ng·mL^{-1} working standard. A 1.00 ng·mL^{-1} working standard should be prepared using the intermediate mercury standard.

5.11 Nitrogen

5.12 Argon or Helium

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected into glass, polyethylene, or fluoropolymer jars. Polyethylene bags are also acceptable for all but very low level and/or very wet solid samples. Dry samples such as coal and ores may be collected and stored in heavy gauge paper pouches.

6.2 Samples containing biota (i.e. wet or dry sludge), and all wet sediment samples are shipped to the laboratory at 0-4 ºC and stored at < -15 ºC for up to 1 year. Dry samples such as ores, paper, and wood may be shipped unrefrigerated and stored indefinitely in a cool, dry location low in mercury.

6.3 Biota samples are to be frozen at < -15 °C (standard freezer on coldest setting) until use. Samples may be stored for a maximum holding time of 1 year.

6.4 Freezing and thawing of sediment samples may adversely affect their homogeneity; therefore, sediment samples should be aliquoted and weighed at the laboratory prior to freezing. To better assure homogeneity, large particles such as rocks and sticks should be removed by screening the samples through a 2.0 mm sieve. If wet sediment samples have been frozen prior to preparation, they must be sequentially homogenized into smaller aliquots as follows. First the whole sample must be emptied into a clean weigh boat and thoroughly homogenized. Then half of the sample is transferred to another

clean weigh boat and thoroughly homogenized. The procedure is continued until the appropriate sample preparation weight is left. Refer to SOP BR-0106 for further discussion of sample homogenization. Additionally, any other associated sample preparations to be performed with the sample (such as percent solids analysis) should homogenized and aliquoted at the same time to ensure that the aliquots are similar in sample characteristic. All remaining sample is stored in the original sample container at < -15 ºC for up to 1 year.

6.5 All dissection, homogenization, and other handling of the samples are to occur by clean room gloved personnel in an environment free of mercury contamination.

7.0 PROCEDURE

7.1 Sample Preparation

7.1.1 General considerations: Dissect and/or homogenize the sample with clean stainless steel tools. Sediment and soil samples may be homogenized with an acid-cleaned fluoropolymer spatula.

7.1.2 Hot re-fluxing HNO_3/H_2SO_4 digestion: This procedure is used for biota, wood, paper, tissue, sludge, or other soils high in organic content. An aliquot of homogenized sample is weighed directly into a glass vial. HNO_3 and H_2SO_4 are pipetted into the sample, and the preparation is swirled.

Fluoropolymer cones or glass marbles are placed on each glass vial to allow refluxing of the preparation. Samples are next placed in a sand bath or on a hotplate, and brought up to a refluxing boil in temperature increments to avoid excessive foaming, especially common with tissue samples. The samples are allowed to cool prior to removal from the sand bath or hotplate. BrCl is added to each sample, and then the samples are diluted with ultra pure deionized water.

7.1.3 Alternative cold aqua regia digestion: This procedure is for geological media such as coal, ores, sediments, and soils. Since the matrix is leached rather than dissolved, the sample must be pulverized prior to digestion if the total mercury content is desired.

Weigh sample into a Digestion Tube. In a fume hood, add HCl, swirl, and add HNO_3. The vial may be loosely capped or covered with a clean glass marble or fluoropolymer cone. The preparation should then be allowed to digest at room temperature overnight.

Add BrCl, dilute the digestate, shake vigorously, and allow to fully settle prior to analysis.

7.2 Analysis: Analysis is performed very similarly to water samples, which is described in BRL SOP-0011.

8.0 QUALITY CONTROL

Current method detection limits are listed in Table 1. For easy reference for QC criteria refer to Table 2, which outline typical run sequences and required QA samples and Table 3, which describes all required QA frequency requirements and QA acceptance criteria along with corrective actions for failed QA.

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration data must be composed of a minimum of 4 calibration blanks (one per bubbler used) and 5 non-zero point standards. Such a calibration must be analyzed daily prior to beginning analysis and run whenever continuing calibration verification (CCV) samples fail to meet acceptance criteria.

8.3 Samples containing high analyte concentrations may be run following dilution. The amount of total mercury measured in the sample aliquot analyzed (P_S) must ultimately fall below the peak area obtained from the highest standard analyzed and above the adjusted PQL.

8.4 Calibration checks must be analyzed after instrument calibration, every ten samples, and at the end of the analytical batch. Calibration checks shall consist of analysis of a certified, traceable standard, referred to as a CCV, at a level in the low to mid-range of the calibration (i.e. 500 pg) and a bubbler blank, also referred to as a continuing calibration blank (CCB). The CCB only needs to be run after the initial CCV. In addition, a standard from a source other than the one used to make the calibration standards must be run prior to the analysis of samples. This standard is referred to as the independent calibration verification (ICV) standard. The ICV is analyzed at the mid-range of the calibration (i.e. 1000 pg). The CCV standards must be within ±23% (77-123%) of the certified value and the ICV standard must be within ±15% (85-115%) for analysis to continue.

Carryover check bubbler blanks must be immediately analyzed following any sample result that exceeds one half of the "carryover threshold". The carryover threshold is determined by repeatedly analyzing standards with higher concentrations until a bubbler blank analyzed immediately after the standard, using the same bubbler/trap combination, yields a result that is > 50 pg and/or deviates from the average calibration blank by more than 20 pg. Currently, the carryover threshold has been determined to be 100,000 pg. Therefore, a carryover check bubbler blank is required following any sample result > 50,000 pg. Neither the bubbler nor the trap may be used to analyze client samples until it has met all bubbler blank criteria. Any samples analyzed using either the bubbler or the trap before the bubbler/trap combination has met the blank criteria must be reanalyzed using a different bubbler/trap combination.

8.5 A minimum of 3 method blanks (BRL routinely prepares 4 method blanks) per batch of 20 client samples must be run. The criterion for the method blanks is average method blank less than two times the MDL and standard deviation less than 0.67 times the MDL or less than $1/10^{th}$ of the associated client samples.

8.6 Matrix spike (MS) and matrix spike duplicate (MSD) recoveries are analyzed at a minimal frequency of one per every 10 client samples. At least one matrix spike sample and matrix spike duplicate sample set must be analyzed per batch and at least two must be analyzed if more than 10 client samples are in a batch. Criterion for MS/MSD analysis is recoveries of 70-130% with a relative percent difference ≤ 30% for sediment and biota and 65-135% with a relative percent difference of ≤ 35% for blood or other samples using the micro method. Spiking levels of MS/MSD should be equal to the regulatory compliance limit, or 1-5 times the background concentration of the sample, whichever is greater. When samples are found to be greater than the spike level, resulting in under spiked MS/MSD samples and possible low recoveries, a post digestion spike (PDS) or bubbler spike should be performed. A spike resulting in a concentration 1-5 times that of the sample native should be added directly into the bubbler using an appropriate calibration standard.

8.7 Certified reference materials (CRM) for mercury in tissues and sediments are analyzed at a minimal frequency of once per every 10 client samples. At least one CRM must be analyzed per batch and at least two must be analyzed if more than 10 client samples are in a batch. At least one appropriate CRM must be run for each different type of matrix being analyzed in a batch. The criterion for CRMs is determined using control charts. If control charts are not available then CRM results should be within 25% of the certified value for the analysis to be considered valid. CRM sample results not meeting this criterion shall be reprepared and analyzed or qualified at the discretion of the lab manager. A list of CRMs currently in stock at BRL is included as Table 4.

8.8 Method duplicate (MD) samples should be prepared and analyzed in conjunction with the MS/MSD samples and whenever samples are deemed to have matrices that are so heterogeneous that it might affect the analysis of the sample. The acceptance criterion for duplicate analysis is RPD ≤ 30% or ± two times the PQL if the sample results are ≤ five times the PQL.

9.0 REFERENCES

Bloom, N.S. and Crecelius, E.A. (1983). "Determination of Mercury in Seawater at Subnanogram per Liter Levels." *Mar. Chem.* 14:49.

Bloom, N.S. and Fitzgerald, W.F. (1988). "Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapour Atomic Fluorescence Detection." *Anal. Chim. Acta.* 208:151.

EPA Appendix to Method 1631. (2001). "Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation."

EPA Method 1631.E. (8/02). "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry."

Fitzgerald, W.F. and Gill, G.A. (1979). "Sub-Nanogram Determination of Mercury by Two-Stage Gold Amalgamation and Gas Phase Detection Applied to Atmospheric Analysis." *Anal. Chem.* 15:1714.

Liang, L. and Bloom, N.S. (1992). "Determination of Total Hg by Single-Stage Gold Amalgamation with Cold Vapor Atomic Spectrometric Detection." *JAAS.* June 8:001

10. TABLES AND BENCHSHEETS

Table 1 Current Method Detection Limits and Minimum Levels Determined at BRL for the Analysis of Total Mercury in Solids Using EPA Method 1631, Appendix

Matrix	Preparation Method	Method Detection Limit (MDL)[1]	Minimum Level (ML)
Sediment/Sludge	Aqua regia cold digestion (regular BrCl level)	0.03 ng/g	0.10 ng/g
Coal (samples high in elemental carbon)	Aqua regia cold digestion (increased BrCl level)	0.20 ng/g	0.60 ng/g
Biota/Sediment	HNO_3/H_2SO_4 hot digestion	0.04 ng/g	0.10 ng/g
Biota/Sediment	Micro volume hot digestion	1.5 ng/g	4.5 ng/g
Hair (w/washing step)	HNO_3/H_2SO_4 hot digestion	0.80 ng/g	2.50 ng/g

NOTES:

1. MDL as determined by the procedure 40 CFR Part 136, Appendix B.

Table 2. - Run Sequence for Total Hg in Solids (suggested)

Run	Run Name	Section Name	Analyze	Requirements
01	Calib. Blank	Calibration Blanks	CB	each CB <50 pg Ave. <25 pg StDev <10 pg
02	Calib. Blank		CB	
03	Calib. Blank		CB	
04	Calib. Blank		CB	
05	25 pg std	Calibration*	25 pg Hg	RSD<15% Rec. Low Std. = 75-125%
06	100 pg std		100 pg Hg	
07	500 pg std		500 pg Hg	
08	2500 pg std		2500 pg Hg	
09	10000 pg std		10000 pg std	
10	OPR (500 pg std)	Ongoing Precision and Recovery	5.0 $ng \cdot L^{-1}$ std	Recovery 77-123%
11	ICV (1000 pg std)	Independent Calibration Verification	10.0 $ng \cdot L^{-1}$ std, different source	Recovery 85-115%
12	CCB	Calibration Check	Calib. Check Blank	< 50 pg, ± 20 pg from ave.
13	Method Blank	Method Blanks	MB	Average < 2 x MDL and St. Dev. < 2/3rd of MDL or High MB < 1/10th sample
14	Method Blank		MB	
15	Method Blank		MB	
16	Method Blank		MB	
17	CRM-1	Certified Reference Materials	CRM	Recovery = 75-125% Blood CRM Rec. = 65-135%
18	CRM-2		CRM	
19	LFB	Laboratory Fortified Blank	Blank Matrix Spiked at 4.0 ng	Recovery = 70-130% (use only if no CRM available)
20	Sample 01	Sample Analysis	Sample 01 Native	RPD≤30% or ±2xPQL if results ≤5xPQL
21	Sample 01-MD	Duplicate Analysis	Sample 01 Duplicate	
22	Sample 01-MS	Matrix Spike Analysis Spike	01 + Spike	Recovery = 70-130%
23	Sample 01-MSD	Duplicate Analysis	01 + Spike	RPD≤30%**
24	Sample 02	Sample Analysis	Sample 02	
25	Sample 03		Sample 03	
26	Sample 04		Sample 04	
27	Sample 05		Sample 05	
28	Sample 06		Sample 06	
29	Sample 07		Sample 07	
30	Sample 08		Sample 08	
31	Sample 09		Sample 09	
32	Sample 10		Sample 10	
33	OPR (500 pg std)	Ongoing Precision and Recovery	5.0 $ng \cdot L^{-1}$ std	Recovery 77-123%
34	Sample 11	Sample Analysis	Sample 11 Native	RPD≤30% or ±2xPQL if results ≤5xPQL
35	Sample 11-MD	Duplicate Analysis	Sample 11 Duplicate	
36	Sample 11-MS	Matrix Spike Analysis Spike	11 + Spike	Recovery = 70-130%
37	Sample 11-MSD	Duplicate Analysis	11 + Spike	RPD≤30%**
38	Sample 12	Sample Analysis	Sample 12	
39	Sample 13		Sample13	
40	Sample 14		Sample 14	
41	Sample 15		Sample 15	
42	Sample 16		Sample 16	
43	Sample 17		Sample 17	
44	Sample 18		Sample 18	
45	Sample 19		Sample 19	
46	Sample 20		Sample 20	
47	OPR (500 pg std)	Ongoing Precision and Recovery	5.0 $ng \cdot L^{-1}$ std	Recovery 77-123%

* Calibration Curve may be adjusted depending on expected concentration range of samples and on the linear range due to instrumentation.

** Matrix spike / spike duplicate acceptance criteria for blood and small mass samples is recovery = 65-135% with an RPD ≤ 35%.

Table 3. Quality control criteria for the analysis of mercury in solids by CVAFS

QC Sample	Measure	Minimum Frequency	Criteria	Corrective Action
Bubbler Blank	Contamination from bubblers	1 per bubbler used prior to analysis, then following initial CCS	each ≤ 50 pg avg ≤ 25 pg std ≤10 pg	Clean and test bubblers until criteria met prior to any analysis
Calibration Standards	Acceptability of the Calibration Curve	Each day prior to analyzing samples and whenever OPR/QCS analysis fails	RSD of response factors ≤ 15%; Recovery of Low Standard = 75 – 125%	Reanalyze suspect calibration standard. If criteria still not met, then remake standards and recalibrate the instrument
Independent Calibration Verification (ICV)	Test of the entire analytical system	1 per batch following the calibration (following calibration blanks if verifying past calibration)	Recovery = 85 – 115%	Correct problem prior to continuing analysis, recalibrate system if required
Ongoing Precision and Recovery (OPR)	Accuracy	2 per batch (one at the beginning and one at the end of each batch)	Recovery = 77 – 123%	Correct problem and reanalyze OPR. If criteria met, reanalyze samples backwards until 2 consecutive results w/RPD ≤ 20%
Carryover Check Bubbler Blank	Contamination due to carryover in the bubbler/trap	On same bubbler/trap following any result exceeding ½ the carryover threshold of 100,000 pg	≤ 50 pg and within ± 20 pg of avg bubbler blank	Clean and continue to test bubbler/trap combo until criteria met prior to further use. Samples analyzed following a result ≥ ½ the carryover threshold must be reanalyzed
Method Blank	Contamination from reagents, lab ware, etc.	3 per batch	Avg < 2 x MDL StDev < 2/3rd of MDL or High MB < 1/10th of associated samples	Correct problem until criteria met. All samples associated with a contaminated method blank must be reanalyzed or qualified accordingly.
Certified Reference Material (CRM)	Accuracy	1 per 10 client samples	Recovery = 75 – 125%; Blood CRM Rec. = 65 – 135%	Correct problem prior to continuing analysis
Matrix Spike/Spike Duplicate	Accuracy and Precision within a given matrix	1 per 10 client samples	Recovery = 70 – 130%; RPD ≤ 30% Blood and Small Mass Criteria Recovery = 65 – 135%; RPD ≤ 35%	If **recoveries** similar but fail recovery criteria, interference may be present in the sample and the result must be qualified. If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples.
Method Duplicate	Precision within a given matrix	In conjunction with MS/MSD samples and when deemed necessary	RPD ≤ 30% Blood and Small Mass Criteria RPD ≤ 35%	If **RPD** criteria not met, then the system is not in control. Correct problem and reanalyze all associated samples or qualify accordingly.

APPENDIX C

SELECTED 2007 RESULTS

SELECTED 2007 RESULTS

This appendix presents selected results from the 2007 nitrate evaluation study (UFI and SU, 2007) in order to assess the need for 1) water column and zooplankton sampling at North Deep in 2008 and 2) collection of water samples for laboratory analysis in conjunction with high resolution rapid profiling ultraviolet spectrophotometry (ISUS) sampling in 2008. Analytical data and ISUS field measurements are presented in the 2007 Data Usability and Summary Report (Exponent, 2008).

Summary of North Deep and South Deep Data

North Deep and South Deep were sampled concurrently on five dates in 2007 to assess variability between the two stations and to determine if South Deep is a representative station for water and zooplankton monitoring in the deep basins of Onondaga Lake. Figures 1 – 5 present the results for total mercury, and methylmercury, and nitrate concentrations in water and total mercury and methylmercury concentrations in zooplankton, respectively.

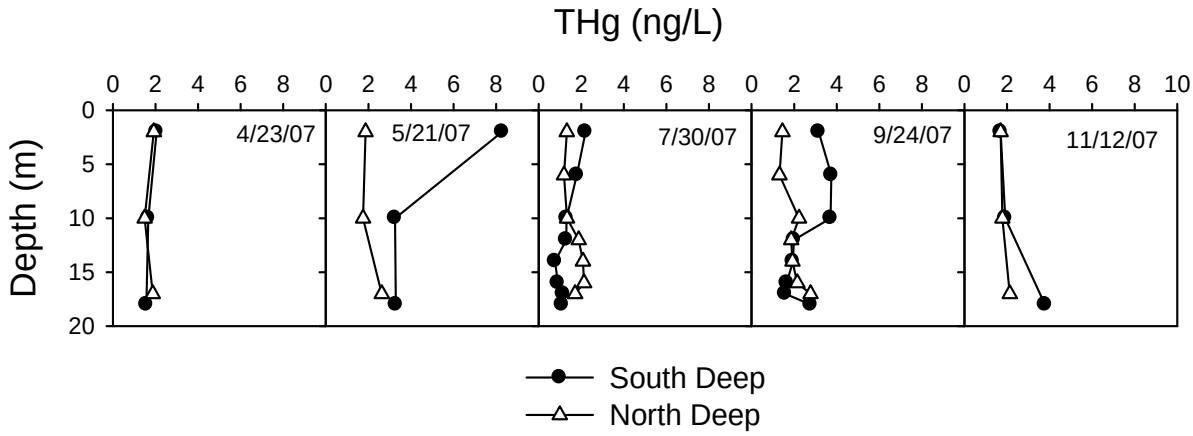


Figure 1. Spatial differences in total mercury concentrations in water of Onondaga Lake

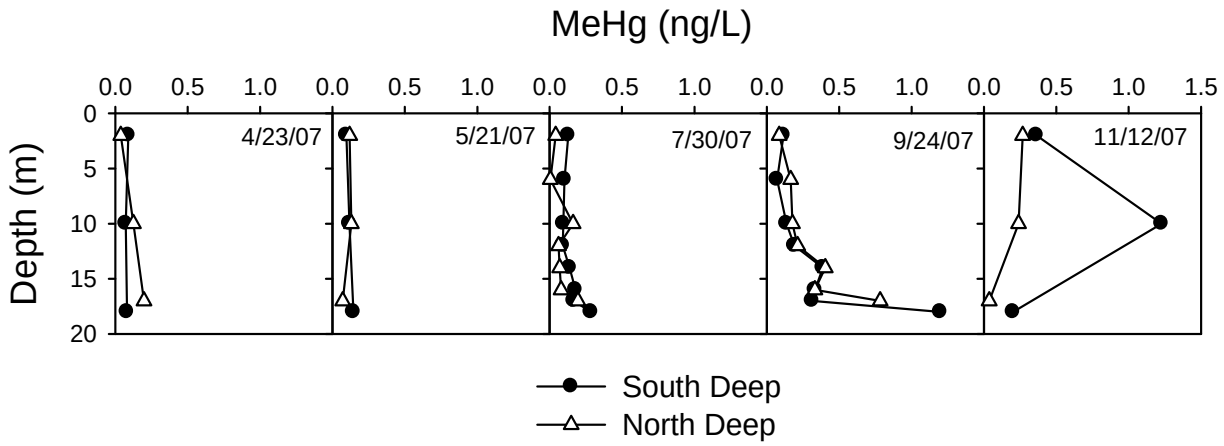


Figure 2. Spatial differences in methylmercury concentrations in water of Onondaga Lake

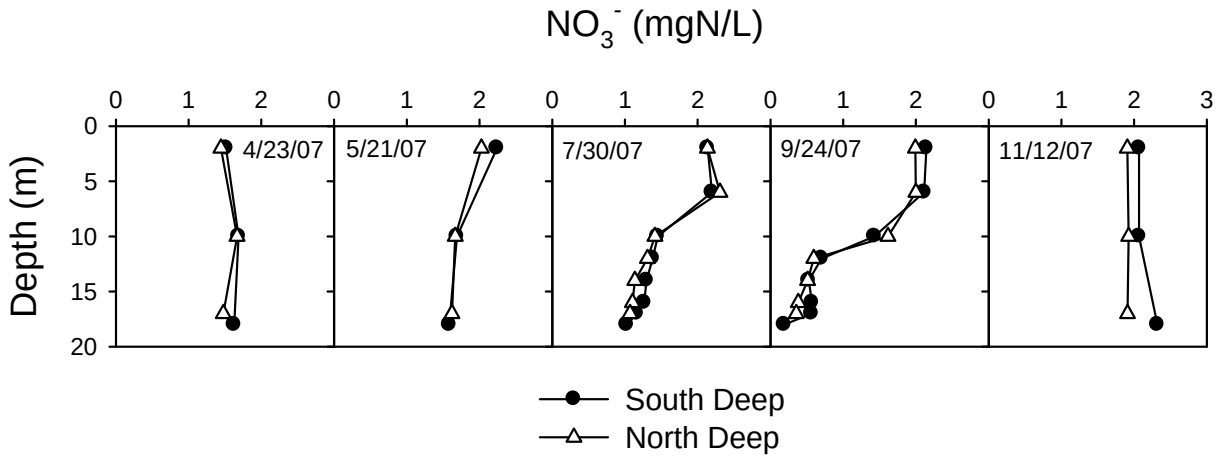


Figure 3. Spatial differences in nitrate concentrations in water of Onondaga Lake

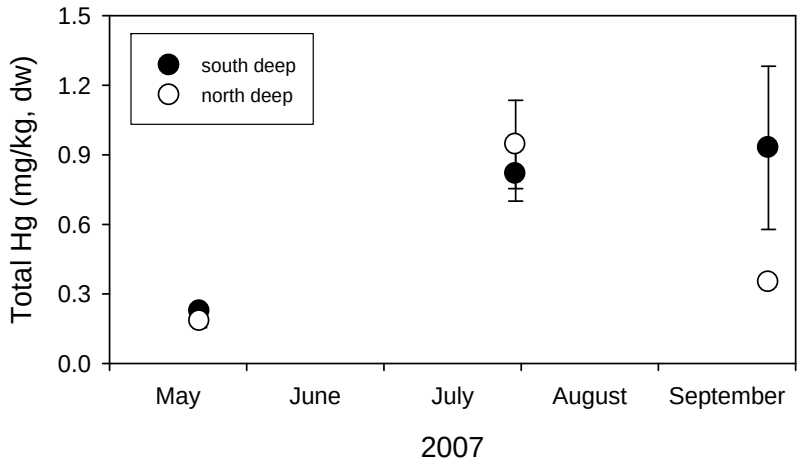


Figure 4. Spatial differences in total mercury concentrations in zooplankton in Onondaga Lake (mean, minimum, maximum of field duplicates)

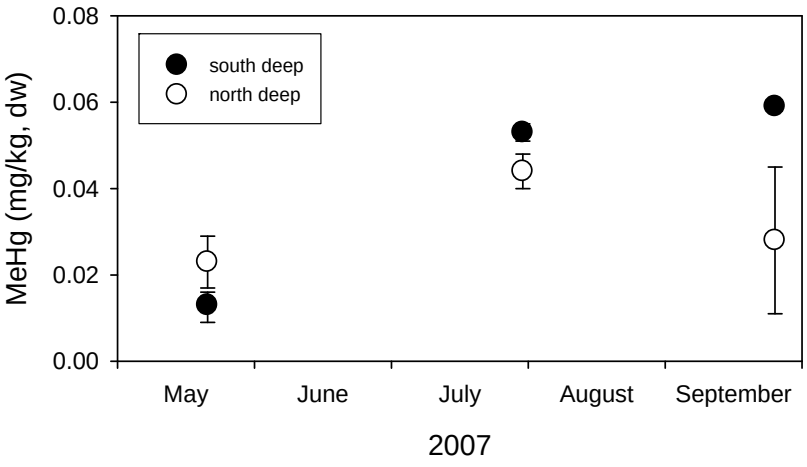


Figure 5. Spatial differences in methylmercury concentrations in zooplankton in Onondaga Lake (mean, minimum, maximum of field duplicates)

Concentrations were generally consistent between the two basins. There were occasional depths and times where South Deep water data were significantly higher than North Deep water data (e.g., total mercury at 2 m depth on 5/21/07; methylmercury at 10 m depth on 11/12/07). A more common occurrence for total mercury in water was slightly higher concentrations at South

Deep than at North Deep, which is consistent with potential resuspension of nearshore mercury-contaminated sediment in the southern part of the lake. In general, these data support the use of South Deep as a representative station for water and zooplankton monitoring in the deep basins of Onondaga Lake.

Summary of Dissolved Oxygen, Nitrate, Total Mercury, and Methylmercury Data Collected in Conjunction with ISUS Sampling

Water samples were collected approximately 1 m above the sediment surface at ISUS gridding locations on two dates in 2007 consistent with the 2007 nitrate evaluation study work plan (UFI and SU, 2007). Figures 6 and 7 present the dissolved oxygen, nitrate, total mercury, and methylmercury concentrations at 12 locations on 9/24/07 and 11 locations on 11/5/07. These data help to address three questions that have arisen in discussions with the SMU8 Technical Work Group: 1) are ISUS measurements of nitrate supported by laboratory analysis?, 2) are redox-dependent parameters consistent with ISUS nitrate measurements?, and 3) when evaluating the spatial distribution of redox-dependent parameters, is water depth or height above sediment surface more important? These data also permit an evaluation of the need for additional laboratory analysis for water samples collocated with ISUS gridding stations.

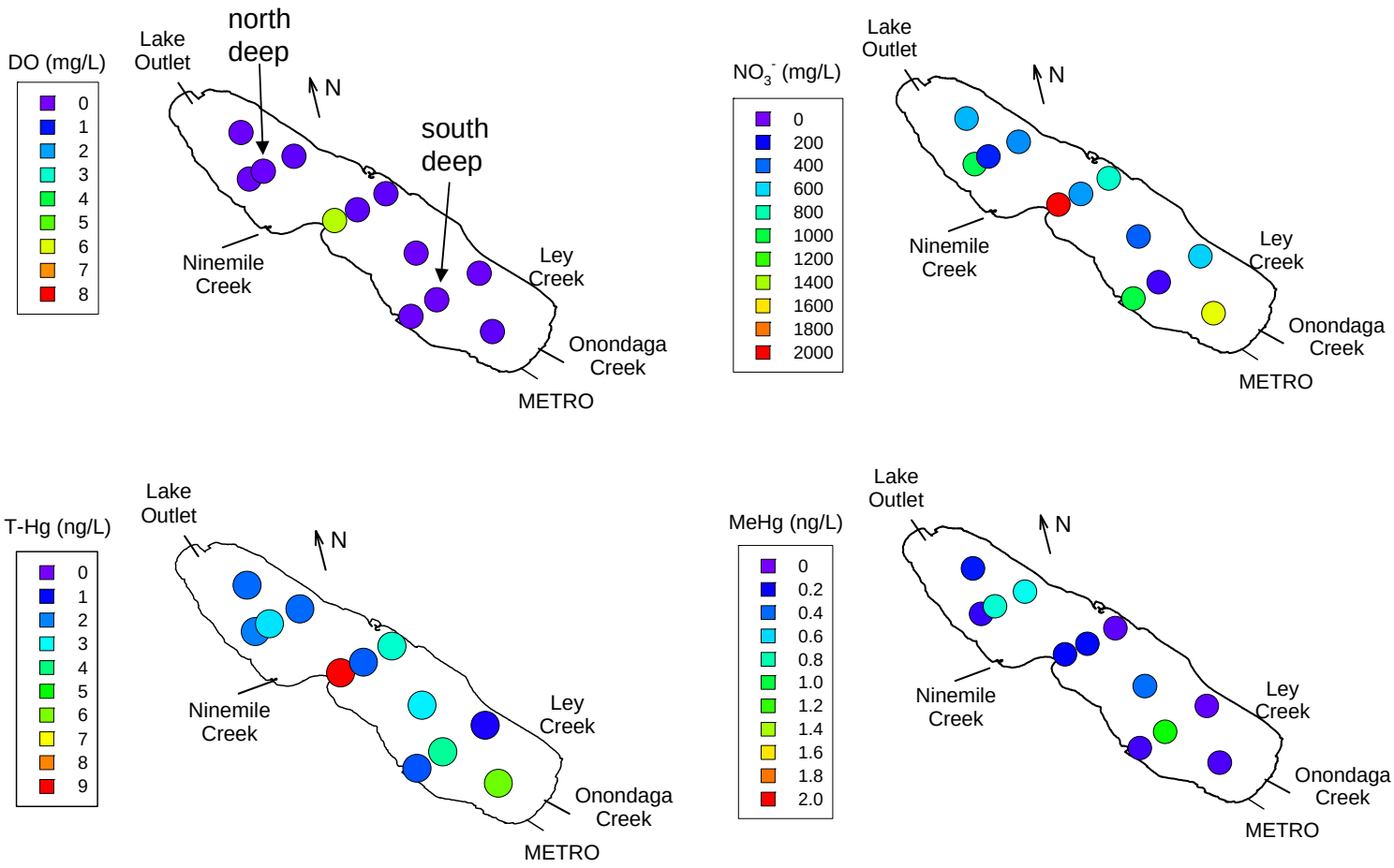


Figure 6. Concentrations of dissolved oxygen, nitrate, total mercury, and methylmercury in water at ISUS gridding locations on 9/24/07. Samples collected at ~ 1 m above sediment surface. The locations of North Deep and South Deep sampling sites are identified on the dissolved oxygen (DO) figure.

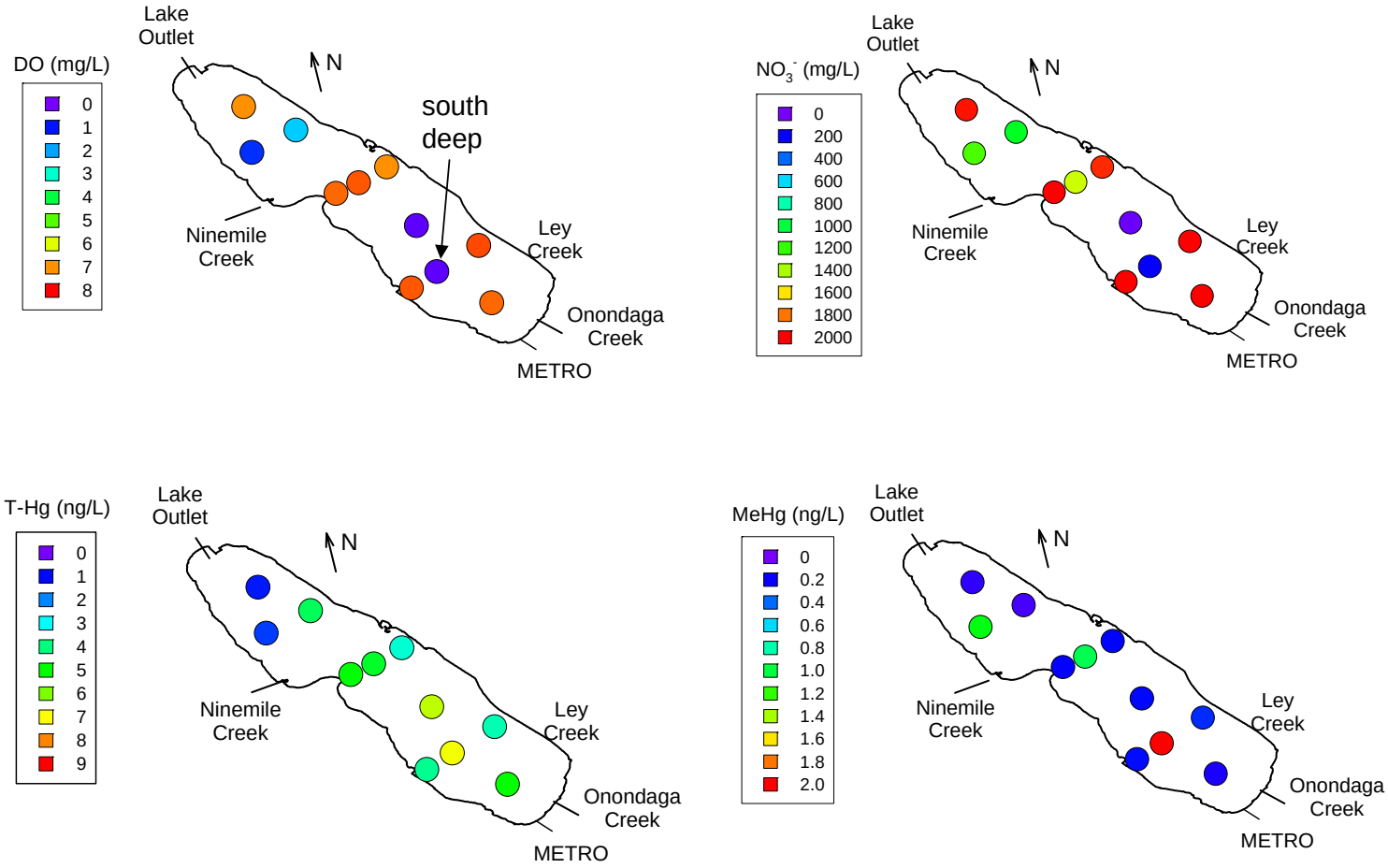


Figure 7. Concentrations of dissolved oxygen, nitrate, total mercury, and methylmercury in water at ISUS gridding locations on 11/5/07. Samples collected at ~ 1 m above sediment surface. The location of South Deep sampling site is identified on the dissolved oxygen (DO) figure.

With respect to the first question, ISUS nitrate values compared very well with lab nitrate values at South Deep (Figure 8). Because there are a large number of data points and the relationship is so strong ($r^2 = 0.9408$) and has such a small intercept and a slope of approximately 1, monitoring of nitrate concentrations by ISUS is considered sufficient and does not require further collection and laboratory analysis of water samples for confirmation.

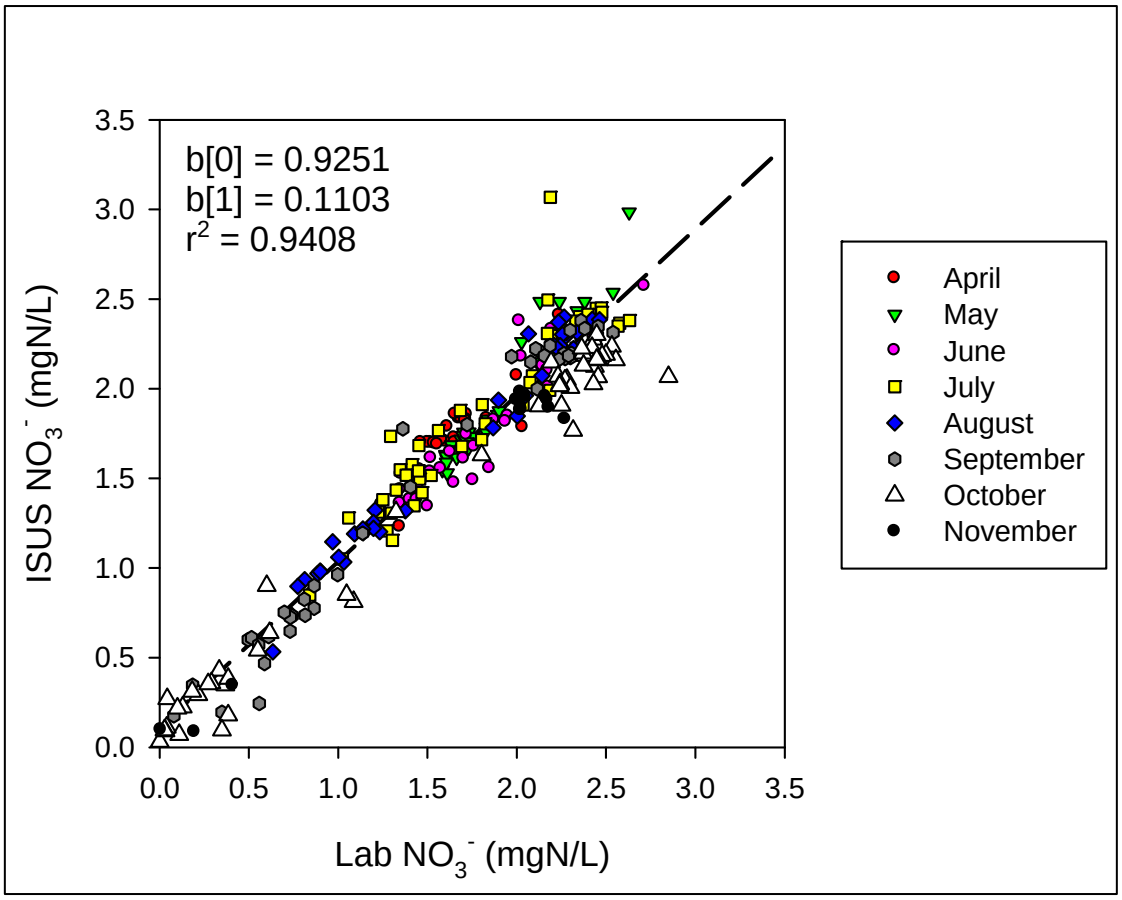


Figure 8. Comparison of 2007 ISUS and laboratory nitrate concentrations

Regarding the second and third questions, concentrations of redox-dependent parameters (dissolved oxygen, methylmercury, and, to some extent, total mercury) in water tend to correlate with ISUS nitrate concentrations and with water depth, rather than with height above sediment (Figures 6 and 7). The exceptions for total mercury were nearshore Locations 9 and 11 on 9/24/07, where higher concentrations were observed than would be expected given the water depth, nitrate concentrations, and total mercury concentrations at adjacent sites. These observations at Locations 9 and 11 on 9/24/07 are consistent with the hypothesis that nearshore sediments contaminated by mercury may be resuspended and result in elevated total mercury concentrations in water.

Conclusions

There are three main conclusions from the 2007 work that is summarized here. First, South Deep is a representative station for water and zooplankton monitoring in the deep basins of Onondaga Lake. Second, the ISUS provides nitrate concentration data that are consistent with laboratory analysis. Third, collection and laboratory analysis of water samples in conjunction with ISUS sampling at other locations besides South Deep are considered unnecessary at this time for the purpose of deep basin water column monitoring. It should be noted that additional water monitoring to provide a basis to establish goals for water quality during implementation of the remedy (one of the data uses identified in the Baseline Scoping Document [Parsons, 2008]) will be addressed in a separate work plan currently being developed by the Dredging and Sediment Consolidation Area (SCA) Operations Technical Work Group. A scope for this monitoring has not yet been formulated, but it will likely include monitoring stations located near planned dredging/capping operations (near-field stations) and monitoring stations in the basins (far-field stations).

References

Exponent. 2008. Draft Data Usability and Summary Report. Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake: 2007 Study. Prepared for Honeywell, Morristown, NJ. Exponent, Maynard, MA. April 2008.

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