ADDENDUM 1 (2009) TO

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

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LIST OF ACRONYMS

Chl	chlorophyll
CH_3Hg	methylmercury
Cl^-	chloride
CPOI	chemical parameter of interest
DOC	dissolved organic carbon
DUSR	Data Usability and Assessment Report
Fe^{2+}	ferrous iron
H_2S	hydrogen sulfide
Hg	mercury
ISUS	high resolution rapid profiling ultraviolet spectrophotometer
mL	milliliter
NO_x	nitrate+nitrite
NYSDEC	New York State Department of Environmental Conservation
OPR	ongoing precision and recovery
ppm	parts per million
QAPP	quality assurance project plan
S^{2-}	sulfide
SO_4^{2-}	sulfate
SOP	standard operating procedure
SU	Syracuse University
TDG	total dissolved gas
TIC	total inorganic carbon
$T\text{-}NH_3$	total ammonia
TOC	total organic carbon
UFI	Upstate Freshwater Institute
USEPA	U.S. Environmental Protection Agency

EXECUTIVE SUMMARY

This addendum to the 2008 Book 1 Work Plan (UFI and SU, 2008) presents the scope for the 2009 deep basin water and zooplankton monitoring in the context of the baseline monitoring program objectives, program elements, and data uses as well as the results of the 2008 program. The 2009 scope is the same as that for 2008 with the exception of minor modifications to optimize the timing and location of water sample collection and eliminate monitoring components no longer considered necessary. In addition, use of sediment traps is being added at one location. Key components of the 2009 scope are 1) water column sampling at multiple depths at South Deep from April through November, 2) zooplankton sampling from April through November, and 3) sediment trap sampling from April through October. Analyses will include measurement of low-level total mercury and methylmercury and ancillary parameters (including nitrate by ISUS) in the water column; total mercury, methylmercury and community composition for zooplankton; and total mercury, solids, and ancillary parameters in settling solids. The rationale for the 2009 scope and modifications to the 2008 scope is presented. The work proposed in this addendum will use the 2008 Book 1 Standard Operating Procedures (SOPs) and Quality Assurance Project Plan (QAPP). New SOPs are provided in Appendix A of this addendum. Revised worksheets for the 2008 Book 1 QAPP are provided as Appendix B of this addendum.

SECTION 1

INTRODUCTION

This addendum to the 2008 Book 1 Work Plan (UFI and SU, 2008) presents the scope for the 2009 deep basin water and zooplankton monitoring in the context of the baseline monitoring program objectives, program elements, and data uses as well as the results of the 2008 program. The rationale for key modifications to the 2008 Book 1 Work Plan is also presented.

The work proposed in this addendum will use the 2008 Book 1 SOPs and QAPP. New SOPs are provided in Appendix A of this addendum. Revised worksheets for the 2008 Book 1 QAPP are provided in Appendix B of this addendum.

1.1 OBJECTIVES AND DATA USES

Program objectives, program elements, and data uses for the deep basin water and zooplankton monitoring previously described in the draft Baseline Monitoring Scoping Document (Parsons, 2008) are presented in Table 1 along with a summary of how each was addressed in 2008 and will be addressed by the work described in this addendum for 2009.

1.2 RATIONALE FOR MODIFICATIONS TO THE 2008 BOOK 1 WORK PLAN

This 2009 addendum includes five key modifications to the 2008 Book 1 Work Plan in order to optimize the timing and location of water sample collection, eliminate monitoring components no longer considered necessary, and add one new component. These modifications and their rationale are as follows:

- Changes to sampling depths:

  Review of the 2008 data indicates that several changes to the sampling depths would result in a more efficient sampling program. First, the 19 m water depth was rarely sampled in 2008 because water levels tended to be low. Depending on the date, the 17 m or 18 m depth was sampled in its place. In 2009, the 18 m depth rather than 17 m or 19 m will be sampled, consistent with previous investigations. Second, the 14 m water depth will be added to the first half of September, primarily to provide consistent sampling depths throughout the month of September. Third, water samples at the 6 m depth will be omitted during and after fall turnover, and water samples at the 14 m and 16 m water depth will be omitted after fall turnover. The 2008 data showed constant concentrations of total mercury and methylmercury throughout the water column following fall turnover, indicating a well-mixed water column. Therefore, the 2 m, 12 m, and 18 m sampling depths will be sufficient for characterizing the water column during this period.

TABLE 1

**ONONDAGA LAKE BASELINE MONITORING
PROGRAM OBJECTIVES, PROGRAM ELEMENTS, AND DATA USES
PERTAINING TO BASELINE MONITORING BOOK 1**

Program Objective	Program Element	Data Use	2008 Book 1	Book 1 Addendum 1 (2009)	Comments
Establish baseline chemical and physical conditions	Lake Water Sampling	**Baseline for Remedy Effectiveness**			
		Provide basis to measure achievement of PRG3 (surface water quality standards)	Book 1 included analysis of unfiltered and filtered (i.e., dissolved) total mercury at 2 m water depth at South Deep. The lowest State of New York mercury surface water quality standards are on a dissolved total mercury basis.	Same as 2008 with slightly less frequency.	Additional CPOIs will be monitored in 2010 or 2011 at South Deep, at nearshore locations where exceedances were previously noted, and/or near source areas. This work may be done in 2009 in conjunction with monitoring by the Operations Technical Work Group for the purpose of establishing water quality goals during implementation.
		Provide basis to measure success in controlling key processes (e.g., mercury methylation, sediment resuspension from the in-lake waste deposit, mercury release from profundal sediment)	Book 1 included analysis of total mercury and methylmercury at multiple water depths and sufficient frequency at South Deep to document mercury methylation and mercury release from profundal sediment. It also included measurement of gas ebullition rates from profundal sediment and high resolution measurements of nitrate using ISUS.	Same water column sampling as 2008 with slightly less frequency and fewer depths. Discontinuation of gas ebullition measurement. Continuation of ISUS nitrate measurements on water column sampling days. Addition of sediment traps to track changes in solids and mercury loading to profundal sediment.	Water column monitoring at South Deep will continue annually through the design phase.
		Baseline for Remedy Design			
		Provide information for design of nitrate addition/oxygenation pilot tests and basis to measure results	Book 1 included analysis of oxygen, nitrate, and methylmercury at multiple water depths and sufficient frequency at South Deep to identify the critical concentrations of oxygen and nitrate associated with limited methylmercury efflux from sediment.	Same as 2008 with slightly less frequency and fewer depths.	Results will be used in design of nitrate addition/oxygenation pilot tests
Provide additional data for future understanding of remedy effectiveness in achieving PRGs	Other biota sampling	**Baseline for Remedy Effectiveness**			
		Assess biological factors that may contribute to variability in fish mercury concentrations	Book 1 included analysis of total mercury and methyl mercury in zooplankton and Daphnia, and zooplankton community composition.	Same as 2008.	Zooplankton monitoring will continue annually through the design phase.

Note: Sediment trap sampling has been added for 2009 to provide additional SMU 8 data about sedimentation characteristics. The value of sediment trap sampling beyond 2009 will be determined after results from 2009 are assessed.

- Reduction of water sampling frequency:

  Biweekly sampling in April, May, and June in 2008 showed that total mercury and methylmercury concentrations remained relatively constant during this period, consistent with historical observations. Therefore, sampling will occur once per month in April, May, and June in 2009. Sampling in July 2009 will be biweekly as it was in 2008. Weekly sampling in August and after turnover in 2008 provided little additional information on the behavior of total mercury and methylmercury in the hypolimnion. During both periods, concentrations of total mercury and methylmercury remained relatively low. Therefore, biweekly sampling is considered sufficient. Weekly sampling in September through fall turnover targets the most critical period of methylmercury accumulation in the hypolimnion.

- Reduction of zooplankton sampling frequency:

  In 2008, zooplankton sampling was conducted biweekly until August 4 and then weekly. Zooplankton data provide only ancillary information to understanding mercury bioaccumulation in fish. In addition, their mercury concentrations tend to be highly variable, complicating data interpretation. In 2009, zooplankton sampling will occur monthly in April, May, and June (consistent with water sampling) and then biweekly for the remainder of the season.

- Discontinuation of gas ebullition measurements:

  Gas ebullition measurements over the period of record shown in Figure 1 were highest in 1989 through 1991, declined considerably by 1993, and have remained approximately in the 10 to 75 $ml/m^2/d$ range since then. Peak methylmercury mass in the hypolimnion has only recently declined significantly as shown in Figure 2 and appears unrelated to the trends in gas ebullition rates and closely related to the increase in nitrate concentrations in the lake in recent years (UFI and SU, 2007a). Therefore, gas ebullition is unlikely to be a significant process with respect to mercury release from profundal sediment.

- Addition of sediment trap sampling and analysis

  Sediment trap sampling and analysis will provide current data to assess gross sedimentation of solids and total mercury during the April to October timeframe. A similar effort was conducted in 1992 during the Onondaga Lake remedial investigation.

Figure 1. Long-term series of gas ebullition rates in Onondaga Lake (UFI, unpublished data)

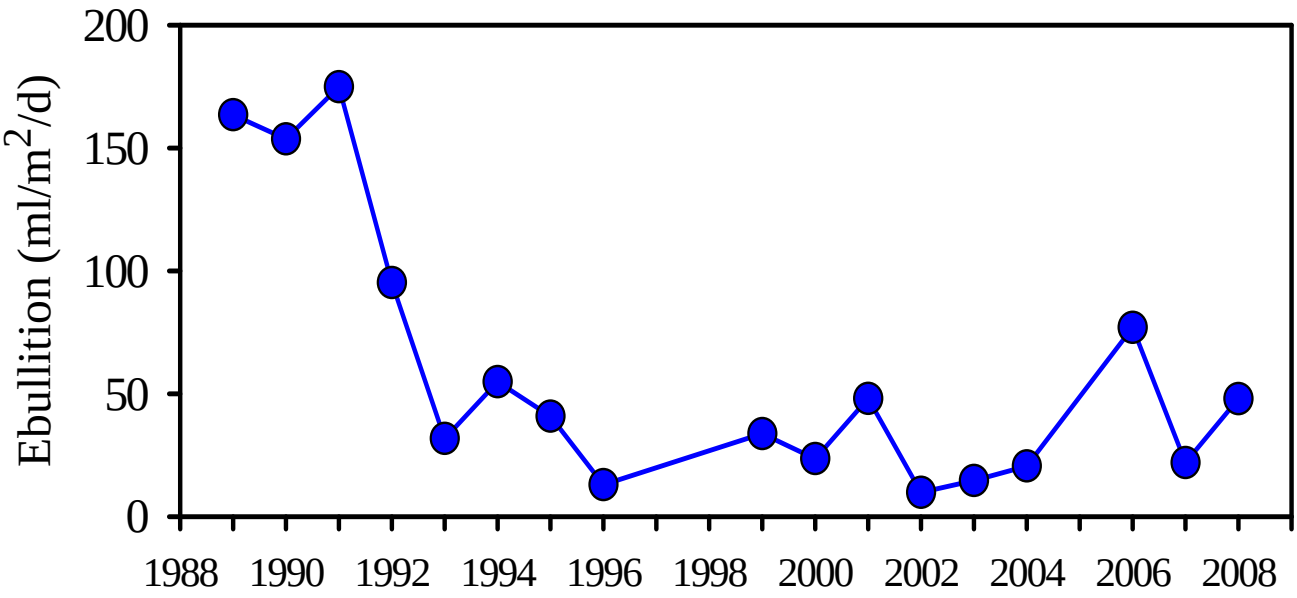
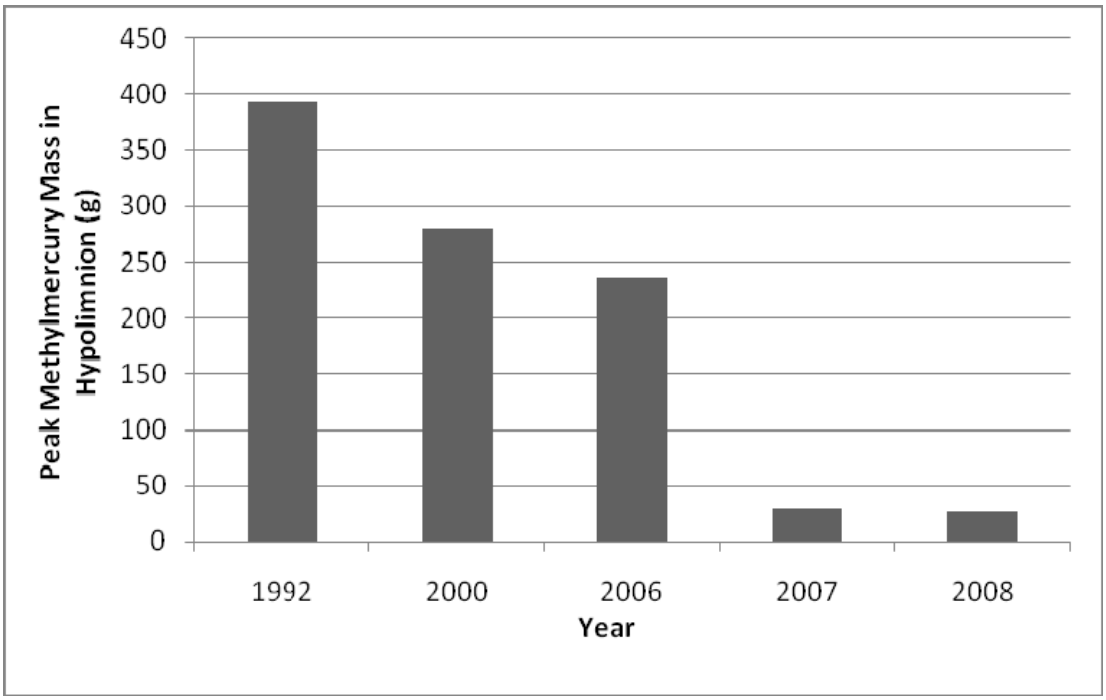


Figure 2. Calculated peak methylmercury mass in hypolimnion (SU and Parsons, unpublished data, presented to Baseline Monitoring Technical Work Group 1/29/09)



SECTION 2

2009 DEEP BASIN WATER, ZOOPLANKTON AND SEDIMENT TRAP MONITORING

The 2009 deep basin water column and zooplankton monitoring program consists of three components: water column, zooplankton, and sediment traps. These components are briefly described below.

2.1 WATER COLUMN

Water column samples will be collected at South Deep at the depths and frequencies specified in Table 2. Analytes will be the same as in the 2008 Book 1 Work Plan and are specified along with sample numbers in Table 3. Profiles of total dissolved gas (TDG) pressure will be observed on a monthly basis and spatially detailed monitoring with the *in situ* ultraviolet spectrophotometer (ISUS) rapid profiling instrument will be conducted on a weekly basis consistent with the 2008 Book 1 Work Plan. The field sampling matrices for laboratory analyses of water samples are shown in Table 4.

As in 2008, *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, at least daily during the April-November interval; however, these data will not be formally part of the Honeywell monitoring program. The data, as previously, will be available online to the public at www.ourlake.org.

2.2 ZOOPLANKTON

Bulk zooplankton samples will be collected in a manner consistent with the 2008 Work Plan on a monthly basis in April, May, and June (concurrent with water sampling) and biweekly thereafter. Analyses are specified in Table 3. If present, *Daphnia* samples will be collected, freeze-dried, digested, and analyzed for total mercury and methylmercury by Syracuse University using low-level USEPA methods. Freeze-drying will permit analysis of very low sample masses (see SOP in Appendix A).

2.3 SEDIMENT TRAPS

UFI's sediment trap design and deployment protocols follow recommendations presented in review and theoretical papers. The sediment traps are simple cylinders constructed of PVC piping, with an aspect ratio of 6:1. Aspect ratios greater than five are recommended to prevent resuspension of particles due to eddies created inside the trap by lake currents and retrieval. Sediment traps are deployed in clusters of three, known as an array, to provide for triplicate analysis. The trap array is deployed vertically, an orientation maintained through use of a sub-surface buoy. Vertical deployment is necessary to avoid "undertrapping", or false low fluxes caused by a reduction of the effective area of the trap opening.

Sediment trap collections will be made at the South Deep sampling site in the deepest area of Onondaga Lake over the April to October interval. The sampling site, located where the water depth of 19.5 m, is generally representative of water quality and sediment deposition conditions in the pelagic area of the lake. In many lakes, turbulent conditions can cause resuspension of sediments from the lake bed. However, resuspension has been shown to be negligible in the deep waters of Onondaga Lake during summer stratification. Sediment traps are deployed below the thermocline (10 m) to measure the net downward flux of particles into the hypolimnion. Sediment traps are generally deployed for seven-day intervals. After retrieval, supernatant is drained off via a stoppered opening located in the side of the traps well above the deposited sediments. The samples are then homogenized, poured into polyethylene bottles and put on ice. There are no chemical treatments applied to sediment traps to inhibit mineralization as this is deemed unnecessary for weekly deployments.

Analytes from each of the three sediment traps will include total suspended solids, fixed and volatile suspended solids, particulate carbon, and total and acidified calcium. One trap from each of the zooplankton collection dates will also be analyzed for total mercury and samples from the remaining two traps will be archived for potential future analyses. Field and analytical SOPs are provided in Appendix A to this addendum. Sample preservation and analytical requirements are presented in QAPP worksheets (see Appendix B to this addendum).

TABLE 2
WATER COLUMN SAMPLING SCHEDULE FOR 2009

Month	Water Column		
	Frequency	**Sampling Date**	**South Deep Depths (m)**
April	once	4/27	2, 12, 18
May	once	5/25	2, 12, 18
June	once	6/22	2, 12, 18
July	bi-weekly	7/6, 7/20	2, 12, 16, 18
August	bi-weekly	8/3, 8/17, 8/31	2, 12, 16, 18
September	weekly	9/7, 9/14, 9/21, 9/28	2, 12, 14, 16, 18
October	weekly	10/5, 10/12, 10/19, 10/26	2, 12, 14, 16, 18
November	Weekly thru turnover, then biweekly	11/1, 11/8	2, 12, 14, 16, 18
		11/23	2, 12, 18

Note: This sampling schedule is based on the lake being stratified from early July until early November. If the timing for stratification is significantly different during 2009 (e.g., turnover occurs earlier), sampling frequency and depths may be adjusted. Any possible adjustments will be discussed with NYSDEC before being implemented.

TABLE 3
SPECIFICATIONS FOR WATER COLUMN AND ZOOPLANKTON MONITORING AT SOUTH DEEP, LABORATORY ANALYTES

Parameter	Method	South Deep Depths (m) and Dates	Total Number of Field Samples for 2009[x]
[@]Chl	EPA 445	2,12 (see Table 2 for dates)	38
NO_X	EPA 353.2	See Table 2	82
NO_2^-	EPA 353.2	See Table 2	82
T-NH_3	EPA 350.1	See Table 2	82
DOC	SM 18-20 5310C	See Table 2	82
TIC	SM 18-20 5310C	See Table 2	82
Cl^-	SM 18-20 4500 Cl^- C	See Table 2	82
[+*]Total Hg	EPA 1631E	See Table 2	82
[+*]Total Hg, dissolved	EPA 1631E	2 m once in April, May, June, bi-weekly thereafter, 14 m biweekly 9/14 to 11/8	19
[+*]CH_3Hg	EPA 1630	See Table 2	82
[#]H_2S method 1	SM 18-20 4500 S^{2-} E	anoxic depths: 1 m intervals (mid-Jul to mid-Nov)	140
°method 2	SM 18-20 4500 S^{2-} G	anoxic depths: 1 m intervals (mid-Jul to mid-Nov)	140
Fe^{2+}	Heaney and Davison (1977)	anoxic depths; 12,16,18 (mid-Jul to mid-Nov)	42
CH_4	Addess (1990)	anoxic depths; 12,16,18 (mid-Jul to mid-Nov)	42
* Zooplankton, Total Hg, and percent solids	EPA Method 1631	13 m vertical tows once in April, May, June, bi-weekly thereafter	14
* Zooplankton, CH_3Hg	EPA Method 1630	13 m vertical tows once in April, May, June, bi-weekly thereafter	14

TABLE 3 (CONTINUED)

Footnotes:

[@] 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 robotic monitoring (RUSS) data.

[x] Field samples only. See QAPP Worksheet #20 for total number of samples to laboratory including field triplicates and blanks for UFI analytes, field blanks and field duplicates at one depth for total mercury and methylmercury, field duplicates for dissolved total mercury and for zooplankton total mercury and methylmercury. 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 mercury analysis of water will be performed by Brooks Rand; methylmercury analysis of water will be performed by Brooks Rand as a subcontractor to Accutest; all other water analyses will be performed by UFI.

[*] Total mercury and methylmercury analysis of zooplankton will be performed by Brooks Rand. In addition, up to 10 samples of large *Daphnia* will be analyzed by Syracuse University for total mercury and methylmercury if sufficient numbers are present to conduct laboratory analyses.

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

TABLE 4
FIELD SAMPLING MATRICES FOR LABORATORY ANALYSES OF WATER SAMPLES[1]

April, May, June, and after turnover 2009

Sampling Depth	Chl	NO_X	NO_2	T-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
18m		X	X	X	X	X	X	X	X

July – August 2009

Sampling Depth	Chl	NO_X	NO_2	T-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	X	X	X	X
16m		X	X	X	X	X	X	anoxic depths	X	X	X	X
18m		X	X	X	X	X	X	anoxic depths	XXX	XXX	X	X

September – turnover 2009

Sampling Depth	Chl	NO_X	NO_2	T-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	X	X	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	XXX	XXX	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 approximately 19 occasions as specified in Table 2.

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 Brooks Rand.

4. Methylmercury analysis will be performed by Brooks Rand.

2.4 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 including deployment and collection of sediment traps 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.

2.5 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. Analytical data generated during this investigation will be reviewed and validated as described in 2008 Book 1 QAPP (UFI and SU, 2008). All analytes will be subject to Level III validation as described in the QAPP for the Phase I Pre-Design Investigation (Parsons, 2005). In addition, 10% of the nitrate, total mercury, and methylmercury results 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. The DUSR will present the results of data validation and data usability assessment. Data interpretation and trend analysis will be discussed with the Baseline Monitoring Technical Work Group.

2.6 REFERENCES

Addess, J. M. 1990. Methane cycling in Onondaga Lake, New York. M.S. Thesis, College of Environmental Science and Forestry, State University of New York, Syracuse, NY.

Heaney, S.I., and W. Davison. 1977. The Determination of Ferrous Iron in Natural Waters with 2,2′-bipyridyl. Limnol. Oceanogr. 22(4):753–759.

Parsons, 2005. Onondaga Lake Pre-Design Investigation: Phase I Work Plan. Prepared for Honeywell, Inc., Morristown, New Jersey. Parsons, Liverpool, NY.

Appendix A *Phase I Sampling And Analysis Plan*

Appendix B *Quality Assurance Project Plan*

Appendix C *Project Safety Plan*

Parsons, 2008. Draft Baseline Monitoring Scoping Document for the Onondaga Lake Bottom Subsite. Prepared for Honeywell, Inc., East Syracuse, NY. Parsons, Liverpool, NY.

UFI and SU, 2007a. Work Plan for Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake, Preliminary Feasibility Analysis and 2006 Study. Prepared

for Honeywell, Inc., East Syracuse, NY. Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Center for Environmental Systems Engineering, Syracuse, NY.

UFI and SU, 2007b. Work Plan for Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake, 2007 Study. Prepared for Honeywell, Inc., East Syracuse, NY. Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Center for Environmental Systems Engineering, Syracuse, NY. May 2007.

UFI and SU, 2008. Onondaga Lake Baseline Monitoring Book 1 Deep Basin Water and Zooplankton Monitoring Work Plan for 2008. Prepared for Honeywell, Inc., East Syracuse, NY. Upstate Freshwater Institute and Syracuse University, Syracuse, NY. May 2008.

APPENDIX A

STANDARD OPERATING PROCEDURES (SOPs)

Reference Number	Title of Standard Operating Procedure (SOP)	Originating Organization
Sampling SOPs		
UFI-ST	Sediment Trap Deployment and Collection	UFI
Analytical SOPs		
UFI-101	UFI SOP 101 Total Suspended Solids	UFI
UFI-202	UFI SOP 202 Fixed and Volatile Suspended Solids	UFI
UFI-205	UFI SOP 205 Total Calcium	UFI
UFI-214	UFI SOP 214 Total Particulate Carbon	UFI
UFI-226	UFI SOP 226 Dissolved Acidified Calcium	UFI
UFI-227	UFI SOP 227 Sediment Trap Sample Preparation	UFI
SU	Nitric Acid Digestion for Methyl Mercury and Total Mercury	SU

10) Reagents and standards: none

11) Reference Solution: none

12) Sample collection, preservation, shipment and storage: Store samples on ice after collection.

13) Quality Control: While deploying be sure that the black rubber stoppers are securely inserted into PVC traps. Make sure the traps are sitting vertical in the water column and verify trap depths after deployment. Upon retrieval log sediment trap depth, water column depth, trap location with GPS coordinates, date and time of deployment and retrieval, and any other appropriate field notes (runoff events or algae blooms during the deployment period) on the sediment trap field sheets. During sample collection, drain water from the trap slowly to prevent in-trap resuspension. Secure caps to sediment trap prior to trap shaking. Pour slowly into collection bottle and use a funnel to prevent spillage. Record all information and complete the chain of custody.

14) Calibration and standardization: none

15) Procedure:

1. Deployment

1) Traps should be deployed so that a metalimnetic trap is 8 to 10 meters below the water surface upon initial deployment (depth is system dependent) and should remain below the upper mixed layer during stratification. Lines should be readjusted as needed. A hypolimnetic trap is placed approximately 1 to 2 meters above the bottom sediments.
2) Traps should be put over the side of the boat and lowered by hand – try not to disturb bottom sediments when deploying to avoid possibility of false high deposition measurements associated with resuspension.
3) Depth of traps should be marked with the depth finder and recorded on the field sheet.
4) The amount of slack line at the surface will be system dependent.

2. Collection

1) Pull the boat up next to the sediment trap buoy.
2) Using the depth finder, check and record the depth of the trap on the field sheet.
3) Pull trap buoy and slack line into the boat (depending on weather conditions, someone may need to keep the boat in position).
4) Pull the sediment trap up through the water column in a steady and consistent manner (~0.5 meter per second).
5) Once trap is in the boat, tie off trap anchor line (or pull into boat).
6) Drain trap by slowing removing plugs from the side of the trap.
7) Once drained, replace plugs and cap traps.
8) Shake up traps until well mixed and pour off into sediment trap bottles (depending on the system, pour all traps into one sample bottle or pour each cylinder into its own sample bottle).
9) Rinse traps (scrub out with brush if necessary) with reservoir water and redeploy.
10) Cap sample bottles and place in a cooler with ice

16) Calculations:

Downward flux (D_F) = $\left(\frac{W}{A \times t}\right)$ where W is the mass of the collected constituents (g), A is the area of the trap opening (m^2), and t is the time of deployment (d).

Settling Velocity (S_V) = $S_V = \left(\frac{D_F}{particle\ conc.}\right)$ where (D_F) is the downward flux ($g/m^2/d$), and particle conc. is the concentration of particles in (g/m^3)

17) Method performance: Under evaluation.

18) Pollution prevention: NA

19) Data assessment and acceptance criteria for quality control measures: NA

20) Corrective actions for out-of-control or unacceptable data: NA

21) Contingencies for handling out of control or unacceptable data: NA

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

23) References:

Bloesch, J., 1996. Towards a New Generation of Sediment Traps and a Better Measurement/Understanding of Settling Particulate Flux in Lakes and Oceans: A Hydrodynamic Protocol. Aquatic Science 58:283-296.

Sediment Trap Sampling Device

Solids, Total Suspended (Solids Method: AH filters)
SOP 101

1) Test Method: <u>SOLIDS, TOTAL SUSPENDED SM 20th ed. 2540 D</u>

2) Applicable Matrix or Matrices: drinking, surface and saline waters, slurries (sediment traps), domestic and industrial wastes.

3) Detection Limit: See UFI control document No. 12.

4) Scope and Application: drinking, surface and saline waters, domestic and industrial wastes.

5) Summary of Test Method: A well mixed sample is filtered though a weighed glass fiber filter and the residue retained on the filter is dried to a constant weight at 103 - 105°C. The increase in weight represents the total suspended solids.

6) Definitions:

Total Suspended Solids- The portion of the total solids retained by a filter.

Desiccant- Any material, such as calcium oxide or silica gel, which has a high affinity for water. Generally it is used as a drying agent.

Desiccator- Any chamber which holds desiccant and is utilized to keep material goods free from atmospheric humidity.

7) Interferences: Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg dried residue. For samples high in dissolved solids thoroughly wash the filter to ensure removal of dissolved materials. Prolonged filtration times resulting from filter clogging may produce high results owing to increased colloidal materials captured on the clogged filter.

8) Safety: No hazardous materials are required for this test. Proper laboratory procedures should be followed at all times.

9) Equipment and Supplies:

- Glass fiber filters (Whatman 934-AH)
- aluminum dishes
- vacuum filter apparatus
- analytical balance
- tongs and tweezers
- calibration weights
- tray
- vacuum pump

10) Reagents and Standards: not applicable**,** calibration weights are used to standardize analytical balances daily.

11) Sample Collection, Preservation, Shipment and Storage: samples should be kept cool and in the dark prior to processing.
Sample holding time is 7 days from collection date.

12) Quality Control: UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization: Analytical balances are calibrated annually. Calibration is checked monthly using a standard weight set, and with each use the 100 mg, 1g and 10g weights are checked and recorded.

14) Procedure:

Preparation of filter – Use tweezers to handle filters and weighing dishes at ALL times.

1) Rinse filters individually with Type II water under vacuum filtration
2) Dry filters at 103-105°C for one hour
3) Ash dried filters at 350°C for one hour
4) Weigh ashed filters on calibrated analytical balance for immediate analysis, record weight as "initial weight".
5) Filter enough sample through to produce at least 2.5mg of dried residue (for sediment traps use 25 ml).
6) Place filter onto filter apparatus.
7) Apply vacuum and wash filter with about 60 ml Type II water, continue suction until the filter is almost dry.
8) Remove filter and place filter into a clean aluminum dish.
9) Dry filter (and dish) in oven for at least 1 hr at 550°C.
10) Remove filters (and dish) from furnace and allow to cool in desiccators.
11) Check scale calibration with three determined weights (100mg, 1g and 10g).
12) Weigh cooled, ashed filter (and aluminum dish), record weight.

Sample analysis

1) Place rinsed, dried, and weighed filter onto filter apparatus, wet filter with Type II water if necessary to seat filter onto apparatus.
2) Mix sample thoroughly by gentle inversion of sample bottle and measure sufficient volume of sample with appropriate graduated cylinder.
3) Filter sample through the filter apparatus, washing down the sides of the graduated cylinder, and adding any remaining sediment to the filtered sample. Wash down the sides of the top of the filtering apparatus to assure all solids are washed onto the filter.
4) Stop suction and carefully remove the filter from the apparatus (using tweezers) and place back into the aluminum dish it was initially weighed in.
5) Dry for at least 1 hr at 103 -105°C in an oven (longer if oven is very full).
6) Remove from oven and cool in a desiccator to room temperature.

7) Check scale calibration with three determined weights (100mg, 1g and 10g).
8) Weigh cooled filters with aluminum dish, record weights.
9) Repeat cycle of drying, cooling, and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. In most cases if the sample is left in the oven for 12-24 hrs. (overnight), it is not necessary to reweigh numerous times. Weighing should occur as rapidly as possible as the sample may absorb water from the atmosphere once it is removed from the desiccator, placing some desiccant in the balance can reduce the effects of atmospheric moisture. If volatile suspended solids are to be determined, the filter (and dish) should be placed in the 550^0C muffle furnace for 1 hour and then weighed a final time.

15) Calculations:

$$\text{Total Suspended Solids (mg/L)} = \frac{(\mathbf{A} - \mathbf{B})\ 1000}{\mathbf{C}\ (\text{L})}$$

where:

A = weight of dried residue, pan and filter (g)
B = weight of pan and filter (g)
C = volume of sample (L)

For Sediment Trap Flux:

Flux $g/m^2/d$ = Concentration (mg/L) / Original Volume (L) / area of trap opening (m^2) / Deployment interval (Days)

16) Method Performance: UFI laboratory follows the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. Samples are done, as possible, following the chart below.
Refer to UFI control document 12 for QC procedure.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP

17) Pollution Prevention: Filters may be placed in the trash once analysis is finalized. Filtrate may be discarded down the drain. For most natural water systems, this procedure has no negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures: Record results from all quality control samples onto the QC file. The control charts are designed so that there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The warning lines are calculated from the previous year's data and are automatically flagged. The process should be shut down for trouble shooting if the following occur:

- A single action outside the control line.
- 2 out of 3 consecutive measurements between the warning and control lines
- 7 consecutive measurements above or below the center line
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Refer to UFI control document 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data: If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: If sufficient sample exists samples should be re-run once the analysis is back in control. If there is insufficient sample data should be flagged with an explanation of the circumstances. Out-of-control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: Used filters may be discarded in the trash. Filtrate may be discarded down the drain.

22) References:

1) Standard Methods 18-20 2540 D. pp 2-57, 58

2) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

Solids, Fixed and Volatile Suspended (Solids Method: AH filters)
SOP 202

1) Test Method: SOLIDS, FIXED AND VOLATILE SM 4500 18th ed 2540 E

2) Applicable Matrix or Matrices: drinking, surface and saline waters, slurries (sediment traps) domestic and industrial wastes.

3) Detection Limit: See UFI control document No. 12.

4) Scope and Application: drinking, surface and saline waters, domestic and industrial wastes.

5) Summary of Test Method: The residue from total solids or total suspended solids is ignited to a constant weight at 550°C. The remaining solids represent fixed total or fixed suspended solids, while the weight lost on ignition is the volatile solids. Volatile solids is a rough determination of organic matter present in the sample.

6) Definitions:

Fixed solids- is the term applies to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature.

Volatile solids- the weight of solids lost upon ignition.

7) Interferences: Negative errors in the volatile solids may be produced by loss of volatile matter during drying. Determination of low concentrations of volatile solids in the presence of high fixed solids concentrations may be subject to considerable error.

8) Safety: No hazardous materials are required for this test. Care should be exercised when handling samples around the muffle furnace, high temperatures are used and burns can occur. Heat protective gloves should be used when placing samples in and out of the furnace.

9) Equipment and Supplies:

- Glass fiber filters (Whatman 934-AH)
- Aluminum weighing dishes
- Vacuum filter apparatus
- Balances
- Tweezers
- Tongs
- Calibration weights
- Oven @ 105° C
- muffle furnace for use at 550°C, and 350°C.

10) Reagents and Standards: None

11) Sample Collection, Preservation, Shipment and Storage: samples should be kept cool and in the dark prior to processing.
Holding time for samples is 7 days from the sampling date.

12) Quality Control: UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization: balances are calibrated annually and checked daily or with each use.

14) Procedure:

1. Rinse filters individually with Type II water under vacuum filtration
2. Dry filters at 103-105°C for one hour
3. Ash dried filters at 350°C for one hour
4. Weigh ashed filters on calibrated analytical balance for immediate analysis, record weight as "initial weight".
5. Filter enough sample through to produce at least 2.5mg of dried residue. (for sediment traps use 25 ml)
6. Ignite the residue produced by total or suspended solids dried at 103 -105°C at a temperature of 550°C . Ash samples for 1 hr.
7. Remove from oven and let pan cool to room temperature in the desiccator.
8. Weigh on calibrated analytical balance and record weights.
9. Repeat cycle of drying, cooling, desiccating and weighing until a constant weight is obtained, or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. In most cases if the sample is left in the oven for 12-24 hours (overnight), it is not necessary to reweigh numerous times. Weighing should occur as rapidly as possible as the sample may absorb water from the atmosphere once it is removed from the desiccator, placing some desiccant in the balance can reduce the effects of atmospheric moisture.

15) Calculations:

$$\text{volatile solids or volatile suspended solids mg/L} = \frac{(\mathbf{A} - \mathbf{B})\ 1000}{\text{volume filtered (L)}}$$

$$\text{fixed solids or volatile suspended solids mg/L} = \frac{(\mathbf{B} - \mathbf{C})\ 1000}{\text{volume filtered (L)}}$$

where:

A = weight of dried (105°C) residue, pan and filter (g)
B = weight of dried residue, pan and filter after ignition at 550°C (g)
C = Initial weight of pan and filter (g)

For Sediment Trap Flux:

Flux $g/m^2/d$ = Concentration (mg/L) / Original Volume (L) / area of trap opening (m^2) / Deployment interval (Days)

16) Method Performance: UFI laboratory follows the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. Samples are done, as possible, following the chart below.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP

17) Pollution Prevention: This procedure has no discernible negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures: Record results from all quality control samples onto the QC file. The control charts are designed so that there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The warning lines are calculated from the previous year's data and are automatically flagged.

The process should be shut down for trouble shooting if the following occur:

- A single action outside the control line.
- 2 out of 3 consecutive measurements between the warning and control lines
- 7 consecutive measurements above or below the center line
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Refer to UFI control document 12 for flags and their meaning.

19) Corrective Actions for Out-of-Control or Unacceptable Data: If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: If sufficient sample exists samples should be re-run once the analysis is back in control. If there is insufficient sample data should be flagged with an explanation of the circumstances. Out-of-Control data is

1) Test method: Sediment Trap Deployment and Collection.

2) Applicable matrix or matrices: water

3) Detection limit: NA

4) Scope and application: drinking, surface and saline waters

5) Summary of test method: A sediment trap is a cylindrical PVC tube with an aspect ratio (height/diameter) of 6 and a diameter of 8.9 cm closed on the bottom and open at the top. These PVC tubes are deployed as assemblages of three (see attached photo). Sediment traps are used to quantify downward flux (D_F) of particles in a water body and the settling velocity of particles (S_V). Routine chemical analyses can be performed on the sediment trap sample as well. Theses analyses include but are not limited to TSS, VSS, FSS, total N, and chlorophyll. A sediment trap assemblage is deployed in the water column at a depth which is site and sampling purpose specific. For example, sediment traps can be deployed just below the thermocline to estimate downward flux of particles from the epilimnion, or sediment traps can be deployed near the bottom of a water body to estimate sediment resuspension.

6) Definitions:

Downward flux (D_F) – The downward movement of particles quantified by mass per unit area per unit time (mass/area/time)

Settling Velocity (S_V) – The settling distance of particles per unit time (length/time) or the ratio of D_F to particle concentration (mass/volume).

7) Interferences: Improper deployment (not vertical) and cleaning, deployment at the incorrect depth (i.e., too close to the benthos), shaking of the traps while collection, improper (too fast) draining of the overlying water in the trap will cause in-trap resuspension and loss.

8) Safety: Standard field procedures involving moderate lifting should be applied. Wear gloves during retrieval and deployment. Keep work area clean and clutter free.

9) Equipment and supplies: Sediment trap assemblage (arrangements of three), deployment rope, sub-surface float, surface float, anchor, black rubber stoppers, cleaning brush, funnel, and collection bottles.

not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: Used filters may be discarded in the trash.

22) References:

1) Standard Methods 20th ed 2540 E. pp 2-58-2-59

2) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

Calcium, Total……..SOP 205

1) Test Method: Total Ca SM 20th ed. 3111B

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Detection Limit (LOD): See UFI control document No. 12.

4) Scope and Application: Drinking, surface and saline waters, sediment traps

5) Summary of Test Method: Atomic absorption (AA) is the process that occurs when a ground state atom absorbs energy in the form of a specific wavelength and is elevated to an excited state. The amount of light energy that is absorbed at this wavelength will increase as the number of atoms of the selected element that are in the light path increases. The relationship between the amount of light absorbed and the concentration of analyte present in known standards can be used to determine unknown concentrations by measuring the amount of light the known concentrations absorb. Instrument readouts can be calibrated to display concentrations directly.

The source energy is heat, in the form of an air-acetylene or nitrous oxide-acetylene flame. The sample is introduced as an aerosol into the flame via a burner head and nebulizer. This system is referred to as flame sampling or flame AA. The flame burner head is aligned so that the light beam passes through the flame, where the light is absorbed.

This method can be used in conjunction with acidified calcium (SOP # 226) to determine total particulate calcium. The dissolved portion of the sample contains background calcium in the water. See sediment trap preparation (SOP # 227) for detailed sample preparation. The filtered water is run using this method, and subtracted from acidified calcium to determine the particulate calcium.

6) Definitions:

Ground State- The lowest energy state or the most stable state of an atom, molecule, or ion.

Excited State- An atom is said to be in an excited state if an electron has absorbed energy sufficient to promote that electron to an energy level which is higher than that in which it finds itself in the ground state.

Absorbance- A measure of the amount of light absorbed by a solution. Absorbance is equal to the logarithm of the ratio of incident light to transmitted light.

7) Interferences: Slight ionization occurs in the air-acetylene flame, and can be controlled by the addition of an alkali salt to samples and standards. Calcium sensitivity is reduced in the presence of certain elements which give rise to stable oxysalts (Al, Be, P, Si, Ti, V, and Zr). This effect is reduced by the addition of 1ml of 1.0% La or Sr.

8) Safety: Standard laboratory procedures involving low hazard methods should be applied. Wear safety glasses, gloves, lab coats /apron as needed and keep work area clean and clutter free. Keep flammable substances away from instrument. Use precautions near open flame.

9) Equipment and Supplies:

- Perkin-Elmer AAnalyst 300
- calcium hollow cathode lamp
- Perkin-Elmer Autosampler AS-90 plus
- 50 ml plastic vials
- 15 ml plastic vials
- Pipettes (assorted)

10) Reagents and Standards:

Calibration standards are made biannually or as needed from an ACS grade or equivalent calcium stock solution (1mL = 1mg Ca, Calcium Carbonate in solvent of 2% Nitric Acid). The table below shows how to make the calibration standards. If running samples in the low range (sediment trap samples) it may be appropriate to reduce the curve to only 5 standards (1mg/L – 27 mg/L)

STANDARD (mg/L)	VOLUME OF STOCK ADDED (ml)	FINAL VOLUME (ml)
1	1	1000
7	7.0	1000
14	14.0	1000
20	20.0	1000
27	27.0	1000
34	34.0	1000
40	40.0	1000

Blank Solution: Add 2.5ml of Nitric Acid (HNO_3) to 1L of Type II water. This is made daily.

Matrix Spike Solution: Pipette 25.0ml of stock standard solution into a 50ml flask and dilute to the 50ml mark. Prepare daily.

Lanthanum Chloride Solution: An ACS grade or equivalent lanthanum chloride solution (Lanthanum Solution: APHA (for metals), containing <6% lanthanum oxide, <10% hydrochloric acid, and water) is used to counteract reduced sensitivity in the presence of certain elements.

Reference Standard**:** Pipette 10.0ml of a secondary ACS grade or equivalent stock solution (1ml= 1mg Ca, Calcium Carbonate in solvent of 2% Nitric Acid) into a 500ml flask and dilute to the 500ml mark to make a concentration of 20.0mg/L. Prepare daily.

11)Sample Collection, Preservation, Shipment and Storage: Samples should be kept cool. Samples are preserved with concentrated nitric acid.
Holding time is six months from sampling date.

12) Quality Control: Quality control is verified in multiple ways, listed below.

Reference Standards (REF): Reference standards are samples of a known concentration made from a secondary ACS grade or equivalent stock solution. One should be run at the beginning of every run as the first sample.

Matrix Spike and Matrix Spike Duplicate(MS/MSD): Pipette out two 9.9ml aliquots of sample into two separate vials. To these samples add 0.1ml of spike solution. A matrix spike should be run once every 20 samples. A matrix spike duplicate should be run once a month or once every 250 samples.

Initial Control Verification (ICV) and Continuing Control Verification (CCV): These are standard samples of known concentrations made from the stock solution. An ICV should be run after an LCS and a CCV should be run every 10 samples following a DUP. Note—Do not vary the concentrations of these samples. Run only the 20mg/L standard.

Initial Calibration Blank (ICB) and Continuing Calibration Blank (CCB): Immediately following a REF an ICB should be run. Following a CCV, a CCB should be run. This is the same blank solution used for the calibration curve.

Laboratory Control Sample (LCS): Pipette out 9.9ml of Type II water into a vial. To this sample add 0.1ml of spike solution. An LCS should be run at the beginning of every run after the ICB.

Duplicates (DUP): Duplicates of samples should be run once every 10 to 15 samples.

13) Calibration and Standardization: The calibration standards are analyzed in order from lowest to highest concentration. The calibration curve for Ca is: a blank, 1mg/L, 7mg/L, 14mg/l, 20mg/L, 27mg/L, 34mg/L, and 40mg/L Confirm that r is equal to or greater than 0.995 and that r^2 is equal to or greater than 0.990. Before proceeding to sample analysis, the calibration must be verified by the analysis of a reference sample.

14) Procedure:

1) Turn the air supply on. The valve is located in the bay near the exit. The valve must be turned so that the handle is in line with the pipe. Turn the air compressor on by moving the red toggle switch away from you.
2) Turn the acetylene gas source on. The tank is located in the CSLAP room. Flow should be set at 15psi. Change tank and reorder if overall pressure is at or below 100psi.
3) Turn the fume hood on.
4) Turn computer on if it is not already on.

5) Turn on the AAnalyzer by using the switch on the right of the lamp housing. Plug in the autosampler. The plug is behind the AAnalyst 300 machine.
6) On the computer open the AA program by double-clicking on the "AA Winlab Analyst (2)" icon on the desktop.
7) As the program starts up, it will check the connections to all components. If they are good, the program will open. If a red X appears in either location, check that the power is on, the air supply is on, the acetylene is on, and then click on "Reset IEEE" to recheck connections.
8) Make sure that the "Technique" lists "Flame" and not "Furnace." If "Furnace" is listed, change to "Flame."
9) In "AA Winlab" window click on the "Use Custom Designed Workspace" icon.
10) Choose the "AUTO.FLM" file.
11) In the workspace that opens, click "Method" in the toolbar at the top of the window.
12) Choose the method "Ca flame w/AS/90" and click OK.
13) Click on the "Calib" tab and then click on "Stand Conc" to check that the standard concentrations listed are correct. Close the window.
14) Click on "Use Entire Sample Info file".
15) For "Sample Info File", click on "Browse" and then click on "CBATCH1.SIF". Click OK.
16) In "Results Data Set", click on "Browse" and create a data file for the analysis. The format used is "Your initials" followed by the date (example: CMS071505). Click OK.
17) Click on Lamp and Flame Off After Analysis.
18) Make sure Print Log is selected.
19) Click on the "Analyze" tab in the "Method" window.
20) In the toolbar at the top of the screen, click on the "Lamps" icon. Select the "Ca, Mg, Zn" element by clicking the circle on the left-hand side. Close the window.
21) Once a week (or whenever the analyte being analyzed is changed) the instrument should be adjusted so that peak absorbance in obtained. The steps to this are found at the end of the "Procedure" section.
22) In the toolbar at the top of the screen, click on the "Sample Info" icon. Sample number 9 will be your REF. Sample 10 will be the ICB. Sample 11 will be the LCS and sample 12 will be the ICV.
23) Starting with Sample number 13, type in the sample ID numbers of the samples you will run. For every 10 samples and at the end of every run, add a DUP followed by a CCV and then a CCB. For every 20 samples, run a Matrix spike. Make sure that the "Sample Units" column is listed as mg/L. Apply this unit to all rows containing samples and click OK.
24) Before closing "Sample Info" window, under "File" menu highlight "Save" and then choose "Sample Info File…" Close the "Sample Info" window.
25) Using a pipette, measure out 10mL of each sample into a sample vial. Make sure to run duplicate samples every 10 samples.
26) Prepare the LCS by adding 0.1mL of spike solution to 9.9mL of Type II water.
27) Prepare the Matrix Spike and any Matrix Spike Duplicate samples by adding 0.1mL of spike solution to two separate 9.9ml aliquots of sample.

28) Prepare all standards that will be run during the analysis by pipetting 10ml Into a sample vial. Prepare all blanks by pipetting 10ml into a sample vial.
29) Add 1ml of 1% lanthanum chloride solution to each sample/standard/QC.
30) Fill the appropriate standard vials (the 50ml vials) with the appropriate standard solutions and place them in positions 1 through 8 of the autosampler. Place your REF in position 9, the ICB in position 10, the LCS in position 11 and the ICV in position 12. Place your remaining samples in the order specified in the Sample file in the autosampler.
31) Add 1ml of 1% lanthanum chloride solution to every 10ml of standard solution and blank used.
32) Make sure that there is Type II water in the wash position of the autosampler (this is the large vial that the autosampler probe rests in) and keep checking the water level periodically to make sure it does not run empty.
33) Turn the flame on by clicking on the on/off switch located in the "Flame Control" window.
34) The flame will come on only if there is a green check mark.
35) If there is a red X, left click on the red X to determine what the problem is.
36) Once the flame is on, click on "Analyze All" in the "Method" window. The machine will now generate a standard curve, test the curve, and then analyze all samples.

Adjusting the peak absorbance reading: Once a week (or whenever the analyte being analyzed is changed) the instrument should be adjusted so that peak absorbance is obtained.

1) Under the "Tools" menu click on "Continuous Graphics."
2) Using the large dial located under the flame unit, turn the flame unit down as far as it will go and then click the "Autozero" icon. Be sure that the absorbance reading in the "Continuous Graphics" window reads 0.000. If it does not, click "Autozero" until it does.
3) Using the large dial bring the burner head up until there is a positive absorbance reading. Turn the flamer unit back down until the absorbance reads zero and then turn it ¼ turn more.
4) Turn the flame on. Place the autosampler probe into the vial containing the highest concentration standard and, using the small dial below the furnace head that sticks straight out at you, adjust the flame unit in order to get the highest absorbance reading possible without exceeding 0.800. Please be sure that the standard the probe is in does not run dry during this step.
5) Place the probe back in the sampler arm.
6) Close the "Continuous Graphics" window.

Analyzer Shut-down:

1) Shut off the air supply valve and the air compressor. Shut off the acetylene tank.
2) In the "Flame Control" window click on the "Bleed Gasses" icon. Wait until the green checkmark becomes a red X.
3) Exit the program.
4) Turn off the power supply for the AAnalyst and unplug the autosampler.

15) Calculations:

Sample concentration (mg/L)= AAS result (mg/L)*Dilution factor

16) Method Performance: UFI laboratory follows the following chart for identifying and running QC samples.
Refer to UFI control document 12 for QC procedures.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP
Reference	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Once at the beginning of every run as the first sample	REF
Continuing Calibration Verification	A standard sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	Run following every DUP	CCV
Initial Calibration Verification	A CCV done at the beginning of the run	Once pre run following the LCS	ICV
Laboratory Control Sample	A spike of unknown concentration to Type II water	One per run following the ICB	LCS
Matrix spike	A spike of known concentration to sample matrix	Every 20 samples or one per batch if less than 20 samples	MS
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	MSD
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB
Initial Calibration Blank	A CCB at the beginning of the run	One per run following the REF	ICB

17) Pollution Prevention: This procedure has no discernible negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures: Record results from all quality control samples onto the QC file. The control charts are designed so that there is

the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The warning lines are calculated from the previous year's data and are automatically flagged.

The process should be shut down for trouble shooting if the following occur:

- A single action outside the control line.
- 2 out of 3 consecutive measurements between the warning and control lines
- 7 consecutive measurements above or below the center line
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Flags and Qualifiers are listed in UFI Controlled Document No.12.

19) Corrective Actions for Out-of-Control or Unacceptable Data: If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: This procedure generates no discernable hazardous waste. Extra samples and standards may be flushed down the sink with the tap running.

22) References:

1) "A Analyst 100/300 Atomic Absorption Spectrometer: Hardware Guide," Perkin-Elmer Manual Part No. 0993-6088 Rev. E, released June 1998

2) "Atomic Absorption Spectroscopy: Analytical Methods," Perkin-Elmer Manual Part No. 0303-0152 Rev. D, released September 1996

3) "AA WinLab: Software Guide," Perkin Elmer Manual Part No. 0993-6190 Rev. B, released July 1996

4) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

5) Standard Methods for the Examination of Water and Wastewater. 20th edition 1998.

Carbon, Total Particulate……..SOP 214

1) Test Method: <u>CARBON, TOTAL PARTICULATE run on the Phoenix 8000 SM 20th ed 5310B</u>

2) Applicable Matrix or Matrices: water, soils, slurries (sediment traps).

3) Detection Limit: See UFI control document 12.

*since this method is dependent on how much carbon is contained in the sample sufficient sample must be used to get a suitable signal.

4) Scope and Application: This method should be used when direct measurement of particulate inorganic carbon is desired. Particulate organic carbon can be fractionated by use of acidification, and particulate inorganic carbon can be determined by difference.

5) Summary of Test Method: Traditionally particulate carbon is determined by the difference between the total and dissolved fractions. In some waters where these two fractions are very similar in magnitude, it is desirable to concentrate the particulate fraction and measure it directly. After concentration the sample is run as a solid using a high temperature combustion method which measures carbon as CO_2 liberated from the combustion.

6) Definitions:

Particulate Organic Carbon (POC)- The carbon retained by a filter with 0.45µm pore size, after acidfication with use of concentrated HCl acid.

Total Particulate Carbon (TPC)- The total amount of carbon retained by a filter with a particle retention size of 0.45 µm.

Particulate Inorganic Carbon (PIC)- The difference between the TPC and POC

7) Interferences: Problems may arise in samples in which there is a lot of suspended material deficient in carbon, it may become difficult to filter sufficient material to yield a suitable signal before the filter becomes clogged. In this case, use of a filter with larger area is recommended.

8) Safety: Always wear safety goggles, gloves and lab coats when handling acids or other toxic substances. Use hoods for mixing solutions that produce fumes. If you spill concentrated acids, bases or other toxic chemicals notify the technical director immediately.

9) Equipment and Supplies:

For sample preparation:

- Whatman 25mm GF/F glass fiber filters ashed at 350°C
- Glass scintillation vials are used to both dry (105 C) and store samples (-20 C for 100 days)
- all identifying notes can be written on the vial label. Be sure to record the volume filtered either on the vial or in the log, it is essential to the calculation of particulate carbon.

- small filtering apparatus (fitted glass microfiltration set up)
- 5 ml and 2 ml wide bore graduated pipette.

10) Reagents and Standards:

Because particulate concentrations are unpredictable the standard curve may vary depending on samples. The high curve should be used from most sediment trap samples, requiring use of the extension range kit.
Working Stock:10,000 mg/L potassium hydrogen phthalate = dry KHP @ 105°C for at least 1 hr. weigh 2.128 g, dilute to 100 ml with Type II water (or 21.28g PHP to make 1 liter).

To make High standard curve Pipette the volume into the platinum sample boat and insert into combustion chamber for the desired mass of carbon to be measured.

ul. of KHP Std (10,000 mg/l)	ug C
20	200
40	400
60	600
80	800
100	1000

11) Sample Collection, Preservation, Shipment and Storage: Collect samples in clean plastic bottles. Process as soon as possible after collection.

TPC

1) Shake sample well and measure a volume into a graduated cylinder, it is extremely important to record the total volume filtered. The total volume required is arbitrary; enough must be filtered to yield a sufficient signal. For water samples 25 ml is a good volume, a slight coloration on the filter is usually a good indicator. Sediment trap samples usually require a volume of around 5 mls for POC samples, and 2mls for TPC samples.

2) Add the sample to the filtering apparatus, rinse the graduate with a squirt of Type II water and once the sample has filtered through, rinse down the sides of the filtering apparatus as well.

3) Using forceps fold the filter in half, place in a labeled vial. The vial (and filter) should be placed in the drying oven at 105°C for at least 24 hrs.

4) Samples frozen -20^{o} C until analysis

POC

1) Shake sample well and measure a volume into a graduated cylinder, it is extremely important to record the total volume filtered! The total volume required is arbitrary,

enough must be filtered to yield a sufficient signal. For water samples 25 ml is a good volume, a slight coloration on the filter is usually a good indicator. Sediment trap samples usually require a volume of around 5 mls for POC samples, and 2 mls for TPC samples.

2) Add the sample to the filtering apparatus, rinse the graduate with a squirt of Type II water and once the sample has filtered through, rinse down the sides of the filtering apparatus as well.

3) For samples containing >40% inorganic Carbon (~Sediment trap samples), contact acidification is required. If samples have less (~water column) skip to step 4. After filtering, remove top part of filtering apparatus and add at least 1ml of concentrated HCl acid directly onto collected sediment until bubbling ceases. If bubble stops immediately, continue adding acid until the 1ml is gone. Replace filtering top and rinse with a small amount of type II water. Skip step 4 if used contact acidification.

4) Only for samples containing < 40% Inorganic Carbon. Vapor acidification is used. Place the filter into a labeled plastic tray, or weighing boat (anything that is not subject to attack by HCl, NO TIN) in a glass desiccator with all desiccant removed with a beaker of concentrated HCl acid for at least 24 hours, up to 48 hours.

5) Using forceps fold the filter in half, place in a labeled vial. The vial (and filter) should be placed in the drying oven at 105°C for at least 24 hrs. **(**POC and TPC samples should be kept in SEPERATE OVENS**)**

6) Samples then frozen -20^{o} C until analysis.

12) Quality Control: UFI's QC parameters are outlined in the Method Performance Section. They are monitored on a variety of levels; by the analyst(s), the Laboratory Director, and the Quality Assurance Officer as needed. In addition, basic knowledge of the characteristic features of the limnological systems may be used to aid in auditing QC data.

13) Calibration and Standardization:

1) Attach the line out from boat sampling module into the Phoenix Copper/Tin scrubber, (in the Copper side).
2) Open the 183 Boat Sampler program from the desktop, and switch the furnace on using the switch on the front of the boat sampler.
3) Ensure the sparger is filled with 21% H_3PO_4 well above the permeated glass, but not to high to avoid acid in the gas flow lines.
4) The use of the extension range kit will be determined by the amount of carbon on the filters being run. This can be used and disengaged as described in the Tekkmar Manuals.
5) Open the valve of the O_2 tank and adjust to 34 PSIG.
6) Click setup, Instrument, and select ready. Under setup, select diagnostics, and deselect all valves and furnaces.

7) Select run, sample setup, sample type, TC Standard, 0.002 – 0.1 ppm, OK. The list will show a variety of available amounts of carbon, for both the high and low curve. Work from lowest to highest amount of Carbon for the curve. Select the lowest, exit, save use.
8) This will prompt you to start your first standard. First ensure the green light is on on the front of the boat sampler, and to first burn off any carbon on the boat and carriage by sliding it in for aprox. 6 mins. Once, this is done, and there is a steady baseline >7 millivolts, you may begin the curve.
9) Using a micropipette, dispense the necessary amount of carbon standard into the boat, close the chamber, and wait for the baseline to stabilize (not always necessary for use with extension range kit). Once stabilized hit run, and a prompt will pop up when the boat should be slide into the furnace, do so, and click ok.
10) Steps 7-9 should be repeated until the desired curve is created with at least 5 points.
11) Click results, calibration, and check off all calibration results and hit re-calc. If the r is below 0.995 then the curve must be re-run.

14) Procedure:

1) Remove the quartz wool from the boat. Samples are placed in the boat via the spring-loaded port on the top of the sample tube.
2) Remove the boat using forceps, place the filter containing the sample into the boat using forceps.
3) Place the boat back into the holder, close the hatch, wait for the baseline to stabilize. Press RUN, the instrument will prompt you indicating that the boat should be slid into the furnace. You should see the baseline rise and then begin to decline on the graph.
4) The sample will finish and be recorded below. After EACH sample run you must select results, multiple analyses, and copy the entire row, and paste it into a spreadsheet. This MUST be done between each sampling. The resulting spreadsheet would be saved under the REPORTS folder in the BOAT folder.

**Two blank filters should be run with each batch of samples, they should be treated in the sample fashion as the samples.

15) Calculations:

$$\text{Calculation for Particulate Carbon } \mu g/l = \frac{\mu g \text{ C (as Returned by Phoenix)}}{\text{ml filtered}} \times 1000$$

TPC – POC = Particulate Inorganic Carbon

16) Method Performance: UFI laboratory follows the following chart for identifying and running QC samples. Each type of sample may not be applicable to every analysis. Samples are done, as possible, following the chart below.

Refer to UFI control document 12 for QC procedures.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP
Reference	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Every sample batch	REF
Continuing Calibration Verification	A standard sample, run throughout the course of the run, generally of varying concentration, and near the expected sample concentration range(s)	First sample, before running others, every 10-15 afterwards, and the last sample of any run NOTE: If curve is not run daily, highest standard must be run as a CCV	CCV
Initial Calibration Verification	A CCV done at the beginning of the run	1st sample	ICV
Laboratory Control Sample or Blank Spike	A spike of unknown concentration to Type II water	One per sample batch	LCS
Matrix spike	A spike of known concentration to sample matrix	Every 20 samples or one per batch if less than 20 samples	MS
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB

The basic performance specification is the amount of mass of carbon in the sample. As you decrease the sample volume and/or the sample concentration, you are decreasing the amount of CO_2 detected by the NDIR.

17) Pollution Prevention: Dispose of the reagents in the combustion tubes in the proper manner. This procedure has no discernible negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures: Record results from all quality control samples onto the QC file. The control charts are designed so that there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The warning lines are calculated from the previous year's data and are automatically flagged.

The process should be shut down for trouble shooting if the following occur:

- A single action outside the control line.
- 2 out of 3 consecutive measurements between the warning and control lines
- 7 consecutive measurements above or below the center line
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Flags and Qualifiers are listed in UFI Controlled Document No.12.

19) Corrective Actions for Out-of-Control or Unacceptable Data: : If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. Causes should be investigated and rectified if possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: Once the samples (filters) are run they can be thrown into the trash.

22) References:

1) Hedges, John, I. and Stern, J.H. 1984. Carbon and Nitrogen Determinations of Carbonate-Containing Solids. Limnology and Oceanography 29(3) pp. 657-663.

2) Standard Methods 18-20th Edition method 5310 B.

3) Installation and Operation of the 183 Boat Sampling Module Revision C. Tekmar-Dohrmann manual.

4) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

Calcium, Dissolved Acidified……..SOP 226

1) Test Method: Total Ca SM 20th ed. 3111A

2) Applicable Matrix or Matrices: drinking, surface and saline waters, domestic and industrial wastes.

3) Level of Detection (LOD): See UFI control document No. 12.

4) Scope and Application: Drinking, surface and saline waters, sediment traps

5) Summary of Test Method: Atomic absorption (AA) is the process that occurs when a ground state atom absorbs energy in the form of a specific wavelength and is elevated to an excited state. The amount of light energy that is absorbed at this wavelength will increase as the number of atoms of the selected element that are in the light path increases. The relationship between the amount of light absorbed and the concentration of analyte present in known standards can be used to determine unknown concentrations by measuring the amount of light the known concentrations absorb. Instrument readouts can be calibrated to display concentrations directly.

The source energy is heat, in the form of an air-acetylene or nitrous oxide-acetylene flame. The sample is introduced as an aerosol into the flame via a burner head and nebulizer. This system is referred to as flame sampling or flame AA. The flame burner head is aligned so that the light beam passes through the flame, where the light is absorbed.

This method is used in conjunction with Total Calcium (SOP # 205) to determine total particulate calcium. The acidified portion of the sample contains both background calcium as well as the particulate portion dissolved by the addition of nitric acid. See sediment trap preparation (SOP # 227) for detailed sample preparation.

6) Definitions:

Ground State- The lowest energy state or the most stable state of an atom, molecule, or ion.

Excited State- An atom is said to be in an excited state if an electron has absorbed energy sufficient to promote that electron to an energy level which is higher than that in which it finds itself in the ground state.

Absorbance- A measure of the amount of light absorbed by a solution. Absorbance is equal to the logarithm of the ratio of incident light to transmitted light.

7) Interferences: Slight ionization occurs in the air-acetylene flame, and can be controlled by the addition of an alkali salt to samples and standards. Calcium sensitivity is reduced in the presence of certain elements which give rise to stable oxysalts (Al, Be, P, Si, Ti, V, and Zr). This effect is reduced by the addition of 0.1ml of 1.0% La or Sr. Nitric acid can modify the matrix and cause a lower absorption reading, so all standards and samples should be of the same concentration of acid.

8) Safety: Standard laboratory procedures involving low hazard methods should be applied. Wear safety glasses, gloves, lab coats /apron as needed and keep work area clean and clutter free. Keep flammable substances away from instrument. Use precautions near open flame.

9) Equipment and Supplies:

- Perkin-Elmer AAnalyst 300
- calcium hollow cathode lamp
- Perkin-Elmer Autosampler AS-90 plus
- 50mL plastic vials
- 15mL plastic vials
- Pipettes (assorted)

10) Reagents and Standards:

Calibration standards are made biannually or as needed from an ACS grade or equivalent calcium stock solution (1mL = 1mg Ca, Calcium Carbonate in solvent of 2% Nitric Acid). The table below shows how to make the calibration standards.

STANDARD (mg/L)	VOLUME OF STOCK ADDED (mL)*	Nitric Acid Added (ml)	FINAL VOLUME (mL)
50	0.5	1	11
200	2.0	1	11
350	3.5	1	11
500	5.0	1	11
650	6.5	1	11
800	8.0	1	11
1000	10	1	11

Each of these should be acidified with 1mL concentrated Nitric Acid. 0.2 ml* of each of these mixtures should be taken and then diluted with 9.8 ml* of Type II water to make 10mL of standard (dilution factor of 50). This is what should be run in the calibration, and the resulting concentrations are shown in the table below. This dilution allows standards to be treated the same as samples as all samples are run with a 50 dilution factor and thus will result in the same concentration of nitric acid. In addition, a vial of 10 ml of water with 1 ml of nitric acid should also be prepared. This will be diluted 1:50 as well for the autozero and ICB/CCB QC. All dilutions should be made with Type II water.

STANDARD (mg/L)	Concentration (mg/l)
1	1
4	4
7	7
10	10
13	13
16	16
20	20

Autozero: *ICV/CCV/LCS*[*]: Add 1 ml of trace metals grade nitric acid to 10 ml type II water. This should then be diluted 50 times with type II water (0.2ml in 9.8 ml)

Lanthanum Chloride Solution[*]: An ACS grade or equivalent lanthanum chloride solution (Lanthanum Solution: APHA (for metals), containing <6% lanthanum oxide, <10% hydrochloric acid, and water) is used to counteract reduced sensitivity in the presence of certain elements.

* If the analyst is having difficulty obtaining acceptable QC values it may be necessary to alter the volumes of sample/dilution water. Recommended alternatives for the 1:50 dilution include 1 ml in 50 ml of water.

11) Sample Collection, Preservation, Shipment and Storage: Samples should be kept cool. Samples are preserved with concentrated nitric acid. Holding time is six months.

12) Quality Control: Quality control is verified in multiple ways, listed below.

ICV/CCV[*]: These should be created by diluting the 500 mg/l standard to 10 mg/l with 0.2 ml of standard with 9.8 ml of type II water.

Matrix Spike Solution[*]: 50 ul of 100 mg/l standard should be added to either diluted sample water or diluted Blank water (above) for a spike nominal of 5 mg/l.

Reference Standard[*]**:** Make intermediate stock with 5 ml reference stock of 1000 mg/l in 5 ml type II water and add 1 ml concentrated trace metals grade nitric acid. This should then be diluted 50 times (0.2 ml in 9.8 ml) to obtain the concentration of 10 mg/l.

Duplicates (DUP): Duplicates of samples should be run once every 10 samples.

13) Calibration and Standardization: The calibration standards are analyzed in order from lowest to highest concentration. 1 ml of lanthanum solution should be added to each standard before analysis. The calibration curve for Ca is: a baseline blank, 1 mg/l, 4mg/l, 7mg/l, 10mg/l, 13mg/l, 16mg/l, and 20mg/l. Confirm that r is equal to or greater than 0.995. Before proceeding to sample analysis, the calibration must be verified by the analysis of initial QC.

14) Procedure:

1) Turn the air supply on. The valve is located in the bay near the exit. The valve must be turned so that the handle is in line with the pipe. Turn the air compressor on by moving the red toggle switch away from you.
2) Turn the acetylene gas source on. The tank is located in the CSLAP room. Flow should be set at 15psi. Change tank and reorder if overall pressure is at or below 100psi.
3) Turn the fume hood on.
4) Turn computer on if it is not already on.
5) Turn on the AAnalyzer by using the switch on the right of the lamp housing. Plug in the autosampler. The plug is behind the AAnalyst 300 machine.
6) On the computer open the AA program by double-clicking on the "AA Winlab Analyst (2)" icon on the desktop.
7) As the program starts up, it will check the connections to all components. If they are good, the program will open. If a red X appears in either location, check that the power is on, the air supply is on, the acetylene is on, and then click on "Reset IEEE" to recheck connections.
8) Make sure that the "Technique" lists "Flame" and not "Furnace." If "Furnace" is listed, change to "Flame."
9) In "AA Winlab" window click on the "Use Custom Designed Workspace" icon.
10) Choose the "AUTO.FLM" file.
11) In the workspace that opens, click "Method" in the toolbar at the top of the window.
12) Choose the method "Ca_DAc w/AS/90" and click OK.
13) Click on the "Calib" tab and then click on "Stand Conc" to check that the standard concentrations listed are correct. Close the window.
14) Click on "Use Entire Sample Info file".
    1. For "Sample Info File", click on "Browse" and then click on "CBATCH1.SIF". Click OK.
    2. In "Results Data Set", click on "Browse" and create a data file for the analysis. The format used is "Your initials" followed by the date (example: CMS071505). Click OK.
15) Click on Flame Off After Analysis.
16) Make sure Print Log is selected.
17) Click on the "Analyze" tab in the "Method" window.
18) In the toolbar at the top of the screen, click on the "Lamps" icon. Select the "Ca, Mg, Zn" element by clicking the circle on the left-hand side. Close the window.

19) Once a week (or whenever the analyte being analyzed is changed) the machine should be adjusted so that peak absorbance is obtained. The steps to do this are found at the end of the "Procedure" section.
20) In the toolbar at the top of the screen, click on the "Sample Info" icon. Sample number 9 will be your ICV. Sample 10 will be the ICB. Sample 11 will be the LCS and sample 12 will be the REF.
21) Starting with Sample number 13, type in the sample ID numbers of the samples you will run. For every 10 samples and at the end of every run, add a DUP followed by a CCV and then a CCB. For every 20 samples, run a Matrix spike. Make sure that the "Sample Units" column is listed as mg/L. Apply this unit to all rows containing samples and click OK.
22) Before closing "Sample Info" window, under "File" menu highlight "Save" and then choose "Sample Info File…" Close the "Sample Info" window.
23) Using a pipette, measure out 0.2mL of each sample into a sample vial and then dilute using 9.8mL of Type II water. Make sure to run duplicate samples every 10 samples.
24) Prepare the LCS
25) Prepare the Matrix Spike and any Matrix Spike Duplicate samples by adding 50 uL of 1,000 mg/L standard to the diluted sample for a nominal concentration of 5 mg/L.
26) Prepare all standards that will be run during the analysis by pipetting 10mL into a sample vial. Prepare all blanks by pipetting 10mL into a sample vial.
27) Add 1mL of 1% lanthanum chloride solution to each sample.
28) Fill the appropriate standard vials (the 50mL vials) with the appropriate standard solutions and place them in positions 1 through 8 of the autosampler. Place your ICV in position 9, the ICB in position 10, the LCS in position 11 and the REF in position 12. Place your remaining samples in the order specified in the Sample file in the autosampler.
29) Add 1mL of 1% lanthanum chloride solution to every 10mL of standard solution and blank used.
30) Make sure that there is Type II water in the wash position of the autosampler (this is the large vial that the autosampler probe rests in) and keep checking the water level periodically to make sure it does not run empty.
31) Turn the flame on by clicking on the on/off switch located in the "Flame Control" window.
32) The flame will come on only if there is a green check mark.
33) If there is a red X, left click on the red X to determine what the problem is.
34) Once the flame is on, click on "Analyze All" in the "Method" window. The machine will now generate a standard curve, test the curve, and then analyze all samples.

Adjusting the peak absorbance reading: Once a week (or whenever the analyte being analyzed is changed) the machine should be adjusted so that peak absorbance is obtained.

1.) Under the "Tools" menu click on "Continuous Graphics."
2.) Using the large dial located under the flame unit, turn the flame unit down as far as it will go and then click the "Autozero" icon. Be sure that the absorbance

reading in the "Continuous Graphics" window reads 0.000. If it does not, click "Autozero" until it does.

3.) Using the large dial bring the burner head up until there is a positive absorbance reading. Turn the flamer unit back down until the absorbance reads zero and then turn it ¼ turn more.
4.) Turn the flame on. Place the autosampler probe into the vial containing the highest concentration standard and, using the small dial below the furnace head that sticks straight out at you, adjust the flame unit in order to get the highest absorbance reading possible without exceeding 0.800. Please be sure that the standard the probe is in does not run dry during this step.

5.) Place the probe back in the sampler arm.
6.) Close the "Continuous Graphics" window.

Analyzer Shut-down:

1.) Shut off the air supply valve and the air compressor. Shut off the acetylene tank.
2.) In the "Flame Control" window click on the "Bleed Gasses" icon. Wait until the green checkmark becomes a red X.
3.) Exit the program.
4.) Turn off the power supply for the AAnalyst and unplug the autosampler.

15) Calculations:

Concentrations, as of 07/30/07, are collected in mg/L, therefore no conversion is needed. Matrix Spike Percent Recovery is automatically calculated by the template and Data Base. Subsequent calculations are as follows:

Sample concentration (mg/L)= AAS result (mg/L)*Dilution factor

16) Method Performance: UFI laboratory follows the following chart for identifying and running QC samples.

QC Sample Type	Description/Definition	Frequency performed	Abbreviation
Duplicate	An identical sample to another one, from the same sample container	Every 10 samples, or one per sample batch, if less than 10	DUP
Reference	A standard sample, made from either a different lot # solution, a different manufacturer, or another method (dissolving a solid)	Once at the beginning of every run as the first sample	REF
Continuing Calibration	A standard sample, run throughout the course	Run following every DUP	CCV

Verification	of the run, generally of varying concentration, and near the expected sample concentration range(s)		
Initial Calibration Verification	A CCV done at the beginning of the run	Once per run following the LCS	ICV
Laboratory Control Sample	A spike of unknown concentration to Type II water	One per run following the ICB	LCS
Matrix spike	A spike of known concentration to sample matrix	Every 20 samples or one per batch if less than 20 samples	MS
Matrix Spike Duplicate	Same as above, repeated	One per month or ~250 samples	MSD
Continuing Calibration Blank	Blank Sample	Every ten, or one per batch, following CCV	CCB
Initial Calibration Blank	A CCB at the beginning of the run	One per run following the REF	ICB

17) Pollution Prevention: This procedure has no discernible negative impact on the environment.

18) Data Assessment and Acceptance Criteria for Quality Control Measures: Record results from all quality control samples onto the QC file. The control charts are designed so that there is the mean displayed through the middle, with an upper warning line, a lower warning line, an upper control line and a lower control line. The upper and lower warning lines are 2 standard deviations from the mean. The upper and lower control lines are three standard deviations from the mean. The process should be shut down for trouble shooting if the following occur:

- A single action outside the control line.
- 2 out of 3 consecutive measurements between the warning and control lines
- 7 consecutive measurements above or below the center line
- 6 consecutive measurements all steadily increasing or all steadily decreasing wherever they are located
- 14 consecutive points alternating up and down, regardless of where they are located
- an obvious non random pattern (Harris)

Once data is analyzed, if there are any discrepancies with how samples were treated from the proper way to treat them, the data associated with those discrepancies are flagged. Flags and Qualifiers are listed in UFI Controlled Document No. 12.

19) Corrective Actions for Out-of-Control or Unacceptable Data: : If QC measures are determined to be outside acceptable limits the analysis is considered Out-of-Control and the data is to be considered suspect. Causes should be investigated and rectified if

possible. Samples should be re-run, if sufficient sample exists. Otherwise, data will be flagged accordingly.

20) Contingencies for Handling Out-of-Control or Unacceptable Data: If sufficient sample exists, samples should be re-run once the analysis is back in control. If there is sufficient sample data, the data should be flagged with an explanation of the circumstances. Out-of-Control data is not to be used in maintaining quality control charts for the method, as they may cause unduly large control limits.

21) Waste Management: This procedure generates no discernable hazardous waste. Extra samples and standards may be flushed down the sink with the tap running.

22) References:

1) "AAnalyst 100/300 Atomic Absorption Spectrometer: Hardware Guide," Perkin-Elmer Manual Part No. 0993-6088 Rev. E, released June 1998

2) "Atomic Absorption Spectroscopy: Analytical Methods," Perkin-Elmer Manual Part No. 0303-0152 Rev. D, released September 1996

3) "AA WinLab: Software Guide," Perkin Elmer Manual Part No. 0993-6190 Rev. B, released July 1996

4) Harris, Daniel C. Quantitative Chemical Analysis. 2003. W.H. Freeman and Company, New York.

5) Standard Methods for the Examination of Water and Wastewater. 20th edition 1998.

Sediment Trap Sample Preparation……..…SOP 227

1) Test Method: <u>Preparation of Sediment Traps for Multiple Analysis</u>

2) Applicable Matrix or Matrices: Sediment traps water/Slurries

3) Detection Limit: N/A

4) Scope and Application: Sediment traps/slurries

5) Summary of Test Method: This SOP is intended to aid in the complex process of preparing sediment traps for a variety of test methods. There is no actual analysis, as it is only the method for fractionating the sample, and following the correct preservation/filtration steps as necessitated by each respective analysis.

This SOP is a supplement to help process the sediment trap sample correctly for each desired method, and should only be used in conjunction with the SOP for each desired analysis.

6) Definitions:

Supernatant: The excess water overlying the sediments in the sample after all solids have settled.

Sediment trap water: the combined mixture of collected sediments and water measured after removal of supernatant.

Sediment trap: A cylinder deployed in the water column designed to collect depositing particles

Sonication: the act of applying sound energy to agitate particles in a sample, for various purposes.

7) Interferences: Refer to the respective SOP for each analytical test.

8) Safety: Use appropriate safety apparel for working with strong acids (Eyewear, gloves lab coat) and use acid only under a vacuum hood

9) Equipment and Supplies:

- Glass filtration apparatus (top and bottom)
- plastic suction filtration vessel, sonicator
- 5 ml wide bore graduated class A pipette
- 2 ml wide bore graduated class A pipette
- 25 ml wide bore class A pipette
- 1 ml adjustable pipette
- plastic disposable pipette
- scintillation vial (for samples)

- nalgene filtering apparatus
- various sized glass fiber filters (25, 47 mm). Pore size is dependent on analysis

10) Reagents and Standards: concentrated nitric acid (trace metals grade), Hydrochloric acid.

11) Sample Collection, Preservation, Shipment and Storage: Samples need to be allowed to settle ~2-3 days at 4^{o} C; thereafter the overlying supernatant should be carefully suctioned off. This needs to be done carefully as to not remove any particulates and to leave adequate volume for sediment re-suspension in water (~150ml).

12) Quality Control: N/A

13) Calibration and Standardization: N/A

14) Procedure:

Removal of supernatant: Allow the sediment traps to settle for ~2-3 days at 4^{o} C. Remove sample containers from the fridge CAREFULLY as to not stir up settled material. Use the large plastic suction filtration flask and tube to slowly and carefully remove the supernatant from the sample container. This is done by placing the tube AT the waters surface, NOT in the sample, to reduce turbulence while removing the overlying water (Fig. 1). Reduce the volume to approximately 150 ml, or more, allowing adequate space between the top layer of the deposited sediment and the water (Fig. 2). Ensure no sediments are suctioned through the vacuum tube. Measure and record the original volume of the trap. Homogenize sample transfer to a plastic sample bottle. See next section or freeze until analysis.

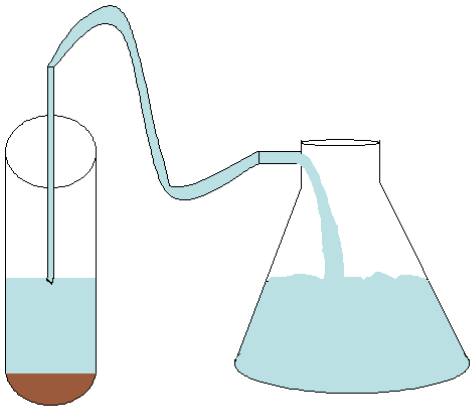


Figure 1

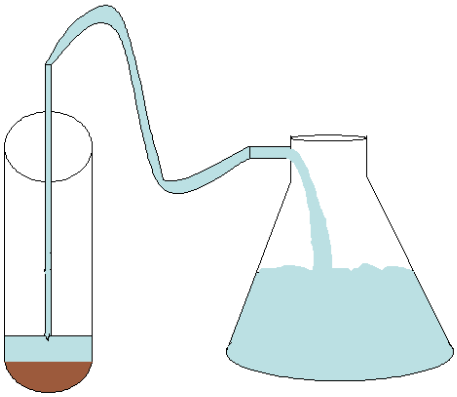


Figure 2

Fractionation of sample for analysis: Remove sample from freezer and allow sample to fully thaw before beginning. After sample has thawed, place sample into the sonicator ¼ filled with water and turn on. The volume of water in the sonicator must be adjusted so that sample bottles do not tip over. Sonicator water will periodically warm up and may melt sample bottles,

so water must be changed every 15-20 minutes or cooled with an adequate amount of ice. After samples have been sonicated for approximately 15 minutes, the samples are removed and placed on a stir plate to be continuously stirred while they are fractionated for analysis. When removing sediment trap sample from the sample container only pipette from the middle of the bottle mid-way down.

- For TSS, FSS, VSS (SOP # 101,202) filter 25 ml of sample through a pre-ashed AH filter paper and follow respective SOP guidelines.
- For Total Particulate Carbon , PIC, and POC (SOP # 214) filter 2 ml of sample through a 25 mm GFF filter paper, dry filter paper then freeze (TPC), save filtrate for dissolved calcium. Filter 5 ml of sample through 25 mm GFF filter, directly acidify sediment on filter paper with concentrated HCl, rinse dry and freeze filter paper (POC).
- For total calcium, pipette 5 ml of sample into a glass vial and acidify with 0.5 ml concentrated trace metal grade nitric acid for 24 hrs, filter, and keep filtrate in refrigerator until analysis.

Follow the Table below for summary instructions of how to prepare the sediment trap sample for each respective analysis:

Desired Analyate	Required Filtering Apparatus	Required Filters	Reagents	Normal Volume	Sample Type	Notes	Storage
TSS,FSS,VSS	Nalgene	AH 47 mm	N/A	25 ml	Filter		Desicator
TPC,PIC,POC	Glass	GFF 25 mm	HCl	2 - 5 ml	Filter	Dried	Freezer
Calcium Total	Glass	GFF 25 mm	Nitric	5 ml	Dissolved		Refrigerator
Calcium Dissolved	Glass	GFF 25 mm	N/A	2 ml	Dissolved		Refrigerator

15) Calculations: N/A

16) Method Performance: N/A

17) Pollution Prevention: Neutralize acidic waste from POC with enough baking soda until fizzing ceases before washing down the drain.

18) Data Assessment and Acceptance Criteria for Quality Control Measures: N/A

19) Corrective Actions for Out-of-Control or Unacceptable Data: N/A

20) Contingencies for Handling Out-of-Control or Unacceptable Data: N/A

21) Waste Management: There should be no waste from this method

22) References: N/A

Nitric Acid Digestion for Methyl Mercury (MeHg) and Total Mercury (T-Hg)

Summary:
The purpose of the Nitric Acid digestion is to analyze limited material samples for T-Hg and MeHg and to calculate the percentage MeHg/T-Hg from the same aliquot. The MDL from spiked digestion solution is 2.04 ng/g for MeHg (attachment a), and the calculated MDL for T-Hg is 14 ng/g of Hg (attachment b).

Material and Reagents:
4M Nitric acid - 25.6g of Optima Grade Nitric Acid brought to 100mL in Milli-Q water
3 ml Teflon Vial- Purchased from Savillex

Procedure:
Weigh Teflon vials, and place 20 to 50 animals in Teflon vial. The average weight of mature daphnia is 16.41 ug. Estimated weights of dried sample for 20 to 50 animals are 328 to 821 ug. Freeze the sample and freeze dry in the same Teflon vial.

Weigh the Teflon vial, and add 1 mL of 4M nitric acid solution to digest the sample. Place in a 65^{o} C oven for 24 hours, and then weigh the Teflon vial after digestion.

Holding time and sample container:
Zooplanktons are collected using method AP #CESE-ENV-310 “Standard Operating Procedure for Zooplankton Sample Collection andPreservation and Secchi Depth Measurement Field Procedures”. In the laboratory 20 -50 animals (preferable 50) are picked and placed in a weighed Teflon vial for freeze drying and digestion.

After digestion samples should be analyzed within 7 days for MeHg.

Analytical batch:
The analytical batch consist of 20 samples, a method blank, laboratory control standard, quality control sample, laboratory control standard duplicate and quality control sample duplicate.

Method Blank- all reagents added to a Teflon vial.

Laboratory Control Sample/laboratory control standard Duplicate-add 100 ul of 10 ng/ml of MeHg to 1ml of 4M nitric acid digestion solution.

Quality Control sample/Quality control Sample duplicate-Weigh 3-5 mg of 2976 certified mussel standards.

MeHg Analysis:
100 mg aliquot is analyzed using method AP #CESE-ENV-Z-1630 “Methyl Mercury in Biomass by Digestion, Aqueous Ethylation, Purge and Trap, and CVAFS”

T-Hg Analysis:
Place a 500*u*L aliquot in Total mercury vial and bring to 49.500g.
Add 500*u*L of BrCl solution to further oxidize the Hg.
The diluted sample is analyzed using method AP #CESE-ENV-1631 “Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry”

Attachment A MDL Study						
Nitric Acid Digestion						
Sample Name	**ng on col.**	**%R**	**sample used**	**digested volume (g)**	**sample used (g)**	**Final concentration (ng/g)**
MDL1	0.00195	97.6	0.001	1.000	0.100	19.51
MDL2	0.00197	98.7	0.001	1.000	0.100	19.75
MDL3	0.00191	95.3	0.001	1.000	0.100	19.06
MDL4	0.00190	95.0	0.001	1.000	0.100	18.99
MDL5	0.00204	102.1	0.001	1.000	0.100	20.42
MDL6	0.00185	92.5	0.001	1.000	0.100	18.50
MDL7	0.00188	94.0	0.001	1.000	0.100	18.81
Average	0.00193	96.5				19.29
STDEV	6.48E-05					0.65
MDL(3.143)(STDEV)	2.04E-04					2.04

Attachment B Theoretical Calculation of T-Hg (ng/g)						
MDL (ng/L)	Analyzed volume(L)	aliquot (g)	total digest (g)	Total ng of Hg	sample used (g)	MDL (ng/g)
0.14	0.05	0.5	1	0.014	0.001	14

APPENDIX B

REVISED WORKSHEETS FOR THE QUALITY ASSURANCE PROJECT PLAN

APPENDIX B
ADDENDUM 1 (2009)
REVISED WORKSHEETS FOR
QUALITY ASSURANCE PROJECT PLAN
ONONDAGA LAKE BASELINE MONITORING
BOOK 1
DEEP BASIN WATER AND ZOOPLANKTON MONITORING WORK PLAN FOR 2008

Prepared for:

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SEPTEMBER 2009

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Project Name: Onondaga Lake Baseline Monitoring Projected Date(s) of Sampling: **April–November 2009** **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
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John McAuliffe	Project Manager	Honeywell	315-431-4443	John.mcauliffe@ honeywell.com	Overall Project Manager
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Robert Montione	Scientist	Earth Tech	518-951-2226	robert.montione@ earthtech.com	Technical support to NYSDEC
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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. The Technical Work Group met on January 29, 2009 to discuss baseline monitoring needs for 2009.

Action Items: Parsons and SU/UFI submitted draft work plan addenda for 2009 on March 10 and July 10, 2009 which NYSDEC has approved.

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 sediment traps. 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 third component, sediment traps, permits the estimation of mercury and solids settling on a weekly basis.

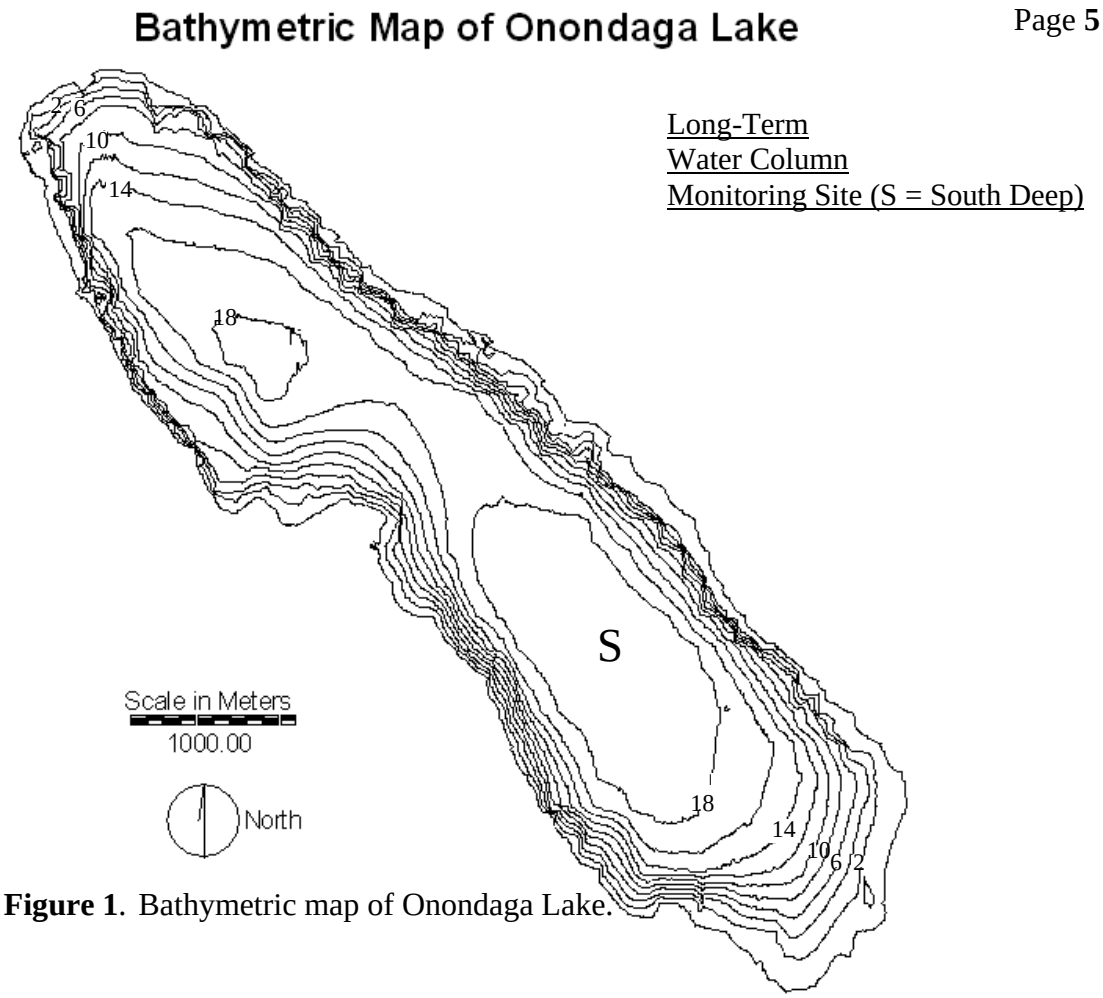

Figure 1. Bathymetric map of Onondaga Lake.

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.

Sediment trap monitoring will measure total mercury, total suspended solids, fixed and volatile suspended solids, particulate carbon, and total and acidified calcium in sediment collected from the traps on a weekly basis.

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.. 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 lateApril until the end of November (as feasible) using field sampling techniques summarized in Worksheet #21 and provided as attachments to the work plan. Sampling frequency may be adjusted if the timing for stratification is significantly different during 2009 than during 2008. Water and zooplankton samples for laboratory analysis will be collected at depths and frequency specified in Worksheet #17. *In situ* rapid profile water monitoring will be conducted on a weekly basis from April until the end ofNovember (as feasible) at multiple depths along transects shown in the 2008 Book 1 work plan. Sediment traps will be deployed and collected from South Deep from April to October.

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 Brooks Rand.

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.

Matrix	Sediment slurry
Analytical Group[1]	Total suspended solids
Concentration Level	Average

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-6	L-20	Precision	RSD 50%	Field triplicate samples	S&A
		Contamination	Less than LOD (1.0 mg/L)	Method blanks	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.

Note: Performance criteria for fixed suspended solids are identical to performance criteria for total suspended solids. Volatile suspended solids are determined based on the difference between total suspended solids and fixed suspended solids.

Matrix	Sediment slurry
Analytical Group[1]	Particulate Inorganic Carbon
Concentration Level	Average

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-6	L-21	Precision	RSD 50%	Field triplicate samples	S&A
		Accuracy/Bias	Within three standard deviations of the mean for control limits	Reference sample	A
		Sensitivity	Within three standard deviations of the mean for control limits	ICV, CCV	A
		Contamination	Less than LOD (50 µgC/L)	Instrument and Method blanks	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	Sediment slurry
Analytical Group[1]	Particulate Calcium
Concentration Level	Average

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-6	L-22	Precision	RSD 50%	Field triplicate samples	S&A
		Accuracy/Bias	Within three standard deviations of the mean for control limits	Reference sample	A
		Sensitivity	Within three standard deviations of the mean for control limits	ICV, CCV	A
		Contamination	Less than LOD (0.3 mg/L)	Instrument and Method blanks	A
		Matrix Effects	Within three standard deviations of the mean for control limits	Matrix spike	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	Sediment slurry
Analytical Group	Total mercury
Concentration Level	Low

Sampling Procedure[1]	Analytical Method/SOP[2]	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-6, S-7	LB-1	Accuracy	< sample-specific RL, or associated samples >5× blank values	Laboratory or equipment blank	A
			Control limit recovery 85-115%	Laboratory control sample	A
			Control limit recovery 85-115%	Matrix spike	A
			80-120% of expected value for ICV; 67-133% of expected value for CCV samples	Initial and continuing calibration verification samples	A
		Precision – Field	RSD 30%	Field duplicate	S&A
		Precision – Lab	RPD 30%	Matrix spike duplicate	A
		Sensitivity	0.034 μg/g	Reporting limits	S&A
		Representativeness	Use of standardized collection and analytical methods	Field audits and laboratory audits	S&A
		Completeness	95%	Comparison of number of confident quantifications to total quantifications	S&A
		Comparability	Based on accuracy and media comparison	Use of standardized SOPs by field and analytical contractors	S&A

[1]Reference number from QAPP Worksheet #21.
[2]Reference number from QAPP Worksheet #23.

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. Sediment Trap Monitoring 4. The work plan documents the details of sample locations, depths, SOPs, and water sample collection.

Analysis Tasks

1. UFI will analyze water and sediment trap 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. Brooks Rand will analyze water, zooplankton, and sediment (from trap) for total mercury and for methylmercury.
3. SU will freeze dry, digest, and analyze the daphnia portion of zooplankton samples for total mercury and for methyl mercury.

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 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: Sediment Slurry
Analytical Group: Total Suspended Solids
Concentration Level: Average

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total Suspended Solids	NA	NA	2.5 mg/L dry weight	NA	NA	1.0 mg/L dry weight	2.5 mg/L dry weight

[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: Sediment Slurry
Analytical Group: Particulate Inorganic Carbon
Concentration Level: Average

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits2	
				MDLs	Method QLs	MDLs	QLs
Particulate Inorganic Carbon	NA	NA	50 µg carbon	NA	NA	NA	50 µg carbon

[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: Sediment Slurry
Analytical Group: Particulate Calcium
Concentration Level: Average

Analyte	CAS Number	Project Action Limit	Project Quantitation Limit	Analytical Method[1]		Achievable Laboratory Limits2	
				MDLs	Method QLs	MDLs	QLs
Particulate Calcium	NA	NA	1.1 mg/L	0.08 mg/L	0.2 mg/L	0.3 mg/L	1.1 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: Sediment Slurry
Analytical Group: Mercury
Concentration Level: Low

Analyte	CAS Number	Project Action Limit (applicable units)	Project Quantitation Limit (applicable units)	Analytical Method[1]		Achievable Laboratory Limits[2]	
				MDLs	Method QLs	MDLs	QLs
Total mercury	7439-97-6	NA		0.007 µg/g	0.034 µg/g	0.007 µg/g[3]	0.034 µg/g[3]

[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.
[3]The MDL and QL concentrations are dependent on the sample mass. For an analysis of 0.3 g, the MDL is 0.007 µg/g.

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
Sediment trap monitoring	UFI	April	October	NA	NA
Water column monitoring	UFI	April 27	November 23	NA	NA
Zooplankton sampling	UFI	April 27	November 23	NA	NA
In situ/in vivo monitoring	UFI	April 27	November 23	NA	NA
Scientific oversight	Exponent	continuous	continuous	NA	NA
Sample analysis	UFI/Test America	late-April	December	Unvalidated data	Quarterly
Data Usability and Summary Report (DUSR)	Parsons or Exponent	January following field season	March 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 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. Sediment trap sampling will also occur at South Deep, consistent with UFI's long-term monitoring program.

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	once	4/27	2, 12, 18
May	once	5/25	2, 12, 18
June	once	6/22	2, 12, 18
July	bi-weekly	7/6, 7/20	2, 12, 16, 18
August	bi-weekly	8/3, 8/17, 8/31	2, 12, 16, 18
September	weekly	9/7, 9/14, 9/21, 9/28	2, 12, 14, 16, 18
October	weekly	10/5, 10/12, 10/19, 10/26	2, 12, 14, 16, 18
November	Weekly through turnover then bi-weekly	11/1, 11/8	2, 12, 14, 16, 18,
		11/23	2, 12, 18

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 (18 m). In addition, when the lake is stratified (July – October), samples will be collected at 16 m 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 7. After turnover, sampling depths will return to 2, 12, and 18 m. This plan will provide increased coverage during the critical fall turnover period. 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. These 2 m samples will be collected once in April, May, and June, and biweekly thereafter. In addition, dissolved mercury samples will be collected on a biweekly basis at 14 m depth starting on September 14 through turnover (estimated to occur by November 8).

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	84 (38 env + 38 dups + 8 blanks)	S-1	See Worksheet #17
South Deep	Water	See Worksheet #17	NO_x and NO_2	Low	128 (82 env + 38 dups + 8 blanks)	S-1	
			T-NH_3	Low	128 (82 env + 38 dups + 8 blanks)		
			DOC and TIC	Low	128 (82 env + 38 dups + 8 blanks)		
			Chloride	Low	128 (82 env + 38 dups + 8 blanks)		
			Total mercury	Low	109 (82 env + 19 dups + 8 blanks)	S-3	
			Methyl mercury	Low	109 (82 env + 19 dups + 8 blanks)		
South Deep	Water	2 m once in April, May, June, bi-weekly thereafter; 14 m biweekly starting 9/14 to 11/8	Filtered total mercury	Low	27 (19 env + 5 dups + 3 blanks)	S-3	
South Deep	Water	Anoxic depths; 12, 16, 18 m (mid July – mid-November)	Ferrous iron	Low	75 (42 env + 28 dups + 5 blanks)	S-1 S-2	
			Dissolved methane	Low	75 (42 env + 28 dups + 5 blanks)		
South Deep	Water	Anoxic depths; 1-m intervals (mid July – mid-November)	Sulfide method 1[2]	Low	173 (140 env + 28 dups + 5 blanks)	S-1 S-2	

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
			Sulfide method 2[2]	Low	173 (140 env + 28 dups + 5 blanks)		
South Deep	Zooplankton[4]	13 m vertical tow bi-weekly once in April, May, June; bi-weekly thereafter	Total mercury and percent solids	Low	16 (14 composites + 2 dups)	S-4	
			Methyl mercury	Low	16 (14 composites + 2 dups)		
South Deep	Sediment Slurry	10 m deployment sampled weekly mid-April to October	Total mercury	Low	37(includes 7 dups)	S-6	
			Total suspended solids	Average	90 (30 triplicate samples)		
			Particulate inorganic carbon	Average	90 (30 triplicate samples)		
			Particulate calcium	Average	90 (30 triplicate samples)		

[1] Total does not equipment rinsate blanks for mercury analyses. For analytes other than mercury, two field duplicates are collected for each sampling event. For mercury, one field duplicate is collected for each sampling event. Blanks are collected monthly.
[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 ($T\text{-}NH_3$)	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)
Sediment Slurry	Total Mercury	Average	LB-1	2-10 g	Plastic or Teflon bottle (250-500 mL)	Cool, 4°±2C, Refrigerate 4°±2C	6 months (preserved)
Sediment Slurry	Total suspended solids	Average	L-20	25 mL	Opaque plastic bottle (1 L)	cool, 4°C, dark	7 days
Sediment Slurry	Particulate inorganic carbon	Average	L-21	7 mL	Opaque plastic bottle (1 L)	filter, freeze	90 days
Sediment Slurry	Particulate calcium	average	L-22	7 mL	Opaque plastic bottle (1 L)	cool, 4°C, dark	6 months

[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, 19 sampling trips (38 samples)	Triplicate sets 19 (38 samples)		8			84
Water	Nitrate/Nitrite as N (NO_x)	Low	L-2	1 station, 3–5 depths, 19 sampling trips (82 samples)	Triplicate sets 19 (38 samples)		8			128
Water	Nitrate as N (NO_2)	Low	L-2	1 station, 3–5 depths, 19 sampling trips (82 samples)	Triplicate sets 19 (38 samples)		8			128
Water	Ammonia as N ($T\text{-}NH_3$)	Low	L-3	1 station, 3–5 depths, 19 sampling trips (82 samples)	Triplicate sets 19 (38 samples)		8			128
Water	Organic Carbon, Total/Total Dissolved as C (DOC)	Low	L-4	1 station, 3–5 depths, 19 sampling trips (82 samples)	Triplicate sets 19 (38 samples)		8			128
Water	Carbon, Inorganic Dissolved and Total (TIC)	Low	L-7	1 station, 3–5 depths, 19 sampling trips (82 samples)	Triplicate sets 19 (38 samples)		8			128

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, 3–5 depths, 19 sampling trips (82 samples)	Triplicate sets 19 (38 samples)		8			128
Water	Ferrous iron	Low	L-10	1 station, 3 depths, 14 sampling trips (42 samples)	Triplicate sets 14 (28 samples)		5			75
Water	Dissolved methane	Low	L-9	1 stations, 3 depths, 14 sampling trips (42 samples)	Triplicate sets 14 (28 samples)		5			75
Water	Sulfide as S (Method 2)	Low	L-6	1 station, ~10 depths, 14 sampling trips (140 samples)	Triplicate sets 14 (28 samples)		5			173[5]
Water	Total mercury	Low	L-11	1 station, 3–5 depths, 19 sampling trips (82 samples)	19		8	4		113
Water	Filtered mercury	Low	L-11	1 station, 1-2 depths, 14 sampling trips (19 samples)	5		2	1		27

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, 3–5 depths; 19 sampling trips (82 samples)	19		8	4		113
Zoo-plankton assembla-ges	Total and methyl mercury	Low	L-12, L-13	1 station, 14 sampling trips (14 samples)	2					16
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					11
Sediment Slurry	Total mercury	Low	LB-1	1 station, 1 trap, 30 sampling trips	7					37
Sediment Slurry	Total suspended solids	Average	L-20	1 station, triplicate traps, 30 sampling trips (90 samples)						90
Sedimen Slurryt	Particulate inorganic carbon	Average	L-21	1 station, triplicate traps, 30 sampling trips (90 samples)						90
Sediment Slurry	Particulate calcium	Average	L-22	1 station, triplicate traps, 30 sampling trips (90 samples)						90

[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]Blanks collected monthly. 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.
S-6	UFI SOP ST Sediment trap deployment and collection	UFI	Sediment trap assemblage (arrangements of three), deployment rope, sub-surface float, surface float, anchor, black rubber stoppers, cleaning brush, funnel, and collection bottles.	N	Includes descriptions and procedures for deployment and collection of sediment traps.

Reference Number	Title, Revision Date and/or Number[1]	Originating Organization	Equipment Type	Modified for Project Work? (Y/N)	Comments
S-7	UFI SOP 227 Sediment trap sample preparation	UFI	Plastic suction filtration flask and tube to remove supernatant from settled sediment trap sample.	NA	Description of sampling sediment slurry from sediment trap for chemical analysis

SOPs S-1 through S-5 are available as attachments to Appendix B, the Quality Assurance Project Plan for the 2007 Nitrate Evaluation Study (UFI and SU, 2007). SOPs S-6 and S-7 are provided in Appendix A to Addendum 1 (2009) to the 2008 Book 1 work plan (UFI and SU, 2009).

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.]

UFI and SU. 2008. Onondaga Lake Baseline Monitoring Book 1 Deep Basin Water and Zooplankton Monitoring Work Plan for 2008. Prepared for Honeywell, Inc., East Syracuse, NY. Upstate Freshwater Institute and Syracuse University, Syracuse, NY. May 2008.

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-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	Brooks Rand	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

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-20	UFI SOP 101 – Total Suspended Solids (SM 20th 2540D) and UFI SOP 202 – Fixed and Volatile Suspended Solids	Definitive	Suspended Solids	Sartorious Analytical Balance	UFI	N
L-21	UFI SOP 214 – Carbon, Organic and Total Particulate (SM 20th 5310B)	Definitive	Particulate Inorganic Carbon	Tekmar Dohrmann Phoenix 8000	UFI	N
L-22	UFI SOP 205 – Calcium, Total UFI SOP 226 – Calcium, Acidified (SM 20th 3111B)	Definitive	Particulate Calcium	Perkin Elmer AAnalyst 300 AAS	UFI	N
LB-1	Mercury (Cold Vapor Technique) [SW-846 Method 7471A], BR-ME-004, Revision 11	Definitive	Total mercury (tissue and sediment slurry	Mercury Auto-Analyzer; Leeman Labs PS 200 and Leeman Labs Hydra AA with Autosampler or equivalent	Test America	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, 2007). L-16 through L-19 are provided in Attachment 1 to the 2008 Book 1 QAPP. L-20 through L-22 and LB-1 are provided in Appendix A to Addendum 1 (2009) to the 2008 Book 1 work plan (UFI and SU, 2009). LB-1 is provided in Appendix A to the 2008 Book 2 Work Plan (Parsons, Exponent, and QEA, 2008).

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.]

UFI and SU. 2008. Onondaga Lake Baseline Monitoring Book 1 Deep Basin Water and Zooplankton Monitoring Work Plan for 2008. Prepared for Honeywell, Inc., East Syracuse, NY. Upstate Freshwater Institute and Syracuse University, Syracuse, NY. May 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
Tekmar Dohrmann Phoenix 8000 Carbon analyzer	See UFI SOP 110 See UFI SOP 203 See UFI SOP 214	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 ,L-7.L21

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
Santorius Analytical Balance	See UFI SOP 101	Annual balance calibration. Calibration is checked with certified weights before each use.	±2% of certified mass	Replace desiccant in scale, re-tare scale, and re-analyze certified weights. If acceptable values cannot be attained balance must be recalibrated.	Laboratory Staff	L-20

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Perkin Elmer AAnalyst 300 AAS	See UFI SOP 205 See UFI SOP 226	Standards are placed at the start of every sample run. Calibration standards are run as the first sample, before running others, every 10 afterwards, and as the last sample of any run.	The software calculates the standard curves and QC acceptance limits. The R^2 for the standards should be no less than 0.995. • 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. Reanalyze and/or report data as associated with failed CCV, repeat calibration and analysis if necessary.	Laboratory Staff	L-22
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

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
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 in Aqueous and Solid Samples by Cold Vapor Atomic Fluorescence, Methods 1631E and MCAWW 245.7	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
		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		

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
Brooks Rand Model III CVAFS	See Brooks Rand SOP #BR-0011	Initial calibration after instrument set up	5 standards with the RSD ≤15%, Low Std. or R2 ≥ 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
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		

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
		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
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

Instrument	Calibration Procedure	Frequency of Calibration	Acceptance Criteria	Corrective Action (CA)	Person Responsible for CA	SOP Reference[1]
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]
Sartorius Analytical Balance	Desiccant changed, balance pan cleaned	Semi-annual PT samples	Visual inspection of scale with each use	With each use	Calibration checked with certified weights within 2%	Change desiccant, re-tare scale, Investigate and document potential problems.	Laboratory Staff	L-20
Tekmar Dohrmann Phoenix 8000 Carnon Analyzer	Check tubing, clen lines, clean boat sampler	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 wit $R^2 >$ 0.995	Remake standards, investigate and document any potential problems	Laboratory Staff	L-21
Perkin Elmer AAnalyst 300 AAS	Check lamp life, flume alignment, auto sampler tubes, aspirator, gas pressure, fuel pressure, and waste catch	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-22
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

Instrument/ Equipment	Maintenance Activity	Testing Activity	Inspection Activity	Frequency	Acceptance Criteria	Corrective Action	Responsible Person	SOP Reference[1]
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).

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.
- Sediment slurry samples from sediment traps will be collected by UFI personnel for the purpose of determining chemical concentrations.
- 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	Sediment Slurry
Analytical Group	Total mercury
Concentration Level	Low
Sampling SOP	S-6, S-7
Analytical Method/ SOP Reference	LB-1
Sampler's Name	Staff
Field Sampling Organization	UFI
Analytical Organization	Test America
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	Samples are collected in duplicate	RPD 35%			Precision - Field	RPD 35%
Method blank	1 per every batch of samples	<1/2 RL	• Reanalyze for verification • If criteria are still not met, reprepare and reanalyze batch.	Lab	Contamination	<1/2 RL
Initial and continuing calibration verification samples (ICV/CCV)	Immediately after initial calibration, after every 10 samples, and at the end of each run	90-110% for ICV; 80-120% for CCV	• Reanalyze • If criteria are still not met, repeat initial calibration • All samples analyzed after the last passing CCV must be reanalyzed	Lab	Accuracy	90-110% for ICV; 80-120% for CCV

Laboratory control samples (LCS)	1 with every batch of samples	85-115%	• 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	Lab	Accuracy	85-115%
Matrix spike and matrix spike duplicate samples (MS/MSD)	1 with every batch of 20 samples	85-115%	• If Recovery and/or RPD is not within QC limits, evaluate LCS. If LCS is within limits, flag data.	Lab	Accuracy	85-115%

Matrix	Sediment Slurry
Analytical Group	Total Suspended Solids
Concentration Level	Average
Sampling SOP	S-6, S-7
Analytical Method/ SOP Reference	L-20
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
Field triplicate	Every sample	RSD 50%	Reanalyze and/or flag data appropriately	Lab Staff	Precision Lab/field	RSD 50%

Matrix	Sediment Slurry
Analytical Group	Particulate Inorganic Carbon
Concentration Level	Average
Sampling SOP	S-6, S-7
Analytical Method/ SOP Reference	L-21
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
Field triplicate	Every sample	RSD 50%	Reanalyze and/or flag data appropriately	Lab Staff	Precision Lab/field	RSD 50%
Reference	One per analytical batch	Control limits are ±3 standard deviations of the mean value	Reanalyze once. If still outside of limits remake and reanalyze standards and reference	Lab Staff	Accuracet/bias	Control limits are ±3 standard deviations of the mean value. The mean is based on a monthly moving average (minimum of 10 samples)

Initial and continuing calibration verification (ICV, CCV)	Beginning of run, every 10 samples, and at end of run.	Control limits are ±3 standard deviations of the mean value	Reanalyze once. If still outside of limits remake and reanalyze standards and reference	Lab Staff	Precision Lab/field	Control limits are ±3 standard deviations of the mean value. The mean is based on a monthly moving average (minimum of 10 samples)

Matrix	Sediment Slurry
Analytical Group	Particulate Calcium
Concentration Level	Average
Sampling SOP	S-6, S-7
Analytical Method/ SOP Reference	L-22
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 50%	Reanalyze and/or report a failed triplicate samples.	Laboratory staff	Precision - Field	RSD 50%
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)

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 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	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	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	• Warning Limits: within 2 standard deviations of the mean value • Control Limits: within 3 standard deviations of the mean value	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	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	Brooks Rand 3958 6th Ave. NW Seattle, WA, U.S.A 98107	N/A
Water	Methyl mercury	Low	South Deep	L-18	28 days	Brooks Rand 3958 6th Ave. NW Seattle, WA, U.S.A 98107	N/A
Zooplankton	Total and methyl mercury	Low	South Deep	L-19 and L-18	28 days	Brooks Rand 3958 6th Ave. NW Seattle, WA, U.S.A 98107	Syracuse University will perform mercury analyses on daphnia samples
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

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	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
Sediment Slurry	Total mercury	Low	South Deep	LB-1	28 days	Brooks Rand ? 3958 6th Ave. NW Seattle, WA, U.S.A 98107	N/A
Sediment Slurry	Total suspended solids	Average	South Deep	L-20	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Sediment Slurry	Particulate inorganic carbon	Average	South Deep	L-21	60 days	UFI PO Box 506 Syracuse, NY 13214 MaryGail Perkins 315-431-4962 ext. 104	N/A
Sediment Slurry	Particulate calcium	Average	South Deep	L-22	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 analyses 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).