Work Plan for
Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake, 2007 Study

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TABLE OF CONTENTS

Executive Summary

A work plan for a study that advances the assessment of the feasibility of controlling methylmercury production in Onondaga Lake through nitrate addition is presented here. This is a continuation of a more detailed study conducted in 2006. The overarching goals of this 2007 study are to:

- continue to stay apprised of the role of nitrate in controlling methylmercury production in Onondaga Lake;
- continue to investigate the interaction between methylmercury production and related metabolic and redox processes, with particular emphasis on oxygen and nitrate;
- assess spatial differences in water chemistry based on five paired profiles from the north and south basins of the lake collected over the spring to fall interval and the collection of 10 samples on two occasions from multiple locations in the lake;
- assess spatial patterns of nitrate, bisulfide, and ancillary parameters through collection and interpretation of weekly gridding data from the ISUS rapid profiling instrument;
- specify mercury concentrations and taxonomy of the pelagic zooplankton community, including seasonal patterns.

Five work components are identified and described as follows:

1. water column monitoring
2. quantification of the flux of ebullitive gas from the sediments
3. rapid profiling with ISUS and measurement of total dissolved gas pressure (TDG)
4. zooplankton monitoring
5. professional interpretations and analyses of monitoring data

Introduction

1. Background

The sediments, water column, and biota of Onondaga Lake are contaminated with mercury (Hg). Methylmercury (CH_3Hg) is the form of primary concern because it is a neurotoxin that strongly bioaccumulates in food webs. Sulfate (SO_4^{2-}) reducing bacteria are responsible for the methylation of ionic mercury. In 2005, a new approach was suggested by Upstate Freshwater Institute and Syracuse University to potentially abate the production and accumulation of CH_3Hg in the hypolimnion of the lake. In this approach, nitrate (NO_3^-) would be added to the hypolimnion of the lake to abate SO_4^{2-} reduction and the production of CH_3Hg. In 2006, Upstate Freshwater Institute and Syracuse University conducted a water quality monitoring program to evaluate the role of NO_3^- in controlling CH_3Hg production in Onondaga Lake. Nitrate addition and hypolimnetic oxygenation will be evaluated as methods to reduce internal CH_3Hg production (NYSDEC 2006 Consent Decree). Regardless of the means used to control CH_3Hg, major demands will be placed on monitoring to effectively represent spatial and temporal patterns of key substances. Such information will need to be comprehensive and available in a timely manner. The scope of work presented here for 2007 includes components that will address these needs.

2. Overarching Goals

The overarching goals of the proposed 2007 study are to:

- continue to stay apprised of the role of nitrate in controlling methylmercury production in Onondaga Lake;
- continue to investigate the interaction between methylmercury production and related metabolic and redox processes, with particular emphasis on oxygen and nitrate;
- assess spatial differences in water chemistry based on five paired profiles from the north and south basins of the lake collected over the spring to fall interval and the collection of 10 samples on two occasions from multiple locations in the lake;
- assess spatial patterns of nitrate, bisulfide, and ancillary parameters through collection and interpretation of weekly gridding data from the ISUS rapid profiling instrument;
- specify mercury concentrations and taxonomy of the pelagic zooplankton community, including seasonal patterns.

Monitoring Components/Matrix for 2007 Study

The nitrate/methylmercury monitoring program for 2007 described herein is partitioned into four components, water column, ebullition, *in situ/in vivo*, and zooplankton. The *in situ/in vivo* component will consist of profiles of total dissolved gas pressure (TDG) and spatially detailed monitoring with the ISUS rapid profiling instrument. A sampling schedule for the 2007 program, based on collecting data during five water quality regimes, is presented in Table 1. Sample locations and analyses for

water column monitoring are summarized in Appendix A. *In situ* robotic measurements (dissolved oxygen, temperature, specific conductance, pH, fluorometric chlorophyll, and turbidity) will be made at one meter depth interval profiles at south deep (Figure 1), at least daily during the April-October interval. These data will be available at *ourlake.org*, a public website. The laboratory analyses 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 quality assurance project plan (QAPP) is presented in Appendix B. Much of the 2007 work follows the same field and laboratory standard operating procedures (SOPs) provided in the 2006 QAPP and appended to the NYSDEC-approved 2006 work plan (UFI and SU 2007). However, some SOPs were updated and new SOPs were added. The new SOPs include field SOPs for zooplankton sampling and ISUS sampling as well as laboratory SOPs for determination of biomass and taxonomy of zooplankton assemblages. Finally, the 2007 work will follow the 2006 project safety plan in Appendix C of the 2006 work plan (UFI and SU 2007).

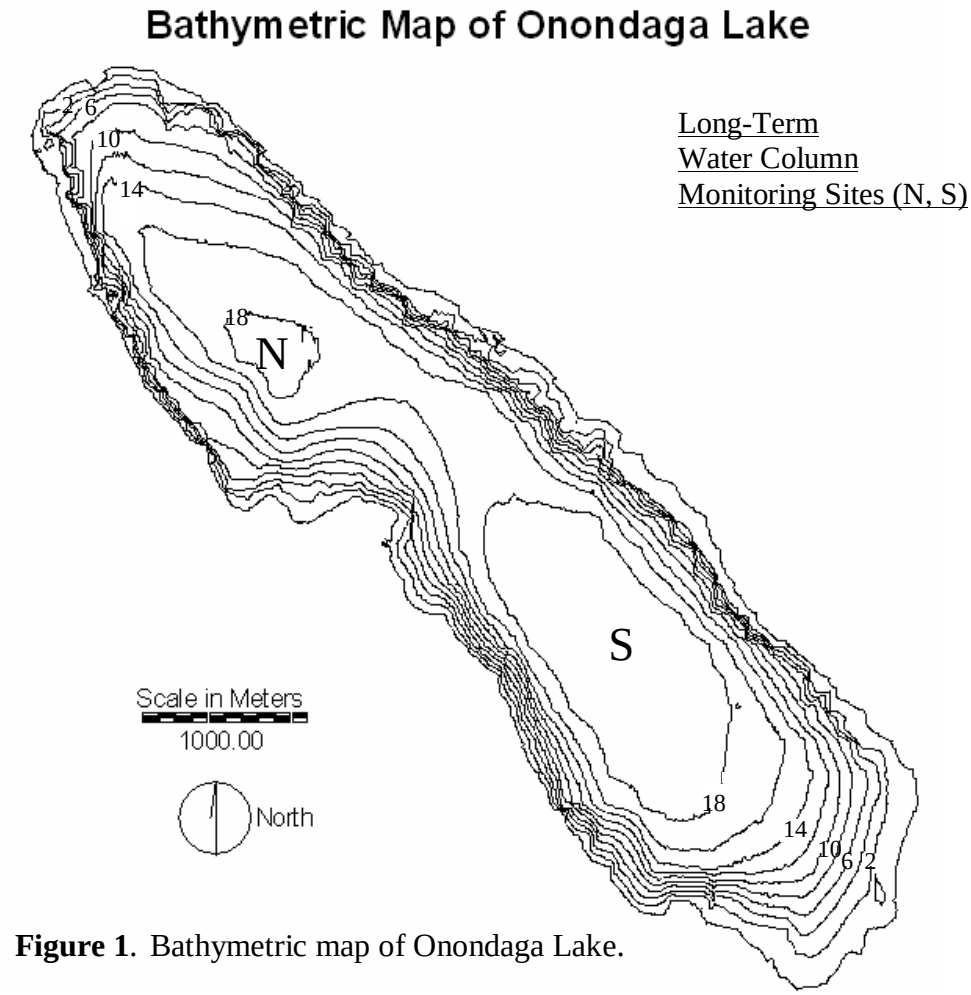

Figure 1. Bathymetric map of Onondaga Lake.

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

1. **Water Column Monitoring** - laboratory analyses of lake water samples
    a. Goals
        i. assess temporal and spatial patterns of mercury speciation in Onondaga Lake
        ii. assess temporal and spatial patterns of an array of constituents that include important redox constituents and indicators of primary production and decomposition processes
        iii. further document the relationship(s) between the patterns of mercury and redox constituents
    b. Specifications
        i. timing – specified in Table 1
        ii. space - at long-term (south deep) monitoring site (S, Figure 1) and at north deep (N, Figure 1); depths as specified in Tables 2 and 3 according to analyte; in addition, 10 samples will be collected in both August and October, in conjunction with ISUS gridding, to evaluate lateral heterogeneity (Table 4). The locations of these samples will be discussed with and approved by NYSDEC prior to sampling. Dissolved oxygen (DO) measurements will be made with calibrated probes at all locations where water samples are collected.
        iii. sample collection as per NELAC and EPA specifications
        iv. parameters - listing, methods, and depths are presented in Tables 2, 3, and 4
2. **Monitoring of Ebullition** – assessment of gas ebullition with inverted cones
    a. Goals:
        i. quantify the upward flux of ebullitive gas from the sediments
        ii. support the evaluation of the potential for increases in ebullition associated with a shift to an increased role for nitrate in supporting decomposition in the hypolimnion (a potential impact of nitrate treatment)
    b. specifications:
        i. inverted cone design as per long-term UFI program, LEXAN construction, 0.75 m diameter, inverted graduated separatory funnel collection
        ii. deployment/collection - 2 m above bottom, one unit at south deep and one unit in the deep portion of north basin
        iii. timing - weekly collections, April - November
        iv. parameters
            (1) upward flux for both cones
3. ***in situ*/*in vivo* monitoring**
    a. Measurements with rapid profiling instrumentation
        i. Goals:

(1) validate ISUS measurements of nitrate (NO_3^-) and bisulfide (HS^-),
(2) assess spatial patterns of nitrate (NO_3^-), bisulfide (HS^-), beam attenuation coefficient (**c**; surrogate of TSS and turbidity), specific conductance (SC) and ancillary parameters, with high spatial resolution, over short time intervals (three dimensional resolution within several hours)
(3) develop monitoring protocols with this instrumentation capable of assessing the efficacy of NO_3^- treatment, through resolution of the spatial patterns of NO_3^- and primary by-products of sulfate reduction (e.g., HS^-); for monitoring during implementation of rehabilitation
(4) develop rapid results - turn-around capabilities with this instrumentation to potentially assist in future nitrate and/or oxygenation pilot studies

ii. protocols and content
(1) "south deep" and "north deep" and X-Y gridding (15 to 30 sites); see Figure 2 for example gridding locations
(2) vertical resolution ~ 0.25 m
(3) frequency – weekly
(4) April - November
(5) parameters measured by sensors as specified in Table 5

b. Measurements of total dissolved gas pressure (TDG)
i. Goals:
(1) evaluate the potential for dissolved gas supersaturation (DGS) and gas bubble trauma (GBT) in fish through measurements of TDG

ii. protocols and content
(1) vertical profiles with a calibrated tensionometer at “south deep” on 9 occasions and “north deep” on 4 occasions
(2) vertical resolution of 1 m

4. **Zooplankton Monitoring**
a. zooplankton taxonomy and mercury concentrations
i. Goals:
(1) specify seasonal patterns in the taxonomy and biomass of the pelagic zooplankton community through enumeration of five samples to genus or species (in most cases) level
(2) determine concentrations of total and methylmercury in the pelagic zooplankton assemblage on a seasonal basis
(3) if possible, determine concentrations of total and methylmercury in large daphnids

ii. Specifications:
(1) “south deep” and “north deep”
(2) five samplings at “south deep” and one at “north deep” under five water quality regimes as described in Table 1

(3) 13 m vertical tows with a non-metallic 64µm mesh zooplankton net
(4) three tows per sampling - two tows for mercury analyses (i.e., field duplicates) and one tow for enumeration
(5) the zooplankton assemblage samples will be analyzed for total mercury and methylmercury. If large daphnids are present, they will be picked from the sample and analyzed for total mercury and methylmercury

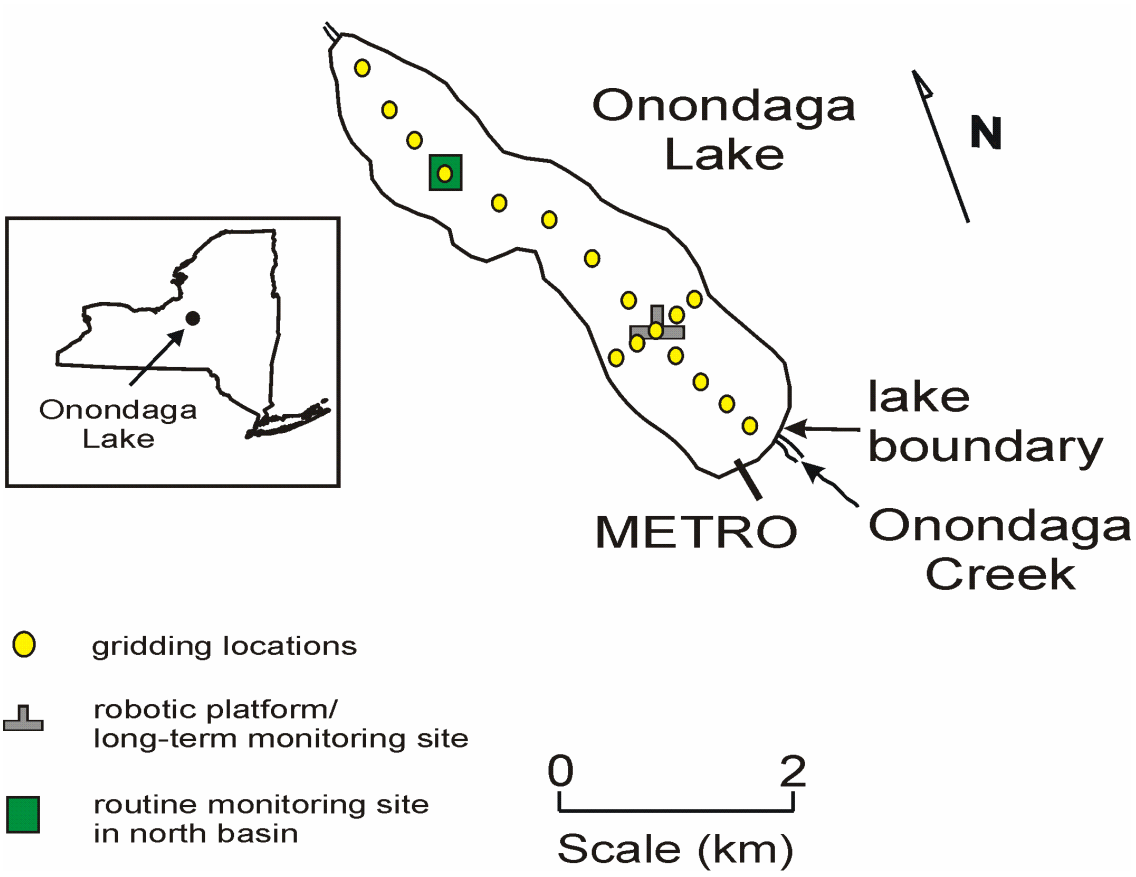

Figure 2. Map of Onondaga Lake that identifies locations for an example ISUS gridding.

Table 1: Sampling schedule for 2007 based on five water quality regimes: (1) spring turnover; (2) stratified conditions with both DO and NO_3^- present throughout the hypolimnion; (3) stratified conditions with NO_3^- present and DO depleted from the hypolimnion; (4) stratified conditions with both DO and NO_3^- depleted from the hypolimnion; and (5) fall turnover. Specified dates are approximations based on the conditions of 2006. Near-real-time information from the ISUS and the robotic buoy will be used to guide the 2007 sampling schedule.

Regime	Approximate Date (week of)	Water Column			Zooplankton	
		South Deep	North Deep	ISUS Gridding	South Deep	North Deep
1	April 23	•	•		○	
2	May 21	•	•		○	
3	June 18	▲				
	July 2	▲	▲		○	
4	August 27	▲	▲	◊	○	○
	September 24	▲				
5	October 22	▲		◊		
	November 5	•	•		○	
	November 19	•				

Notes:

- 3-depth event (South Deep and North Deep)

▲ 8-depth event at South Deep, 7-depth event at North Deep

◊ locations and depths for samples associated with ISUS gridding to be determined with NYSDEC (2 events with 10 samples each)

○ zooplankton sampling; Regime 5 event may be moved to week of November 19 based on the timing of fall turnover.

Table 2: Specifications for water column and zooplankton monitoring at south deep, laboratory analytes.[x]

Parameter	Method	South Deep Depths (m)	Total Number of Analyses[x]
Chl	EPA 445	2,10,18 (Apr, May, Nov twice) 2, 6,10,18 (Jun-Oct)	59
NO_X	EPA 353.2	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
NO_2^-	EPA 353.2	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
T-NH_3	EPA 350.1	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
DOC	SM 18-20 5310C	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
TIC	SM 18-20 5310C	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
Fe^{2+}	Heaney and Davison (1977)	anoxic depths, 1 m intervals	54
H_2S method 1	SM 18-20 4500 S^{2-} E	anoxic depths, 1 m intervals	54
°method 2	SM 18-20 4500 S^{2-} G	anoxic depths, 1 m intervals	79
CH_4	Addess 1990	anoxic depths, 1 m intervals	54
N_2	Addess 1990	anoxic depths, 1 m intervals	54
Cl^-	SM 18-20 4500 Cl^- C	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
+*Total Hg	EPA 1631E	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
+*CH_3Hg	EPA 1630	2,10,18 (Apr, May, Nov twice) 2,6,10,12,14,16,17,18 (Jun-Oct)	79
#Zooplankton Total Hg	EPA Method 7473 or 1631E	Apr, May, Jul, Aug, Nov	10
#Zooplankton CH_3Hg	EPA Method 1630	Apr, May, Jul, Aug, Nov	10

[x] Includes trip blanks and field triplicates at one depth. UFI trip blanks are sample bottles that are filled in the laboratory, transported to the field and then back to the laboratory for analysis.

[+] Measurements performed in laboratory at Syracuse University, all others in laboratory at the Upstate Freshwater Institute

* Includes one field duplicate, one field blank, and one equipment blank per sampling event.

° Approximately 25 samples will be collected outside of the monthly sampling program and analyzed for sulfide to support validation of ISUS measurements.

[#] Duplicates will be collected during each of 5 events for a total of 10 samples. In addition, up to 10 samples of large *Daphnia* will analyzed if sufficient numbers are present. For zooplankton assemblages, EPA Method 7473 will be used for total Hg analysis. For *Daphnia*, EPA Method 1631E will be used for total Hg analysis.

Table 3: Specifications for water column and zooplankton monitoring at north deep, laboratory analytes.

Parameter	Method	North Deep Depths (m)	Total Number of Analyses
Chl	EPA 445	2,10,17 (Apr, May, Nov) 2, 6,10,17 (Jul, Aug)	17
NO_X	EPA 353.2	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	23
NO_2^-	EPA 353.2	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	23
T-NH_3	EPA 350.1	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	23
DOC	SM 18-20 5310C	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	23
TIC	SM 18-20 5310C	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	23
Fe^{2+}	Heaney and Davison (1977)	anoxic depths, 1 m intervals	24
H_2S method 1	SM 18-20 4500 S^{2-} E	anoxic depths, 1 m intervals	24
method 2	SM 18-20 4500 S^{2-} G	anoxic depths, 1 m intervals	24
CH_4	Addess 1990	anoxic depths, 1 m intervals	24
N_2	Addess 1990	anoxic depths, 1 m intervals	24
Cl^-	SM 18-20 4500 Cl^- C	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	23
[+*]Total Hg	EPA 1631E	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	28
[+*]CH_3Hg	EPA 1630	2,10,17 (Apr, May, Nov) 2, 6,10,12,14,16,17 (Jul, Aug)	28
[#]Zooplankton Total Hg	EPA Method 7473 or 1631E	Aug	2
[#]Zooplankton CH_3Hg	EPA Method 1630	Aug	2

[+] Measurements performed in laboratory at Syracuse University, all others in laboratory at the Upstate Freshwater Institute

* Includes one field duplicate per sampling event. One field blank and one equipment blank per sampling event are included in the South Deep analyses total.

[#] Duplicates will be collected during the August sampling event for a total of 2 samples. In addition, up to 10 samples of large *Daphnia* will analyzed if sufficient numbers are present. For zooplankton assemblages, EPA Method 7473 will be used for total Hg analysis. For *Daphnia*, EPA Method 1631E will be used for total Hg analysis.

Table 4: Number of laboratory analyses for south deep, north deep, ISUS gridding, and total.

Parameter	South Deep	North Deep	ISUS Gridding	Total Number of Analyses
Chl	59	17		76
NO_X	79	23	20	122
NO_2^-	79	23	20	122
T-NH_3	79	23	20	122
DOC	79	23		102
TIC	79	23		102
Fe^{2+}	54	24		78
H_2S method 1	54	24		78
method 2	79	24	20	123
CH_4	54	24		78
N_2	54	24		78
Cl^-	79	23		102
Total Hg	79	28	24	131
CH_3Hg	79	28	24	131
[#]Zooplankton Total Hg	10	2		12
[#]Zooplankton CH_3Hg	10	2		12

[#] Up to an additional 12 samples will analyzed if sufficient large *Daphnia* are present.

Table 5: Specifications for ISUS rapid profiling instrumentation

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

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

Professional Analyses of 2007 Work Elements

The results of the 2007 study will be analyzed by an interdisciplinary team of experts to identify and evaluate noteworthy findings consistent with the overarching and specific goals identified for the study above. The details of these analyses will doubtless evolve, and in some cases shift, through the study interval based on continuing inputs from the Honeywell team, and perhaps other parties, and observed lake conditions. **The following outline of activities is representative and valuable for planning purposes. However, changes in the details of organization and composition are to be expected during these analyses, and will be consistent with inputs from the Honeywell team during these activities.**

1. **Water Column Monitoring of Indicators of Lake Metabolism**
    a. specification of concentration and mass patterns of constituents related to Hg cycling in time and space
    b. comparisons of contemporary and earlier patterns, including identification of substantive changes
    c. presentation of 2007 findings in context of the UFI long-term data base; have substantial changes occurred in lake chemistry?
    d. evaluate ISUS performance in measuring NO_3^- and HS^-
    e. description of the temporal and vertical progression of redox/decomposition pathways in the lake's lower layers
    f. couple these patterns to those for species of mercury
    g. evaluate the consistency of the temporal patterns redox constituents with the sequence expected from thermodynamic considerations
    h. calculation of key transformation (net process) rates for redox constituents, including nitrate depletion (ISUS) and hydrogen sulfide accumulation (ISUS)
    i. correction of apparent rates for the effects of vertical mixing/exchange
    j. evaluate the extent of spatial heterogeneity of NO_3^- and HS^-, and related processes in the lake, and drivers
    k. quantify the upward flux of ebullitive gas from the sediments to support the evaluation of the potential for increases in ebullition associated with increased denitrification

2. **Mercury Monitoring - Water Column and Zooplankton**
    a. specification of concentration and mass patterns of species of Hg in time and vertically
    b. comparisons of contemporary and earlier patterns, including identification of substantive changes
    c. coupling of mercury patterns to those for lake metabolism including redox constituents/processes
    d. particular focus on temporal and vertical inflections of methylmercury and corresponding metabolism/redox conditions

e. consideration of the potential relative importance of selected mechanisms and processes in the lake for the mercury cycle based on the reported patterns
f. specification of taxonomy, biomass, and Hg concentrations of the zooplankton community, including seasonal patterns; determine Hg concentrations in large *Daphnia* if they are present
g. evaluation of results in context of related literature

Deliverables

1. All data in acceptable electronic formats
2. Draft data submitted to NYSDEC on a quarterly basis (e.g., April data will be submitted in July), unless agreed to otherwise by NYSDEC
3. Presentation of progress to Honeywell team and other parties (as specified by Honeywell team) in the form of PowerPoint presentation(s) and/or technical memos
4. 2007 Data Usability Summary Report

    UFI and SU will assist Exponent in preparing the data usability summary report. The report will present the results of data validation and data usability assessment. It will also present the findings of the 2007 study in graphical and tabular formats. This is intended to be a "rapid-turn-around" document following the field season. The text treatment will be brief and will highlight findings that are believed to be the most important.

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.

UFI and SU. 2007. Work plan for evaluation of nitrate addition to control methylmercury production in Onondaga Lake, preliminary feasibility analysis and 2006 study. Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Center for Environmental Systems Engineering, Syracuse, NY.

TIMELINE

	2007												2008				
	J	**F**	**M**	**A**	**M**	**J**	**J**	**A**	**S**	**O**	**N**	**D**	**J**	**F**	**M**	**A**	**M**
Develop work plan for 2007 study	→	→	→	→	→												
2007 field study																	
set-up			X	X													
water column monitoring				→	→	→	→	→	→	→	→						
scientific oversight			→	→	→	→	→	→	→	→	→	→					
data handling/analysis				→	→	→	→	→	→	→	→	→	→				
data report											→	→	→	→			
data analysis/interpretation				→	→	→	→	→	→	→	→	→	→	→	→	→	
Meetings/Teleconferences		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

APPENDIX A

Field Sampling Matrix

APPENDIX A

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

Sampling Depth	Chl	NO_X	NO_2	$T\text{-}NH_3$	TIC	DOC	Cl^-	[3]Total Hg	[3]CH_3Hg
2m	XXX	XXX	XXX	XXX	XXX	XXX	XXX	XX	XX
10m	X	X	X	X	X	X	X	X	X
18m	X	X	X	X	X	X	X	X	X

Field Sampling Matrix for Laboratory Analyses of Water Samples, June – October[1]:

Sampling Depth	Chl	NO_X	NO_2	$T\text{-}NH_3$	TIC	DOC	Cl^-	[2]Fe^{2+}	[2]H_2S	[2]CH_4	[2]N_2	[3]Total Hg	[3]CH_3Hg
2m	XXX	XXX	XXX	XXX	XXX	XXX	XXX					XX	XX
6m	X	X	X	X	X	X	X					X	X
10m	X	X	X	X	X	X	X	anoxic depths				X	X
12m		X	X	X	X	X	X	anoxic depths				X	X
14m		X	X	X	X	X	X	anoxic depths				X	X
16m		X	X	X	X	X	X	anoxic depths				X	X
17m		X	X	X	X	X	X	anoxic depths				X	X
18m	X	X	X	X	X	X	X	anoxic depths				X	X
19m								anoxic depths					

NOTES:

X represents one laboratory analysis.

[1] South Deep is the primary sampling site and will be sampled on 9 occasions as specified in Table 1; North Deep will be sampled on 5 occasions as specified in Table 1. The deepest sample at North Deep will be collected from 17 m, the maximum depth of this basin.

[2] Reduced species (CH_4, N_2, H_2S, Fe^{2+}) are collected at all anoxic depths and one meter above the uppermost anoxic depth (oxic sample).

[3] Measurements performed at Syracuse University; all other parameters will be analyzed at UFI