### **ADDENDUM 3 (2011) TO**

### ONONDAGA LAKE BASELINE MONITORING BOOK 1

### DEEP BASIN WATER AND ZOOPLANKTON MONITORING WORK PLAN FOR 2008

Prepared for:

# Honeywell

301 Plainfield Road, Suite 330 Syracuse, NY 13212

Prepared by:

#### **PARSONS**

301 Plainfield Road, Suite 350 Syracuse, New York 13212

and



420 Lexington Avenue, Suite 1740 New York, NY 10170



### TABLE OF CONTENTS

|   | Page   |
|---|--------|
| LIST OF ACRONYMS  | iii    |
| EXECUTIVE SUMMARY   | ES-1   |
| SECTION 1 INTRODUCTION  | 1-1    |
| 1.1 OBJECTIVES AND DATA USES  | 1-1    |
| 1.2 RATIONALE FOR MODIFYING 2010 WORK SCOPE                               | 1-1    |
| SECTION 2 2011 DEEP BASIN WATER, ZOOPLANKTON AND SEDIMENT TRAP MONITORING | 2-1    |
| 2.1 WATER COLUMN  | 2-1    |
| 2.2 ZOOPLANKTON   | 2-1    |
| 2.3 SEDIMENT TRAPS  | 2-1    |
| 2.4 HEALTH AND SAFETY   | 2-2    |
| 2.5 QUALITY ASSURANCE, DATA MANAGEMENT AND REPORTI                        | NG 2-2 |
| 2.6 REFERENCES  | 2-3    |



#### TABLE OF CONTENTS (CONT.)

#### LIST OF FIGURES

- Figure 1 Volume-Weighted Hypolimnion Average Concentrations of Key Indicators (10 to 19-Meter Water Depths)
- Figure 2 Onondaga Lake Zooplankton Mercury Concentrations: 2008-2010

#### LIST OF TABLES

- Table 1 Onondaga Lake Baseline Monitoring Program Objectives, Program Elements, and Data Uses Pertaining to Baseline Monitoring Book 1
- Table 2 Water Column Sampling Schedule for 2011
- Table 3 Specifications for 2011 Book 1 Baseline Monitoring Laboratory Analytes
- Table 4 Field Sampling Matrices for Laboratory Analyses of 2011 Water Samples
- Table 5 List of ISUS (Water) Parameters
- Table 6 QAPP Worksheet 20 Field Quality Control Sample Summary Table



#### LIST OF ACRONYMS

Chl chlorophyll  $CH_3Hg$  methylmercury

Cl<sup>-</sup> chloride

DOC dissolved organic carbon

DUSR Data Usability and Assessment Report

Fe<sup>2+</sup> ferrous iron

H<sub>2</sub>S hydrogen sulfide

Hg mercury

ISUS in situ ultraviolet spectrophotometer

JSA Job Safety Analysis

NO<sub>x</sub> nitrate+nitrite

NYSDEC New York State Department of Environmental Conservation

QAPP quality assurance project plan SMU Sediment Management Unit

 $S^{2-}$  sulfide

SOP standard operating procedure

SU Syracuse University
TDG total dissolved gas
TIC total inorganic carbon

T-NH<sub>3</sub> total ammonia

UFI Upstate Freshwater Institute

USEPA United States Environmental Protection Agency



#### **EXECUTIVE SUMMARY**

This third addendum to the 2008 Book 1 Work Plan (UFI and SU, 2008) presents the scope for the 2011 deep basin water and zooplankton monitoring that is part of Honeywell's baseline monitoring program for Onondaga Lake prior to lake remediation. The baseline monitoring program objectives and program elements remain unchanged for 2011.

The 2011 Book 1 work scope is the same as the Book 1 work scope for 2010 with two modifications required for the nitrate addition pilot test that will be implemented in 2011 (Parsons and UFI, 2011). These modifications are:

- The addition of surface water and zooplankton monitoring at North Deep from late April through November
- The addition of monthly water sampling and analysis for mercury from deep water at the 10 *in situ* ultraviolet spectroradiometer (ISUS) locations

Analyses will include measurements of low-level total mercury and methylmercury and other baseline parameters (such as nitrate) in the water column; total mercury, methylmercury, total solids content, and community composition for zooplankton; and total mercury and other parameters in sediment trap solids. The rationale for the 2011 Book 1 work scope is presented herein focusing on modifications to the 2010 Book 1 work scope (Parsons and Exponent, 2010).

The field and laboratory work proposed in this addendum will be based on the 2008 Book 1 Standard Operating Procedures (SOPs) and Quality Assurance Project Plan (QAPP). No new SOPs will be implemented during 2010. The only worksheet revised from the QAPP is Worksheet 20 presented as Table 6.



#### **SECTION 1**

#### INTRODUCTION

This third addendum to Honeywell's 2008 Baseline Monitoring Book 1 Work Plan for Onondaga Lake (UFI and SU, 2008) presents the work scope for Honeywell's 2011 deep basin water and zooplankton monitoring effort. This work scope is consistent with the baseline monitoring program objectives, program elements, and data uses, and the work scope has been developed in part based on results from the 2008, 2009, and 2010 Book 1 work efforts. Rationale for modifying the 2010 work scope (Parsons and Exponent, 2010) is also presented. Sampling and analysis work proposed in this Book 1 Work Plan Addendum for 2011 will use the existing, approved Book 1 SOPs and QAPP.

#### 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 2008-2010 and will be addressed during 2011 by the work described in this addendum. The objectives, elements, and data uses described in this work plan are the same as those described previously.

#### 1.2 RATIONALE FOR MODIFYING 2010 WORK SCOPE

Deep basin conditions were very similar from 2007 through 2010 as summarized in Figure 1. This 2011 work plan addendum includes two modifications to the 2010 Book 1 work scope that are required for the nitrate addition pilot test (Parsons and UFI, 2011). These two modifications for 2011 and their rationale are as follows:

#### • Surface water and zooplankton sampling at the North Deep location

During 2011, surface water and zooplankton sampling will be conducted at the North Deep location at the same frequency as conducted during 2010 and planned for 2011 at the South Deep location. This additional work at North Deep is based on 2011 being the first year of the nitrate addition pilot test in the profundal zone of Onondaga Lake. Zooplankton samples will again be collected weekly beginning in mid-September based largely on zooplankton mercury levels measured in samples collected during early October 2009 and to a lesser extent on zooplankton mercury levels measured during September 2010 (see Figure 2). The total number of zooplankton sampling efforts cannot be determined at this time, because the timing of fall turnover cannot be predicted.

### Surface water analyses for mercury monthly from deep water at the 10 ISUS locations

This additional work is also based on 2011 being the first year of the nitrate addition pilot test in the profundal zone of Onondaga Lake. Total mercury and

# ONONDAGA LAKE BASELINE MONITORING BOOK 1 DEEP BASIN WATER AND ZOOPLANKTON MONITORING WORK PLAN ADDENDUM 3 (2011)



methylmercury will be measured approximately 1 meter above the lake bottom at each of the 10 ISUS locations monthly as a comparison to nitrate concentrations measured as part of the pilot test work. Analyses of these samples are being accounted for as part of the nitrate addition pilot test.



#### **SECTION 2**

## 2011 DEEP BASIN WATER, ZOOPLANKTON AND SEDIMENT TRAP MONITORING

The components of the 2011 deep basin water column, zooplankton, and sediment trap monitoring program are briefly described below.

#### 2.1 WATER COLUMN

Water column samples will be collected at South Deep and at North Deep at the depths and frequencies specified in Table 2. Deep water samples will be collected monthly from June through October at a water depth in the lower hypolimnion near the sediment-water interface at each of 10 ISUS locations for analysis of total mercury and methylmercury. (Details are provided in the work plan for the nitrate addition pilot test.) Analytes will be the same as during 2008 - 2010 (see Table 3). Profiles of total dissolved gas (TDG) pressure will be observed monthly. Spatially detailed monitoring with ISUS rapid profiling instrument will be conducted weekly consistent with the 2008 Book 1 Work Plan. The field sampling matrices for laboratory analyses of water samples are shown in Table 4. The ISUS parameters and methods are provided in Table 5.

As during 2008, 2009, and 2010, *in situ* robotic measurements (dissolved oxygen, temperature, specific conductance, pH, fluorometric chlorophyll, and turbidity) will be made during 2011 at 1-meter depth interval profiles at South Deep, at least daily during the April-November interval; however, these data will not be presented formally as part of the Honeywell monitoring program. Instead, the robotic data will again be available online at www.ourlake.org.

#### 2.2 ZOOPLANKTON

Zooplankton samples will be collected at South Deep and at North Deep in a manner consistent with the zooplankton collections conducted from 2008 through 2010. Zooplankton samples will be enumerated by species and analyzed for total mercury, methylmercury, and percent solids (see Table 3).

If present, *Daphnia* samples will be collected, freeze-dried, digested, and analyzed for total mercury and methylmercury from zooplankton tows conducted on up to 10 different dates. Mercury analyses of *Daphnia* will be performed using low-level United States Environmental Protection Agency (USEPA) methods. Freeze-drying will permit analysis of very low sample masses.

#### 2.3 SEDIMENT TRAPS

Sediment trap sampling and analysis provide data to assess gross sedimentation of solids and total mercury during the field sampling season timeframe. Sediment traps were set at South Deep and collected and analyzed for solids content and for mercury during 1992, 2009, and 2010.

# ONONDAGA LAKE BASELINE MONITORING BOOK 1 DEEP BASIN WATER AND ZOOPLANKTON MONITORING WORK PLAN ADDENDUM 3 (2011)



Sediment trap mercury results were generally lower in 2010 than in 2009. The average 2009 and 2010 mercury concentrations in sediment trap solids were 1.7 and 1.0 milligrams per kilogram, respectively.

Sediment trap samples will be collected again during 2011 at South Deep consistent with the 2009 and 2010 monitoring efforts and Upstate Freshwater Institute's (UFI) sediment trap design and deployment protocols. A set of three traps will be deployed weekly from April to October 2011 at the South Deep sampling site below the thermocline (10-meter water depth). Sediment traps will generally be deployed for seven-day intervals. After retrieval, supernatant will be drained off via a stoppered opening located in the side of the traps well above the deposited sediments. The samples will then be homogenized, poured into polyethylene bottles, and put on ice.

Laboratory analyses of sediment trap samples will be consistent with 2009 efforts. Analytes will include total suspended solids, fixed and volatile suspended solids, particulate carbon, total and acidified calcium, and total mercury. One trap from each date when zooplankton will be sampled will be analyzed for total mercury and samples from the remaining two traps on those dates will be archived for potential future analyses.

#### 2.4 HEALTH AND SAFETY

Maintaining health and safety is the highest priority for the Book 1 work efforts. 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 QUALITY ASSURANCE, DATA MANAGEMENT AND REPORTING

Various field and laboratory duplicate and blank samples will be collected and analyzed in accordance with the previously-approved quality assurance project plan for Book 1 work. The extent of field and matrix duplicate and blank sample collection and analysis is summarized in Table 6.

Preliminary, unvalidated data will be submitted to New York State Department of Environmental Conservation (NYSDEC) by late summer prior to data validation, 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 percent of the nitrate, total mercury, and methylmercury results will be validated based on Level IV protocols. Parsons will incorporate the validated results into the Locus Focus database.

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

**PARSONS** 

# ONONDAGA LAKE BASELINE MONITORING BOOK 1 DEEP BASIN WATER AND ZOOPLANKTON MONITORING WORK PLAN ADDENDUM 3 (2011)



validation and data usability assessment. Data interpretation and trend analysis will also be presented to NYSDEC.

#### 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 and Exponent, 2010. Addendum 2 (2010) to Onondaga Lake Baseline Monitoring Book 1 Deep Basin Water and Zooplankton Monitoring Work Plan for 2008. Prepared for Honeywell. April 2010.
- Parsons, Exponent and Anchor QEA, 2010. Baseline Monitoring Scoping Document for the Onondaga Lake Bottom Subsite. Prepared for Honeywell. July 2010.
- Parsons and UFI, 2011. Work Plan for Pilot Test to Add Nitrate to the Hypolimnion of Onondaga Lake. Prepared for Honeywell. Anticipated to be finalized March 2011.
- 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. Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Center for Environmental Systems Engineering, Syracuse, NY.
- UFI and SU, 2008. Onondaga Lake Baseline Monitoring Book 1 Deep Basin Water and Zooplankton Monitoring Work Plan for 2008. Prepared for Honeywell. Upstate Freshwater Institute and Syracuse University, Syracuse, NY. May 2008.
- UFI and SU, 2009. Addendum 1 (2009) to Onondaga Lake Baseline Monitoring Book 1 Deep Basin Water and Zooplankton Monitoring Work Plan for 2008. Prepared for Honeywell. Upstate Freshwater Institute and Syracuse University, Syracuse, NY. September 2009.

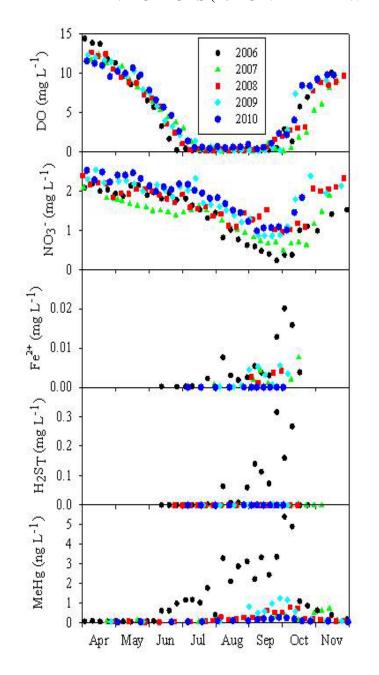




### **FIGURES**



#### FIGURE 1 VOLUME-WEIGHTED HYPOLIMNION AVERAGE CONCENTRATIONS OF KEY INDICATORS (10 TO 19-METER WATER DEPTHS)



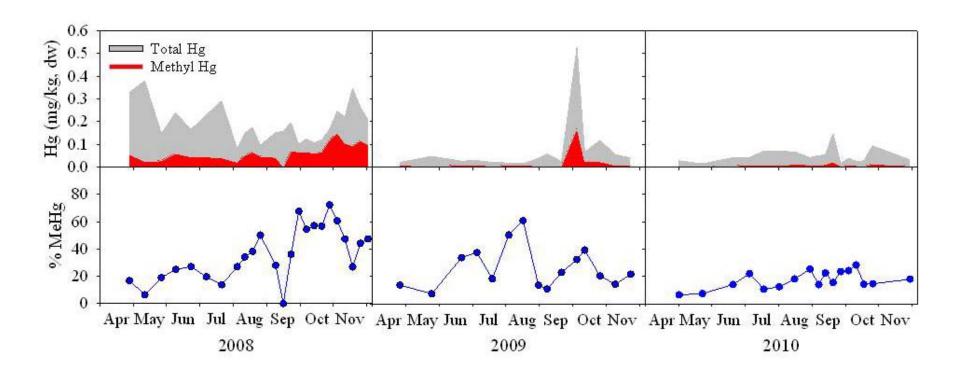
#### Notes:

DO – dissolved oxygen in milligrams per liter NO<sub>s</sub>\* – nitrate (as nitrogen) in milligrams per liter FE<sup>2+</sup> - ferrous iron in milligrams per liter H<sub>2</sub>S<sub>T</sub> – hydrogen sulfide in milligrams per liter MeHg – methylmercury in nanograms per liter

One nanogram is 0.000001 milligram.



## FIGURE 2 ONONDAGA LAKE ZOOPLANKTON MERCURY CONCENTRATIONS: 2008-2010





### **TABLES**

#### TABLE 1

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

| Program  | Program              |   |   | Book 1 Addendum 3   |  |
|--|----------------------|---|---|---|--|
| Objective  | Element              | Data Use  | Book 1 to Date  | (2011)  | Comments   |
|  |                      | Baseline for Remedy Effective   | ctiveness   |   |  |
| nditions   |                      | Provide basis to measure<br>achievement of PRG3<br>(surface water quality<br>standards)   | Book 1 includes 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 2010.   | Additional CPOIs will be monitored in 2011 at South Deep, at nearshore locations where exceedances were previously noted, and/or near source areas. This work will be done in conjunction with monitoring by Honeywell's Operations design work as a continuation of work initiated in October 2010. |
| Establish baseline chemical and physical conditions  | Lake Water Sampling  | Provide basis to measure success in controlling key processes (e.g., mercury methylation, sediment resuspension from the inlake waste deposit, mercury release from profundal sediment) | Book 1 includes 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. | More extensive water column sampling overall than in 2010 based on 2011 being the first year of the nitrate addition pilot test. Sediment trap samples will be collected and analyzed again during 2011 to track changes in solids and mercury loading to profundal sediment. | Water column monitoring at South Deep has been conducted annually for Honeywell since 2007.  |
| blis   |                      |   |   |   |  |
| Esta   |                      | Baseline for Remedy Desi<br>Provide information for<br>design of nitrate<br>addition/oxygenation pilot<br>tests and basis to measure<br>results   | Book 1 includes 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.  | Attempts will be made aagin during 2011 to collect Daphnia. Water Column monitoring at North Deep to be added for 2011 based on 2011 being the first year of the nitrate pilot test.  | Results will be used to assist in evaluation of results from the nitrate pilot test.   |
| ssa  |                      | Descline for Describe Dec   | -4i   |   |  |
| Provide additional data for future<br>understanding of remedy effectiveness<br>in achieving PRGs | Other biota sampling | Baseline for Remedy Effet<br>Assess biological factors<br>that may contribute to<br>variability in fish mercury<br>concentrations   | Book 1 includes analysis of total mercury and methyl mercury in zooplankton including Daphnia, as well as an assessment of zooplankton community composition.   | No change for South Deep. Zooplankton collection and analysis to be added at North Deep based on 2011 being the first year of the nitrate pilot test.   | Zooplankton monitoring has been conducted annually since 2008.   |



## TABLE 2 WATER COLUMN SAMPLING SCHEDULE FOR 2011

| Month     |           | Water Column              |                       |  |  |  |  |  |  |  |  |
|-----------|-----------|---------------------------|-----------------------|--|--|--|--|--|--|--|--|
|           | Frequency | Sampling Date             | South Deep Depths (m) |  |  |  |  |  |  |  |  |
| May       | once      | 5/23                      | 2, 12, 18             |  |  |  |  |  |  |  |  |
| June      | twice     | 6/6, 6/20                 | 2, 12, 18             |  |  |  |  |  |  |  |  |
| July      | bi-weekly | 7/5, 7/18                 | 2, 12, 16, 18         |  |  |  |  |  |  |  |  |
| August    | bi-weekly | 8/1, 8/15, 8/29           | 2, 12, 16, 18         |  |  |  |  |  |  |  |  |
| September | weekly    | 9/6, 9/12, 9/19, 9/26     | 2, 12, 14, 16, 18     |  |  |  |  |  |  |  |  |
| October   | weekly    | 10/3, 10/10, 10/17, 10/24 | 2, 12, 14, 16, 18     |  |  |  |  |  |  |  |  |
| November  | bi-weekly | 11/7, 11/21               | 2, 12, 18             |  |  |  |  |  |  |  |  |

**Note**: This sampling schedule is based on the lake being stratified from early July until the third week of October. If the timing for stratification is significantly different during 2011 (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 2011 BOOK 1 BASELINE MONITORING LABORATORY ANALYTES

| Parameter              | Method                | South Deep Depths (m) and Dates  | Total Number of Field Samples for 2011 <sup>x</sup> baseline monitoring |
|------------------------|-----------------------|--|---|
| <sup>®</sup> Chl       | EPA 445               | 2,12 (see Table 2 for dates)   | 36  |
| $NO_X$                 | EPA 353.2             | Applies to the South Deep and North Deep locations. See Table 2 for April-June and after the week of October 17. Additional samples will be collected (see Table 4 in the work plan for the nitrate addition pilot test).  | 40  |
| NO <sub>2</sub>        | EPA 353.2             | Applies to the South Deep and North Deep locations. See Table 2 for April-June and after the week of October 17. Additional samples will be collected (see Table 4 in the work plan for the nitrate addition pilot test).  | 40  |
| T-NH <sub>3</sub>      | EPA 350.1             | Applies to the South Deep and North Deep locations. See Table 2 for April-June and after the week of October 17. (see Table 4 in the work plan for the nitrate addition pilot test).   | 40  |
| DOC                    | SM 18-20<br>5310C     | See Table 2  | 75  |
| TIC                    | SM 18-20<br>5310C     | See Table 2  | 75  |
| Cl <sup>-</sup>        | SM 18-20<br>4500 Cl C | See Table 2  | 75  |
| <sup>+*</sup> Total Hg | EPA 1631E             | Applies to the South Deep and North Deep locations. See Table 2 for April-June and after the week of October 17. Other samples will be collected weekly from June 27 through October 17 and monthly from the 10 ISUS locations (see Table 4 in the work plan for the nitrate addition pilot test). | 40  |



# TABLE 3 (CONTINUED) SPECIFICATIONS FOR 2011 BASELINE MONITORING LABORATORY ANALYTES

| Parameter  | Method                                 | South Deep Depths (m) and Dates  | Total Number<br>of Field Samples<br>for 2010 <sup>x</sup>  |
|--|--|--|--|
| **Total Hg, dissolved  | EPA 1631E                              | 2 stations, 2 meter water depth once in April, May, June, bi-weekly thereafter plus the 14 meter water depth biweekly 9/12 to 11/7   | 36   |
| +*CH₃Hg  | EPA 1630                               | Applies to the South Deep and North Deep locations. See Table 2 for April-June and after the week of October 17. Other dates are weekly from June 27 through October 17 and monthly from 10 ISUS locations (see Table 4 in the work plan for the nitrate addition pilot test). | 40   |
| *H <sub>2</sub> S method 1   | SM 18-20<br>4500 S <sup>2-</sup> E     | Anoxic water depths at 1-meter intervals (mid-July through Fall turnover)  | 70   |
| °method 2  | SM 18-20<br>4500 S <sup>2-</sup> G     | See Table 4 in the work plan for the nitrate pilot test.   | 0  |
| Ferrous iron (Fe <sup>2+</sup> )   | Heaney and<br>Davison<br>(1977)        | See Table 4 in the work plan for the nitrate addition pilot test.  | 0  |
| Methane (CH <sub>4</sub> )   | Addess (1990)                          | anoxic depths: 12, 16, and 18 meter water depths (mid-July to mid-November)  | 42   |
| Zooplankton: Total Hg, CH <sub>3</sub> Hg, percent solids, and taxonomic enumeration | EPA Methods<br>1630 and 1631<br>for Hg | Vertical tows at 13-meter water depth once in April, May, June, bi-weekly from July to mid-September, weekly mid-September until turnover, and then biweekly through November  | 18 each at South Deep and North Deep (plus up to 10 daphnia zooplankton samples from South Deep) |



## TABLE 3 (CONTINUED) SPECIFICATIONS FOR 2011 BASELINE MONITORING LABORATORY ANALYTES

| Parameter  | Method   | South Deep Depths (m) and Dates  | Total Number<br>of Field Samples<br>for 2010x |
|--|--|--|---|
| Sediment Traps: total<br>suspended solids,<br>fixed and volatile<br>solids, particulate<br>carbon, total and<br>acidified calcium,<br>and total Hg | EPA methods<br>for Hg; see<br>Table 6 for<br>other<br>parameters | Up to 30 weekly trap deployments from April through November. Frequency for Hg analyses will be the same as for zooplankton. | 18 for mercury<br>and 90 for others           |

#### Note:

Analyses of water specified in the work plan for the nitrate pilot test (Parsons and UFI, 2011 – see Table 4) are not included here; those analyses include weekly sampling while nitrate is to be applied. The timing of nitrate application is assumed to be the week of June 20 through the week of October 17 (18 weeks).

#### Footnotes:

- <sup>®</sup> 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 data.
- Field samples only. See QAPP Worksheet #20 (Table 6) 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.
- <sup>+</sup> Total mercury and methyl mercury analysis of water and zooplankton will be performed by a qualified laboratory contracted by Honeywell. In addition, a laboratory to be selected will freeze dry and analyze Daphnia samples for total mercury and methyl mercury. All other water analyses and zooplankton enumeration will be performed by UFI.
- Total number of field samples will depend on the time of year and extent of anoxic conditions in the Sediment Management Unit (SMU 8) hypolimnion. The estimated number of samples assumes five 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 2011 WATER SAMPLES<sup>1</sup>

#### April, May, June, and after turnover 2011

| Sampling<br>Depth | Chl | NO <sub>x</sub> | NO <sub>2</sub> | T-NH <sub>3</sub> | TIC | DOC | Cl  | Total Hg | CH <sub>3</sub> Hg |
|-------------------|-----|-----------------|-----------------|-------------------|-----|-----|-----|----------|--------------------|
| 2m                | XXX | XXX             | XXX             | XXX               | XXX | XXX | XXX | XX       | XX                 |
| 12m               | Х   | Х               | Х               | Х                 | Х   | Х   | Х   | Х        | Х                  |
| 18m               |     | Х               | Х               | Х                 | Х   | Х   | Х   | Х        | Х                  |

#### July - August 2011

| Sampling<br>Depth | Chl | NO <sub>X</sub> | NO <sub>2</sub> | T-NH <sub>3</sub> | TIC | DOC | CI <sup>-</sup> | $^{2}$ H <sub>2</sub> S | Fe <sup>2+</sup> | CH <sub>4</sub> | Total Hg | CH <sub>3</sub> Hg |
|-------------------|-----|-----------------|-----------------|-------------------|-----|-----|-----------------|-------------------------|------------------|-----------------|----------|--------------------|
| 2m                | xxx | XXX             | XXX             | XXX               | xxx | XXX | XXX             |                         |                  |                 | xx       | XX                 |
| 12m               | Х   | Х               | Х               | Х                 | Х   | Х   | Х               | anoxic depths           | Х                | Х               | Х        | Х                  |
| 16m               |     | Х               | Х               | Х                 | Х   | Х   | Х               | anoxic depths           | Х                | Х               | Х        | Х                  |
| 18m               |     | Х               | Х               | Х                 | Х   | Х   | Х               | anoxic depths           | XXX              | XXX             | Х        | Х                  |

#### September – turnover 2011

| Sampling<br>Depth | Chl | NO <sub>X</sub> | NO <sub>2</sub> | T-NH <sub>3</sub> | TIC | DOC | CI. | $^{2}$ H <sub>2</sub> S | Fe <sup>2+</sup> | CH <sub>4</sub> | Total Hg | CH <sub>3</sub> Hg |
|-------------------|-----|-----------------|-----------------|-------------------|-----|-----|-----|-------------------------|------------------|-----------------|----------|--------------------|
| 2m                | XXX | XXX             | XXX             | XXX               | XXX | XXX | XXX |                         |                  |                 | XX       | XX                 |
| 12m               | Х   | Х               | Х               | Х                 | Х   | Х   | Х   | anoxic depths           | Х                | Х               | Х        | Х                  |
| 14m               |     | Х               | Х               | X                 | Х   | Х   | Х   | anoxic depths           |                  |                 | X        | X                  |
| 16m               |     | X               | Х               | X                 | Х   | Х   | Х   | anoxic depths           | X                | X               | Х        | X                  |
| 18m               |     | Х               | Х               | Х                 | Х   | Х   | Х   | anoxic depths           | XXX              | XXX             | Х        | Х                  |

#### **NOTES:**

- **X** Represents one field sample. XX and XXX represent duplicate and triplicate field samples, respectively.
- South Deep and North Deep will be sampled on a total of approximately 18 occasions as specified in
- H<sub>2</sub>S samples will be collected at all anoxic depths and one meter above the uppermost anoxic depth (oxic sample).



#### **TABLE 5**

### LIST OF ISUS (WATER) PARAMETERS

| Parameter                            | Sensor <sup>x</sup> | Performance<br>Accuracy/Resolution    | Attribute/Value                              |
|--------------------------------------|---------------------|---------------------------------------|--|
| +NO <sub>3</sub> -                   | Satlantic ISUS V2   | $0.5  \mu\mathrm{M}  (\mathrm{dl}^7)$ | status, preferred electron acceptor          |
| <sup>+</sup> HS <sup>-</sup>         | Satlantic ISUS V2   |                                       | redox constituent, SO <sub>4</sub> reduction |
| $T^1$                                | SBE 3F              | ± 0.002 °C/0.0003 °C                  | Stratification                               |
| $SC^2$                               | SBE4                | ± 3 μS/cm/0.1 μS/cm                   | tracer/stratification                        |
| <b>c</b> <sub>660</sub> <sup>3</sup> | Wetlabs C-Star      | ± 0.1% transmission                   | particle indicator                           |
| OBS <sup>4</sup>                     | D&A OBS-3           | ± 0.25 NTU/0.1 NTU                    | particle indicator                           |
| Chl <sub>f</sub> <sup>5</sup>        | Wetlabs WETstar     | ± NA/0.1 μg/L Chl                     | vertical pattern of phyto                    |
| PAR <sup>6</sup>                     | Li-Cor LI-193       | ± 5% reading                          | light penetration                            |

x factory calibrated annually, maintained according to manufacturers instructions

<sup>&</sup>lt;sup>+</sup> as described in Johnson and Coletti (2002)

<sup>&</sup>lt;sup>1</sup> temperature

<sup>&</sup>lt;sup>2</sup> specific conductance

<sup>&</sup>lt;sup>3</sup> beam attenuation coefficient at 660 nm

<sup>&</sup>lt;sup>4</sup> optical backscattering

<sup>&</sup>lt;sup>5</sup> chlorophyll fluorescence

<sup>&</sup>lt;sup>6</sup> photosynthetically active irradiance

<sup>&</sup>lt;sup>7</sup> detection limit



## TABLE 6 QAPP WORKSHEET 20 – FIELD QUALITY CONTROL SAMPLE SUMMARY TABLE FOR 2011 BASELINE MONITORING

| Matrix | Analytical Group  | Concentration Level | Analytical and Preparation SOP Reference <sup>1</sup> | No. of Sampling<br>Locations <sup>2</sup>                   | No. of Field<br>Duplicate<br>Pairs                | Inorganic  No. of  MS <sup>3</sup> | No. of<br>Field<br>Blanks <sup>4</sup> | No. of<br>Equip.<br>Blanks | No. of PT<br>Samples | Total No.<br>of<br>Samples<br>to Lab |
|--------|---|---------------------|---|---|---|------------------------------------|--|----------------------------|----------------------|--------------------------------------|
| Water  | Chlorophyll   | Low                 | L-8   | 1 station, 2 depths, 19<br>sampling trips (38<br>samples)   | One<br>Triplicate set<br>per trip (38<br>samples) |                                    | 8                                      |                            |                      | 84                                   |
| Water  | Nitrate/Nitrite as N<br>(NO <sub>x</sub> )                | Low                 | L-2   | 2 stations, 3–5<br>depths, 6 sampling<br>trips (40 samples) | One<br>Triplicate set<br>per trip (12<br>samples) |                                    | 3                                      |                            |                      | 55                                   |
| Water  | Nitrate as N<br>(NO <sub>2</sub> )                        | Low                 | L-2   | 2 stations, 3–5<br>depths, 6 sampling<br>trips (40 samples) | One<br>Triplicate set<br>per trip (12<br>samples) |                                    | 3                                      |                            |                      | 55                                   |
| Water  | Ammonia as N<br>(T-NH <sub>3</sub> )                      | Low                 | L-3   | 2 stations, 3–5<br>depths, 6 sampling<br>trips (40 samples) | One<br>Triplicate set<br>per trip (12<br>samples) |                                    | 3                                      |                            |                      | 55                                   |
| Water  | Organic Carbon,<br>Total/Total<br>Dissolved as C<br>(DOC) | Low                 | L-4   | 1 station, 3–5 depths,<br>19 sampling trips (82<br>samples) | One<br>Triplicate set<br>per trip (38<br>samples) |                                    | 8                                      |                            |                      | 128                                  |
| Water  | Carbon, Inorganic<br>Dissolved and<br>Total (TIC)         | Low                 | L-7   | 1 station, 3–5 depths,<br>19 sampling trips (82<br>samples) | One<br>Triplicate set<br>per trip (38<br>samples) |                                    | 8                                      |                            |                      | 128                                  |



## TABLE 6 (CONTINUED) QAPP WORKSHEET 20 – FIELD QUALITY CONTROL SAMPLE SUMMARY TABLE

| Matrix | Analytical Group           | Concentration Level | Analytical and<br>Preparation<br>SOP Reference <sup>1</sup> | No. of Sampling<br>Locations <sup>2</sup>                      | No. of Field<br>Duplicate<br>Pairs                | Inorganic<br>No. of<br>MS <sup>3</sup> | No. of<br>Field<br>Blanks <sup>4</sup> | No. of<br>Equip.<br>Blanks | No. of PT<br>Samples | Total No.<br>of<br>Samples<br>to Lab |
|--------|----------------------------|---------------------|---|--|---|--|--|----------------------------|----------------------|--------------------------------------|
| Water  | Chloride                   | Low                 | L-1   | 1 station, 3–5 depths,<br>19 sampling trips (82<br>samples)    | One<br>Triplicate set<br>per trip (38<br>samples) |  | 8                                      |                            |                      | 128                                  |
| Water  | Ferrous iron               | Low                 | L-10  | None   | •   |  |  |                            |                      | None <sup>5</sup>                    |
| Water  | Dissolved methane          | Low                 | L-9   | 1 stations, 3 depths,<br>14 sampling trips (42<br>samples)     | One<br>Triplicate set<br>per trip<br>(28 samples) |  | 5                                      |                            |                      | 75                                   |
| Water  | Sulfide as S<br>(Method 2) | Low                 | L-6   | None   |   |  |  |                            |                      | None <sup>5</sup>                    |
| Water  | Total mercury              | Low                 | L-11  | 2 stations, 3 to 5<br>depths, 6 sampling<br>trips (40 samples) | 4   |  | 3                                      | 3                          |                      | 50                                   |
| Water  | Filtered mercury           | Low                 | L-11  | 2 stations, 1-2 depths,<br>14 sampling trips (38<br>samples)   | 8   |  | 4                                      | 2                          |                      | 52                                   |
| Water  | Methyl mercury             | Low                 | L-12  | Same as for total mercury(40 samples)                          | 4   |  | 3                                      | 3                          |                      | 50                                   |



### TABLE 6 (CONTINUED) QAPP WORKSHEET 20 – FIELD QUALITY CONTROL SAMPLE SUMMARY TABLE

| Matrix                                    | Analytical Group           | Concentration<br>Level | Analytical and<br>Preparation<br>SOP Reference <sup>1</sup> | No. of Sampling<br>Locations <sup>2</sup> | No. of Field<br>Duplicate<br>Pairs | Inorganic<br>No. of<br>MS <sup>3</sup> | No. of<br>Field<br>Blanks <sup>4</sup> | No. of<br>Equip.<br>Blanks | No. of PT<br>Samples | Total No.<br>of<br>Samples<br>to Lab |
|---|----------------------------|------------------------|---|---|------------------------------------|--|--|----------------------------|----------------------|--------------------------------------|
| Zooplankton                               | Total and methyl           | Low                    | L-12, L-13  | 2 stations, 19                            | 4                                  |  |  |                            |                      | 42                                   |
| assemblages                               | mercury and percent solids |                        |   | sampling trips (38 samples) <sup>6</sup>  |                                    |  |  |                            |                      |                                      |
| Sediment<br>slurry from<br>sediment traps | Total mercury              | Low                    | LB-1  | 1 station, 1 trap, 19 sampling trips      | 5                                  |  |  |                            |                      | 24                                   |
| Sediment                                  | Total, fixed, and          | Average                | L-20  | 1 station, triplicate                     |                                    |  |  |                            |                      | 90                                   |
| slurry from                               | volatile suspended         |                        |   | traps, 30 sampling                        |                                    |  |  |                            |                      |                                      |
| sediment traps                            | solids                     |                        |   | trips                                     |                                    |  |  |                            |                      |                                      |
| Sediment                                  | Particulate                | Average                | L-21  | 1 station, triplicate                     |                                    |  |  |                            |                      | 90                                   |
| slurry from                               | inorganic carbon           |                        |   | traps, 30 sampling                        |                                    |  |  |                            |                      |                                      |
| sediment traps                            |                            |                        |   | trips                                     |                                    |  |  |                            |                      |                                      |
| Sediment                                  | Total and acidified        | Average                | L-22  | 1 station, triplicate                     |                                    |  |  |                            |                      | 90                                   |
| slurry from                               | calcium                    |                        |   | traps, 30 sampling                        |                                    |  |  |                            |                      |                                      |
| sediment traps                            |                            |                        |   | trips                                     |                                    |  |  |                            |                      |                                      |

- See Worksheet 23 in the Book 1 Work Plan for 2008 (UFI and SU, 2008).
- Samples collected at different depths at the same location are counted separately.
- Matrix spike and matrix spike duplicate samples will be prepared by the laboratory at a frequency of at least one pair per 20 samples.
- 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 analyses. A field blank for total mercury and methylmercury 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.
- These samples and additional samples to be collected during other sampling trips during 2011 for analyses of nitrate/nitrite, nitrate, ammonia, mercury and methylmercury are not accounted for here, because they will be collected as part of the work associated with the nitrate pilot test (Parsons and UFI, 2011).
- In addition, analyses of up to 10 daphnia zooplankton samples will be conducted.