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September 10, 2014

Mr. Timothy J. Larson New York State Department of Environmental Conservation Division of Environmental Remediation Remedial Bureau D 625 Broadway, 12<sup>th</sup> Floor Albany, NY 12233-7016

#### RE: Operations and Monitoring Plan for Adding Nitrate Full Scale to the Hypolimnion of Onondaga Lake August 2014

Dear Mr. Larson:

Enclosed you will find one bound copy, and three electronic versions (PDF & original) of the Operations and Monitoring Plan for Adding Nitrate Full Scale to the Hypolimnion of Onondaga Lake, dated August 2014. We are distributing per your instructions.

Please feel free to contact Dave Babcock at 315-451-9560 or me if you have any questions.

Sincerely,

John F. Muduliffe

John P. McAuliffe, P.E. Program Director, Syracuse

#### Enclosure

cc: Harry Warner, NYSDEC (1 bound, 1 PDF) Bob Nunes, USEPA (1 bound, 3 PDF) Mike Spera, AECOM (1 bound, 1 PDF) Bob Montione, AECOM (1 bound, 1 PDF) Mark Sergott, NYSDOH (1 PDF) Justin Deming, NYSDOH (Cover Ltr Only) Kenneth Lynch, NYSDEC (1 bound) Tara Blum, NYSDEC (1 bound, 1 PDF) Norman Spiegel, Env. Protection Bureau (Cover Ltr Only) Andrew Gershon, Env. Protection Bureau (Cover Ltr Only) Margaret Sheen, Esq., NYSDEC (Cover Ltr Only) Argie Cirillo, Esq., USEPA (Cover Ltr Only) Joseph Heath, Esq., (ec Cover Ltr Only) Thane Joyal, Esq. (1 PDF) Curtis Waterman, Onondaga Nation (1 PDF) Alma Lowry, Onondaga Nation (1 PDF)

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# OPERATIONS AND MONITORING PLAN FOR ADDING NITRATE FULL SCALE TO THE HYPOLIMNION OF ONONDAGA LAKE

Prepared For:



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and



# **AUGUST 2014**

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## LIST OF ACRONYMS

EDD	electronic data deliverable
GPS	global positioning system
ISUS	in situ ultraviolet spectrophotometer
Metro	Metropolitan Syracuse Wastewater Treatment Plant
	(discharge of treated municipal and other pre-treated wastewater into the south [upstream] end of Onondaga Lake)
mg/L	milligrams per liter
NYSDEC	New York State Department of Environmental Conservation
SMU 8	sediment management unit 8
SOP	standard operating procedure
SU	Syracuse University
SUNA	submersible ultraviolet nitrate analyzer
UFI	Upstate Freshwater Institute (based in Syracuse, NY)
USEPA	United States Environmental Protection Agency

# **GLOSSARY OF TERMS**

**Deep Water** (**Profundal**) – Offshore zone within a water body where water depths are greater than the depth to which sunlight can penetrate to support aquatic plants, in contrast with the littoral zone closer to shore. In Onondaga Lake, the profundal zone thermally stratifies typically from May to October, and water depths exceed 30 ft. The profundal zone of Onondaga Lake occupies two-thirds of the lake's surface area.

**Epilimnion** - The upper portion of the water column during summer stratification where water temperatures are warmer than lower waters (typically in the portion of Onondaga Lake where water depths exceed 30 ft [9 meters]). Epilimnion waters are warmer than the underlying hypolimnion layers and mixed wind, waves and tributary inflows.

**Hypolimnion** - The lower portion of the water column during summer stratification where water temperatures are cooler than upper waters (typically in the portion of Onondaga Lake where water depths exceed 30 ft [9 meters]). There is less mixing of hypolimnion waters than takes place in epilimnion waters.

**Methylmercury** - An organic form of mercury that can be created from inorganic mercury by bacteria in sediments and water. Methylmercury is a potential neurotoxin and the form of mercury that can most easily bioaccumulate in organisms.

**SMU 8** – Sediment in the deep water portion of Onondaga Lake where nitrate is to be applied annually from late June or early July until early October.

### OPERATIONS AND MONITORING PLAN FOR ADDING NITRATE TO THE HYPOLIMNION OF ONONDAGA LAKE

#### **EXECUTIVE SUMMARY**

This plan describes operations and monitoring for adding liquid calcium nitrate long term as warranted to the Onondaga Lake hypolimnion (where water depths exceed 30 ft [9 meters]). This work follows the successful three-year nitrate addition pilot test completed in 2013 (Parsons and Upstate Freshwater Institute [UFI], 2014b). The pilot test demonstrated that nitrate addition could be implemented in a way that maintained target concentrations of nitrate, did not interfere with normal usage of the lake, and was sufficiently flexible to address changing lake conditions. The objective for adding nitrate both during the three-year pilot test and over the long-term is to maintain nitrate concentrations in the hypolimnion of Onondaga Lake at levels sufficient to inhibit release of methylmercury from lake sediment to the overlying waters. Methylmercury in surface water bioaccumulates in fish and can potentially pose a risk to wildlife and humans who consume fish.

Beginning in 2014, a full-scale, barge-based system will be used to add liquid nitrate to the hypolimnion. Nitrate additions will be conducted on approximately 20 to 40 non-consecutive days during summer and fall. Nitrate additions will typically start in late June or early July before nitrate-nitrogen concentrations drop below 1.0 milligram per liter (mg/L) at the 60-foot water depth. They will typically continue until early October, a few weeks prior to the fall turnover in the lake. Nitrate will be applied continuously over three to six hours in a single day at one predetermined location. The location for each application will be selected from three predetermined locations based on the most recent available lake monitoring results. The applied nitrate and related water quality parameters will be monitored one to two days each week throughout the deep water portion of the lake while nitrate is being applied. Monitoring results will be reported to the agencies on an annual basis.

#### **1.0 BACKGROUND**

The option to add nitrate to the deep waters of Onondaga Lake was first proposed by researchers at Syracuse University (SU) and Upstate Freshwater Institute (UFI) and was subsequently required as a pilot study in the Statement of Work attached to the Consent Decree between the State of New York and Honeywell (United States District Court, Northern District of New York, 2007). The remedy for the deep waters of Onondaga Lake originally included in the Record of Decision for the lake bottom (NYSDEC and USEPA, 2005) called for an oxygenation pilot study. This was replaced by nitrate addition as explained in an Explanation of Significant Differences currently being prepared by New York State Department of Environmental Conservation (NYSDEC) and United States Environmental Protection Agency (USEPA) that includes a Technical Support Document (Parsons and UFI, 2014b).

The nitrate addition pilot test completed in Onondaga Lake on behalf of Honeywell from 2011 through 2013 was very successful (Matthews et al. 2013; Parsons and UFI, 2014a). The pilot test objective of maintaining nitrate at concentrations sufficient to inhibit release of methylmercury from lake sediment was achieved across the entire lower hypolimnion of the lake. The target minimum nitrate-nitrogen concentration during the pilot test was 1.0 mg/L. Adding nitrate resulted in lower methylmercury concentrations in hypolimnion waters during all three years of the pilot test. Adding nitrate also lowered the concentrations of soluble reactive phosphorus in hypolimnion waters over the same period (Parsons and UFI, 2014a). Early season nitrate-nitrogen concentrations in the lake ranged during the pilot test from 2.0 to 2.9 mg/L and the annual duration of summer stratification in the lake ranged from 163 to 184 days. Therefore, the quantity of nitrate-nitrogen applied each year during the pilot test ranged from 63 to 88 metric tons to respond to these variations.

The combination of nitrification treatment of wastewater provided at Metro and nitrate added during the nitrate addition pilot test resulted in very low zooplankton methylmercury concentrations from 2011 through 2013 (Parsons and UFI, 2014b). This in turn has resulted in lower exposure of fish to methylmercury, given that methylmercury accumulates as it moves up the food chain from zooplankton to other aquatic organisms.

Nitrate addition is sufficiently flexible to accommodate even unlikely extreme future scenarios that might result in undesirably low nitrate levels in lake waters during the spring season. For example, less nitrate would be available in the hypolimnion at the start of each annual application period if Metro's treatment of ammonia to nitrate unexpectedly went offline or if the lake did not mix vertically in early spring prior to summer stratification. Sufficient quantities of nitrate could be added to the lake at a more rapid pace if needed to address these conditions.

The extent of nitrate needed in Onondaga Lake during summer months is expected to decline gradually over the coming years. Therefore, the need for continued nitrate addition will be evaluated annually based on the prior year's results, the lake's fluctuating seasonal hydrologic and nitrate inputs, and other factors. Any proposed changes to the nitrate addition program will be documented in the annual reports or as an addendum to this plan for NYSDEC review and approval. Improved phosphorus removal from Metro discharges since 2005 and the resulting decline in primary production in the lake are expected to reduce the demand for oxygen and

nitrate over time. In addition, ongoing natural recovery due to gradual burial of sediment by solids entering the lake as runoff from upstream areas will reduce the mercury concentrations in surface sediments in the deep water portion of the lake (i.e., sediment management unit (SMU 8)).

#### 2.0 BASIS FOR IMPLEMENTATION

The basis of design developed in 2011 for the nitrate addition pilot test (Parsons and UFI, 2011) continues to be suitable for full-scale nitrate addition efforts over at least the next few years.

Results from the three-year nitrate addition pilot test demonstrated that three locations for applying nitrate are sufficient to enable the added nitrate to spread throughout the entire hypolimnion of Onondaga Lake. Figure 1 shows water depths and the three application locations.

Applying nitrate using a self-propelled barge was effective during the pilot test and will therefore continue for full-scale nitrate addition efforts. Figure 2 is a schematic cross section of the barge used for applying nitrate. The nitrate barge is 40 ft long by 24 ft wide and holds two 2,500-gallon nitrate storage tanks, two large dilution water pumps, hosing for transmitting water and nitrate, a shed, a portajon, and a cast-iron manifold to hold in place the flexible hosing that is extended from the barge down into the lower hypolimnion. Hosing on the nitrate barge is used to withdraw epilimnetic lake water for mixing with the calcium nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>) solution and to deliver the diluted nitrate solution to the hypolimnion. Water depths for releasing the diluted nitrate solution are 50 to 60 ft (15 to 18 meters), approximately 3 to 12 ft (1 to 4 meters) above the lake bottom.

Both barge and pipeline application options were reviewed when the basis for adding nitrate was developed. The barge application was selected in large part because of its effectiveness during the three-year nitrate addition pilot test. Using the barge, nitrate can be added most days as planned. Threats from lightening and excessive wave heights in the lake from high winds were avoided without significantly affecting the schedule for barge use throughout the three-year nitrate addition, the barge had no maintenance challenges during the pilot test that could have prevented nitrate from being applied. With barge applications, in-lake infrastructure is minimized and flexibility to move application locations is maximized.

Installation of pipelines from the western shoreline and possible extension of the Metro outfall to the Onondaga Lake hypolimnion were two alternatives to barge applications that were assessed. However, placing and maintaining pipelines along the lake bottom from shore to SMU 8 would require significant underwater construction and maintenance efforts. While the current plan is to apply nitrate using a barge, placement of one or more pipelines along the lake bottom from shore to the application locations remains an option for the future.

To meet the nitrate addition objective, nitrate will be applied annually in Onondaga Lake as needed during approximately 20 to 40 non-consecutive days between late June and early October. The number of daily applications needed annually will depend primarily on lake conditions at the start of lake stratification in mid-to-late May and meteorological conditions late in the fall as fall turnover approaches. During the three-year nitrate addition pilot test, nitrate was applied between 29 and 40 days annually. Demand for nitrate and the need to add nitrate should

decline over time as more controls of inflows to the lake are implemented and as natural recovery of sediment in SMU 8 continues.

Calcium nitrate was selected as the source of nitrate to add to Onondaga Lake because it is a liquid, available, and commonly used as an agricultural fertilizer. Its chemical content and successful applications to date (Parsons and UFI, 2011) also contributed to the decision. The solution of calcium nitrate applied in Onondaga Lake to date has been provided by Yara North America (<u>www.yara.us</u>) (see Table 1 for product information). The nitrate solution to be applied during full-scale nitrate application operations is expected to have the same general properties.

Property	Description
Chemical form	49.8 percent calcium nitrate (Ca(NO <sub>3</sub> ) <sub>2</sub> ) solution by weight including 8.55% nitrate-nitrogen
Other constituents	Common fertilizer ingredients: 0.02% ammonia nitrogen by weight
Specific gravity	1.48 (based on 1.00 for water)
Weight per gallon, pounds	12.3
Salt out temperature, degrees Fahrenheit	35
рН	5.0 to 7.0
Description	Clear, odorless liquid
Storage and handling	Plastic, fiberglass, or stainless steel
Instructions (for avoiding formation of insoluble precipitates)	Do not mix with phosphate or sulfate-containing materials
Trace contaminant concentrations <sup>(1)</sup>	Arsenic: less than 0.25 mg/L Cadmium: less than 2.0 mg/L Cobalt: less than 5.0 mg/L Lead: less than 1.5 mg/L Mercury: less than 0.02 mg/L Molybdenum: less than 2.5 mg/L Nickel: less than 5.0 mg/L Selenium: less than 0.5 mg/L Zinc: less than 3.0 mg/L

#### PROPERTIES OF THE CALCIUM NITRATE SOLUTION APPLIED TO DATE

TABLE 1

(1) Concentrations are in milligrams per liter (mg/L) as obtained from Yara North America, Inc. and (for lead) from a Honeywell contracted laboratory that analyzed a sample of the calcium nitrate solution.

The amount of nitrate to be added during each application will be quantified every week or two during summer months based on the ongoing demand for nitrate in hypolimnion waters. Concentrations of nitrate decline naturally in the hypolimnion after oxygen levels decline naturally following the onset of summer stratification. In the absence of oxygen, nitrate is depleted in Onondaga Lake at an average rate of 0.8 metric tons per day (Parsons and UFI, 2011). Addition of nitrate to the hypolimnion will approximately track the rate at which it's being utilized. The specific gravity of the nitrate solution applied to date in Onondaga Lake is 1.48, which is almost 50 percent higher than the density of water. In order to achieve neutral buoyancy at the target depth, water less dense than hypolimnetic water must be mixed with the calcium nitrate before it is pumped to the lower hypolimnion. Water from shallower depths above the thermocline (i.e., the epilimnion) is warmer and less dense than hypolimnetic waters. The calcium nitrate solution is diluted with epilimnetic lake water at an approximate ratio of 1:250. This results in the density of the diluted calcium nitrate solution being approximately the same as the density of water where the nitrate is directly applied (at the target water depth in the lower hypolimnion). By matching the density of the diluted calcium nitrate solution with the density of lake water in the lower hypolimnion, the calcium nitrate solution remains near the lake bottom and spreads horizontally due to natural hydrodynamic forces. The field crew on the barge will adjust the dilution water flows to maintain the required dilution ratio based on daily field determinations of water temperature and specific conductance (a surrogate measurement for salinity).

Table 2 presents an example determination of nitrate and epilimnetic water flows to add based on the average demand for nitrate of 0.8 metric tons per day. The determination includes a 20 percent safety factor beyond the average daily demand and applies 40 percent of the weekly nitrate over a single day. Flows of dilution water corresponding to a specific flow rate of nitrate solution will be estimated prior to each application based on the most recent available water quality monitoring results. The flows will be adjusted as warranted based on same-day monitoring in the lake.

### TABLE 2

#### DETERMINATIONS OF RATES FOR ADDING CALCIUM NITRATE AND EPILIMNION DILUTION WATER BASED ON AVERAGE DAILY DEMAND

Items	Value	Units	Note
Fraction of calcium nitrate solution that is $Ca(NO_3)_2$	0.486	Dimensionless	Constant based on information from chemical supplier
Density of calcium nitrate solution	1.48	Gram per cubic centimeter	Constant based on information from chemical supplier
Target average daily flow of nitrate as nitrogen based on a seven-day-per week application	0.80	Metric tons per day	
Target converted to weekly flow	5.600	Metric tons per week	Conversion from daily
Dilution ratio	250	Dimensionless	
Target nitrate loading for an application based on three days of applications weekly with a 20 percent safety factor added	2.24	Metric tons expressed as nitrogen	
Target nitrate for an application	2,240	Kilograms as nitrogen	Same mass in different units
Volume of liquid calcium nitrate for an application	4,755	Gallons	Same mass expressed in terms of volume
Flow rate of liquid calcium nitrate	9.91	Gallons per minute	
Flow rate of epilimnion water to be mixed with calcium nitrate solution based on a 250 to 1 dilution	2,476	Gallons per minute	
Flow rate of epilimnion water and liquid calcium nitrate to enter the hypolimnion based on a 250 to 1 dilution	2,486	Gallons per minute	

Note: Dilution ratio will vary based on salinity and temperature conditions.

#### 3.0 SECURITY, MOBILIZATION AND OPERATIONS

Annual mobilization is anticipated to take approximately two to three weeks during June, following annual procurement of materials and equipment. During mobilization, the barge with its two nitrate storage tanks will be removed from storage, and the pumps, pipes, hosing manifold, and controls will be placed on the barge. After the barge is outfitted, the barge will be moved out into the lake to test the pumps and controls, and the anchor weights will be placed at each of the application locations.

Nitrate will be applied and nitrate concentrations in the lake will be most intensely monitored from late June until early October. Lake waters typically turn over and become mixed again from top to bottom in mid-to-late October, which replenishes the lower waters with oxygen and nitrate. Sufficient nitrate will be applied in the lake hypolimnion by early October to carry through until turnover. One to two weeks are needed following turnover to demobilize the nitrate application equipment. Monitoring will continue in the lake at a lower frequency following turnover until mid-to-late November, weather permitting based on winds and temperatures.

#### 3.1 Security

The lakeshore support areas for nitrate application operations will most likely be located on Honeywell property on or near Wastebed B south of Wastebeds 1 through 8. Wastebed B is being used as the support area for lake dredging and capping operations. Security procedures maintained during ongoing remedial activities have been successful in controlling equipment, materials, and building security. These measures, including controlled access locations and fencing with locked gates around key equipment/storage areas will continue to be implemented as needed for the nitrate addition activities.

#### 3.2 Mobilization

The following mobilization activities will take place each year to prepare for nitrate addition:

- The nitrate barge in storage along the shoreline of Onondaga Lake during winter months will be mobilized.
- Equipment needed to add calcium nitrate will be mobilized including pumps, storage tanks, chemical feed piping, meters, suction piping, and distribution piping to transmit the nitrate-water mixture to predetermined depths in the hypolimnion.
- Monitoring equipment will be tested including a global positioning system (GPS) sensor, the *in situ* ultraviolet spectrophotometer (ISUS) equipment, hand-held real-time monitoring equipment, and a laptop computer containing needed software.
- Software will be checked and modified as needed to allow reliable recording and display of field measurements on the on-board computer.
- Anchor weights will be placed at each of the three application locations in the lake and buoyed.

#### **3.3 Operations**

Operations for adding nitrate to Onondaga Lake include barge operations, loading of nitrate onto the barge, and fueling. The following is a typical sequence of barge operations during a day when nitrate is applied:

- 1. Move the barge with its equipment, field team, and support boat carrying hoses to one of the three application locations and attach at two spots to buoyed anchor weights previously set at each location.
- 2. After the barge is anchored, monitor specific conductance, water temperature and water depth. Quantify the dilution water flow rate for the day's application based on field monitoring results and results from recent application days.
- 3. Clamp hose sections together so the total length reaches down into the lower hypolimnion to approximately 6 ft (2 m) above the lake bottom. Attach the hoses to the manifold. Use the crane located on the barge near the manifold to assist with clamping the hose sections onto the manifold.
- 4. Start up the dilution water and nitrate feed pumps. Establish flow rates so the diluted nitrate can hover slightly above the lake bottom. Flow rates are based in part on real-time lake monitoring conducted from a separate boat. Begin to pump nitrate and dilution water to the lower hypolimnion.
- 5. Once pumps are operating, check the pump gauges and nitrate levels in the feed tanks on the barge regularly and allow them to operate continuously for three to five hours (on average) until the quantity of nitrate targeted for the day's application is reached.
- 6. After the quantity of nitrate is applied, shut down the pumps and retrieve the hoses from the lake. Disassemble the clamped hose sections and place the hose sections on the support boat.
- 7. After hoses are pulled from the lake and the hose sections are placed on the support boat, detach the barge from the anchor weights and move the barge to a safe location such as near the western shoreline of the lake adjacent to Honeywell property.

Liquid nitrate is transported by tanker truck to Syracuse and transferred to a double-walled storage tank on Honeywell property near the lake shoreline. The nitrate is loaded onto the barge by pumping it from the onshore storage tank to the two nitrate storage tanks on the barge.

Fuel is provided to the barge power unit and to the dilution water pumps by pumping either from a fuel supply boat or from a portable fuel tank along the lake shoreline.

#### 3.4 Spill Prevention and Contingency

The storage tanks for the calcium nitrate solution on the barge have secondary containment equivalent to their volumes. Secondary containment will also be provided for the nitrate storage tank located near the lake's shoreline each year from June through October.

Preventive management practices will be employed during activities such as refueling the barge and dilution water pumps or transferring chemicals. These are a second tier of control included in standard operating procedures (SOPs)/job safety analyses that are part of the health, safety and environmental plan previously prepared and implemented for nitrate addition efforts.

The plan is updated on a regular basis. In addition, tanks, hoses, and connection will be regularly monitored as a spill prevention measure.

Spill response procedures are outlined in the project safety plans (Parsons, 2013; UFI and SU, 2007) and will be reviewed periodically by the barge team during the application season. Spill response equipment on the barge includes absorbent booms.

#### 3.5 Unlikely Extreme Future Scenarios

Two independent and unlikely extreme future scenarios have been identified that could occur in future years: (1) the nitrification treatment unit at Metro could go offline for a significant portion of a spring period resulting in lower nitrate concentrations in the lake when summer stratification sets up; and (2) the lake may not turn over following winter stratification which would extend the annual stratification period from late winter until its typical end in late October. Both of these scenarios can be effectively addressed with additional applications of nitrate as warranted. If either of these scenarios arise in future years, the work scope (including additional lake monitoring if warranted) to address either condition would be discussed with NYSDEC prior to being implemented. Either of these scenarios would develop over many weeks, so there would be sufficient time to prepare for action as needed.

If the nitrification unit at Metro would go offline for a long period of time during a spring period, applications of nitrate would need to begin as soon as the lake thermally stratifies. The earliest recorded onset of thermal stratification in Onondaga Lake is early May. Early-season applications of nitrate would be conducted as needed to maintain a minimum nitrate-nitrogen concentration of 1 milligram per liter at lower depths in the profundal zone. A typical lake nitrate-nitrogen concentration prior to the Metro nitrification unit going online in 2004 was 1 milligram per liter. The average demand for nitrate in the deep waters of the profundal zone is 0.8 metric ton per day (Parsons and UFI, 2011 and from pilot test results). Assuming an early set-up of thermal stratification on May 1 and a late fall turnover on November 7, the demand for nitrate would total 153 metric tons of nitrate as nitrogen (0.8 metric ton per day for 191 days) which at an application capacity based on the current barge of 2.4 metric tons would total 64 applications of nitrate over 21 weeks from mid-May until mid-October or three applications per week which is implementable. Representatives from Onondaga County's Department of Water Environment Protection and members of the nitrate addition team are regularly in contact about lake conditions. Metro effluent concentrations are monitored regularly by Onondaga County. The nitrate team would know many weeks prior to the nitrification unit at Metro going offline for a long period of time.

Since observations began in the 1980's, Onondaga Lake has experienced a spring turnover every year except for two years (i.e., 1993 and 1994). No spring turnover would mean the stratification period would start approximately two months earlier in March. Winter stratification in Onondaga Lake typically does not lead to significant anoxic conditions based on available data; dissolved oxygen concentrations during winter months are typically at 5 milligrams per liter or above. Two additional months of nitrate applications at the average pilot test application rate of two per week equates to 16 additional nitrate applications which could be conducted as needed at a frequency as high as five applications per week and thereby require a minimum of 3.2 weeks from late April through mid-May to complete.

#### 4.0 MONITORING

The in-lake monitoring program will be conducted before, during, and following each annual nitrate addition program. Data collected as part of the nitrate addition monitoring program will be used to guide rates and locations for future applications of the diluted calcium nitrate, track the fate of the chemical addition, and verify there are no adverse impacts to water quality (none are expected, based on pilot test results). The three components to the overall monitoring program to support nitrate addition are discussed in the three subsections below. They include: (1) fixed frequency monitoring to assess various water quality parameters associated with nitrate operations and mercury concentrations in lake water; (2) three-dimensional specification of nitrate addition.

#### 4.1 Fixed Frequency Monitoring

This component of monitoring nitrate applications allows for assessment of (1) in-lake conditions to establish the need for initiating and continuing nitrate addition; (2) the effectiveness of nitrate addition; (3) important fluctuations and systematic changes that may influence the nitrate addition effort; and (4) the fate of the chemical addition and any unanticipated adverse impacts. Water column monitoring will be conducted weekly at South Deep during the period of nitrate addition (from approximately July until fall turnover in mid-to-late October) and bi-weekly from mid-May through June and from fall turnover until late November. Monitoring parameters, sampling depths, analytical methods for laboratory analyses, parameter justifications, and typical numbers of samples are summarized in Tables 3, 4, and 5. The laboratory will make provisional data for key parameters (e.g., nitrate) available to the Honeywell team within one week of sample collection; formal data packages will be available to Honeywell within one month of sample collection.

Fixed-frequency monitoring will focus on sample collection at the South Deep location because water quality at the South Deep location is representative of water quality conditions throughout Onondaga Lake's profundal zone. Modifying this focus of fixed frequency monitoring to include, for example, monitoring at the North Deep location could be considered in future years if warranted to do so.

During the pilot test, fixed-frequency monitoring included calcium which is not included in Tables 3 through 5. Monitoring during the pilot test demonstrated that elevated calcium concentrations are not a concern at the rate nitrate will continue to be applied in Onondaga Lake. In addition, there are no applicable New York State surface water quality standards or guidelines for calcium.

Concentrations of manganese measured in hypolimnion waters by Onondaga County unexpectedly increased during the 2013 application period. County data from 2013 indicate manganese concentrations increased in the hypolimnion over time in a manner that roughly tracked with increases in nitrate concentrations. The sequence of electron acceptor utilization is oxygen followed by nitrate followed by manganese followed by iron followed by sulfate. The 2014 fixed-frequency monitoring program will include manganese given its role as an electron acceptor.

Time Period	Sampling Frequency	South Deep Water Depths to Sample (m)			
Mid-May to late June	Once in May and twice in June	2, 12, 18			
July	Weekly	2, 12, 16, 18			
August	Weekly	2, 12, 16, 18			
September	Weekly	2, 12, 16, 18			
October until fall turnover	Weekly	2, 12, 16, 18			
Fall turnover to late November	Bi-weekly	2, 12, 18			

# TABLE 3 ANNUAL WATER COLUMN SAMPLING SCOPE

#### Notes:

- (1) This surface water sampling scope is based on the lake being stratified from mid-May until the end of October and nitrate being added from late June until mid-October. Any significant adjustments due to weather or variations in lake inflows or lake conditions will be discussed with NYSDEC before being implemented.
- (2) The total number of annual water column samples for forms of nitrogen and mercury is 83 based on three sampling events through June, four sampling events in July four in August, four in September, four in October until the lake turns over, and two in November following lake turnover.
- (3) The number of water depths to monitor in the hypolimnion at South Deep starting in 2014 has been reduced by one for September and October until fall turnover based on pilot test results that show little variation of results in the hypolimnion with depth.

Parameter Method		South Deep Depths (m) and Frequency	Total Number of Field Samples <sup>x</sup>
WATER			
Nitrate plus nitrite (NO <sub>X</sub> )	EPA 353.2	See Table 3	83
Nitrite $(NO_2^-)$	EPA 353.2	See Table 3	83
Total ammonia (T-NH <sub>3</sub> )	EPA 350.1	See Table 3	83
Manganese	SM 3500 Mn-B (persulfate)	Ten dates from mid-June to late October at water depths of 14 m, 16 m and 18 m	30
*Total mercury	EPA 1631E	See Table 3	83
*Total mercury, dissolved	EPA 1631E	2-meter water depth once in June, bi- weekly thereafter to early November, plus the 16-meter water depth biweekly from early September to early November.	15
*Methylmercury	EPA 1630	See Table 3	83
Ferrous iron (Fe <sup>2+</sup> )	Heaney and Davison (1977)	Ten dates from mid-June to late October at water depths of 14 m, 16 m and 18 m	30
Soluble reactive phosphorus	SM 18-20 4500-PE	Ten dates from mid-June to late October at water depths of 14 m, 16 m and 18 m	30
Total dissolved gases (TDG)	TDG sensor	Ten biweekly profiles from June 30 to late October.	

# TABLE 4 ANNUAL LAKE MONITORING LABORATORY ANALYTES

Notes:

x Numbers of field samples are based on the sampling timeframes and water depths presented in Table 3. See Table 5 for total numbers of samples to be analyzed.

 $SM-Standard \ method$ 

#### TABLE 5

### **QAPP WORKSHEET 20 – QUALITY CONTROL SUMMARY TABLE**

Matrix	Analytical Group <sup>1</sup>	Concen- tration Level	No. of Annual Field Samples for Laboratory Analyses <sup>2</sup>	No. of Field Duplicates	No. of Field Blanks <sup>3</sup>	No. of Equip. Blanks	Total No. of Samples to Laboratory
Water	Nitrate + Nitrite as N (NO <sub>x</sub> )	Low	83	22	22		127
Water	Nitrate as N (NO <sub>2</sub> )	Low	83	22	22		127
Water	Ammonia as N (T-NH <sub>3</sub> )	Low	83	22	22		127
Water	Manganese	Mod	30	10	10		50
Water	Ferrous iron	Low	30	10	10		50
Water	Soluble reactive phosphorus	Low	30	10	10		50
Water	Total mercury	Low	83	22	22	11	138
Water	Filtered mercury	Low	15	2	2	2	21
Water	Methylmercury	Low	83	22	22	11	138

Notes:

<sup>1</sup> See Worksheet 23 in the Quality Assurance Project Plan for analytical methods (Parsons, Anchor QEA and UFI 2012, draft).

<sup>2</sup> See Tables 3 and 4. Samples to be collected at different depths at the same location are counted separately.
 <sup>3</sup> Field blanks will consist of analyte-free water transported from the lab to the field and then poured into a second clean sample bottle prior to transport.

In addition, matrix spike and matrix spike duplicate samples will be prepared by the laboratory at a frequency of one per sample delivery group.

Robotic monitoring at South Deep will allow for assessment of the dynamics of density stratification, dissolved oxygen resources, and an array of auxiliary limnological conditions, with high time (daily) and depth (1 meter) resolution. Specifications of probe measurements for robotic monitoring are presented in Table 6. Although robotic data will not be presented formally as part of the nitrate addition work, robotic data will be available online at www.upstatefreshwater.org within a few hours of data collection.

Parameter	Probe (YSI <sup>*</sup> )	Performance Accuracy/Resolution	Attribute/Value			
Dissolved oxygen (optical sensor)	6562	0.1 mg/L/0.01 mg/L	Electron acceptor			
Temperature	6560	± 0.15 °C/0.01 °C	Thermal stratification, mixing			
Specific conductance	6560	$\pm$ 0.5% reading/1 µS	Tracer, signature of injected chemical			
рН	6565	$\pm$ 0.2 units/0.01 units	Chemical equilibria, sulfide species			
Fluorometric chlorophyll	6025	$\pm$ NA/0.1 µg/L Chl	Metric of phytoplankton biomass			
Redox potential	6565	$\pm$ 20 mVs/ 0.1 mV	Indicator of redox status			
Turbidity	6136	± 2 NTUs/0.1 NTU	Vertical pattern of particles			

TABLE 6
<b>SPECIFICATIONS OF PROBES FOR ROBOTIC MONITORING AT SOUTH DEEP</b>

 $\mu S-microsiemens$ 

mV - millivolt

 $\mu g/L$  – micrograms per liter

NTU – Nephelometric turbidity units

Two acoustic doppler velocimeters (hereafter called velocity meters) will be deployed near the South Deep location and in the North Basin near the North application location each year that nitrate is applied. Each velocity meter will be housed in a stationary steel-framed cage to ensure sensors remain in a fixed position approximately one meter above the lake bottom.

#### 4.2 Three-Dimensional Specification of Nitrate and Sulfide Levels

An important component of the nitrate addition program is near-real-time feedback on the detailed spatial resolution of the nitrate pool in the hypolimnion to assess the transport and fate of the added nitrate and guide subsequent additions. A three-dimensional representation of the distribution of nitrate must be obtained over a short interval during nitrate addition. Further, measurements of sulfide within the hypolimnion over three dimensions will help to identify the potential for occurrences and sources of methylmercury. These monitoring efforts will be conducted with the same rapid profiling instrumentation used during the nitrate addition pilot test, which includes the ISUS technology to measure nitrate and sulfide concentrations in lake water (Prestigiacomo et al., 2009). A submersible ultraviolet nitrate analyzer (SUNA) is used by UFI as a backup for the ISUS equipment.

The ISUS provides well-resolved patterns of both nitrate and sulfide within a single day, with results typically available in graphical form prior to the end of the sampling day. Approximately 30 profiles are needed to support the needed measuring resolution. Profiles will

be collected at 34 locations (see Figure 3) once weekly while nitrate is being applied and at 15 locations a second time during the same weeks. One of the lessons learned during the nitrate addition pilot test is that two ISUS profiles per week at 34 locations are not needed to effectively monitor nitrate concentrations in the lake. Nitrate concentrations do not change at a rate that is sufficiently rapid to require multiple profiles each week at 34 locations. However, it is important to collect data more than once weekly at the deepest locations. Therefore, the second day of lake nitrate monitoring each week will include collecting nitrate profiles at 10 locations along two transects plus five additional profiles near where nitrate is applied. The primary transect is along the lake's main axis and includes the South Deep and North Deep locations. The secondary transect is a lateral line of locations passing through South Deep. If nitrate concentrations at any of the 34 monitoring locations drop below 1 mg/L, then that location will be monitored again as part of the next nitrate monitoring effort. Other sensors in the rapid profiling "package" (Table 6) provide information related to lake stratification and turbidity. The goal is to provide viewerfriendly spatial patterns (e.g., contours) of the nitrate, sulfide, and other related characteristics within the same day of field measurements. This information will then be used to guide decisions on appropriate rates of application and near-future locations for adding nitrate. Backup ISUS instrumentation (a SUNA) is available to minimize the potential for down time if the ISUS equipment unexpectedly becomes inoperable.

The nitrate objective in the hypolimnion is a concentration of at least 1 mg/L as nitrogen. If nitrate measurements using the ISUS show concentrations significantly below this objective, water samples and analyses for low-level total mercury and low-level methylmercury will be conducted in the vicinity of that location until nitrate-nitrogen concentrations increase to the target level of 1 mg/L or higher. This additional monitoring will be triggered if nitrate-nitrogen concentrations are below 0.7 mg/L on two consecutive monitoring days.

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Parameter	Sensor	Performance Accuracy/Resolution	Attribute/Value
Nitrate	Satlantic ISUS V2	$\pm 0.028$ mg per liter as	Calcium nitrate being added
Bi-sulfide	Satlantic ISUS V2	$\frac{+0.064 \text{ mg per liter as}}{\text{sulfur}}$	Redox constituent, sulfate reduction
Temperature	SBE 3F	± 0.002 °C/0.0003 °C	Stratification
Specific conductance	SBE4	$\pm$ 3 µS/cm/0.1 µS/cm	Tracer/stratification
Beam attenuation coefficient	Wetlabs C-Star	$\pm 0.1\%$ transmission	Particle indicator
Optical backscattering	D&A OBS-3	± 0.25 NTU/0.1 NTU	Particle indicator
Chlorophyll-a	Wetlabs WETstar	$\pm$ NA/0.1 µg/L Chl-a	Indicator of phytoplankton biomass
Photosynthetically active irradiance	Li-Cor LI-193	± 5% reading	Light penetration

# TABLE 7 SPECIFICATIONS FOR THREE-DIMENSIONAL ISUS-SUNA MONITORING

#### 4.3 On-Barge Measurements

Three types of monitoring are planned to be conducted on-board the vessel during nitrate addition: (1) measurements to assess the density of the calcium nitrate and discharge solution; (2) measurements of volumetric flow rates for calcium nitrate and the discharge solution; and (3) measurements of specific conductance in hypolimnion waters. Density is a function of temperature and salinity. Salinity will be assessed by measuring specific conductance. Densities of the chemical solution and the diluted form to be added to the lake will be calculated in near-real-time by an on-board computer to guide the details of nitrate addition, including the extent of on-board dilution and depth(s) of discharge.

Measurements of flow rates of calcium nitrate, dilution water, and discharge solution will be conducted to demonstrate closure of a total flow budget (chemical solution volume plus dilution volume equals discharge volume) and use of calcium nitrate.

#### 5.0 HEALTH AND SAFETY

The safety of all members of the project team and the general public is the highest priority for Honeywell and for Parsons. Written safety procedures will be prepared as needed to supplement the Project Safety Plan for Parsons' nitrate addition efforts (Parsons, 2013) and the UFI Safety Plan (Appendix C in UFI and SU, 2007). Job safety analyses are task-specific assessments of work procedures that are an important safety tool when they are prepared and periodically reviewed. This safety documentation will be updated if needed and strictly followed by nitrate addition team members. If work activities are identified in the future that are not

included in relevant Onondaga Lake plans referenced herein, then new operating procedures and job safety analyses will be prepared prior to starting the activity.

Various project-specific safety elements will be emphasized. For example, suitable personal flotation devices are essential for persons working over water or along the shoreline and docks (see specific requirements below). Slip-resistant surfaces and electrical protection around water will be emphasized. Suitable hand and eye protection will be instituted as appropriate when working with the nitrate solution. Working conditions at this time of the year could include very warm weather; therefore, shade and plenty of water will be provided for the field team.

Safe operation of water craft is essential during nitrate applications. There will be some days during summer months and into early fall when conditions will not be safe for anyone to be on the nitrate barge or support boat due to weather such as thunder and lightning storms or strong winds. Anyone on the nitrate application team will have the ability to terminate work if unsafe conditions arise.

The nitrate barge and support boat will be spudded to the lake bottom to limit movement when near the lakeshore. While working on a barge or boat, the field team will be instructed to be aware of other boaters and weather conditions that may influence operations. All personnel will be required at a minimum to wear Level D personal protective equipment. Approved Coast Guard life vests must be worn at all times by any team member on a boat or barge, and anyone involved in loading or unloading the barge from shore or docks must wear an approved flotation device.

#### 6.0 SCHEDULE CONSIDERATIONS

Nitrate will be added to the lake's lower hypolimnion starting in late June or early July depending on lake conditions and ending in early October prior to fall turnover. "Blackout" dates, when nitrate will not be added, will be established to the extent practicable based on scheduled dates for public events on the lake between mid-June and late October.

NYSDEC, USEPA, and the Onondaga County Department of Water Environment Protection will be notified prior to initiating nitrate addition each year consistent with the notification protocol successfully implemented during the three-year nitrate addition pilot test completed in 2013. Every reasonable effort will be made to give agencies at least one week of notice during June prior to commencing annual nitrate additions. Every reasonable effort will also be made to notify NYSDEC in a timely manner of any schedule changes.

#### 7.0 QUALITY ASSURANCE

Site work efforts are outlined as written operating procedures in the job safety analyses (Parsons, 2013). These procedures will be followed and updated as warranted if procedures change significantly over time.

Laboratory procedures will be conducted in accordance with the current quality assurance plan for Onondaga Lake construction and post-construction media monitoring efforts (Parsons, Anchor QEA and UFI, 2012).

Confirmation of ISUS real-time nitrate concentrations with laboratory measurements will be completed periodically during each application year.

#### 8.0 DATA MANAGEMENT AND REPORTING

Because this work is required under a Consent Order through NYSDEC, approval of this operations maintenance and monitoring plan will be used as a notice to proceed and a permit from NYSDEC will not be required to conduct this work.

Project information will be recorded electronically to the extent practical. Field data will be recorded primarily in field instruments and electronic files using a laptop computer on the nitrate barge. Laboratory data will be provided in electronic format by laboratories and will include field chains of custody in addition to laboratory results as specified in the quality assurance plan.

Laboratory output will be coordinated through a database manager as described in the SOP for data management that is part of the quality assurance plan. Data queries will be completed working with the database manager for quality control purposes.

Each electronic data deliverable (EDD) provided by a laboratory will be loaded to the temporary holding table where the validator can login, view the data and complete the data validation. Once validation is complete and the results have been entered, the dataset will be saved and inserted into the final permanent database tables. EDDs provided to NYSDEC have a format that is separate from the Honeywell EDD format (NYSDEC, 2011). The database manager will prepare EDDs for NYSDEC from laboratory deliverables and send them to 'NYENVDATA' in coordination with the Project Manager.

Annual data reports of nitrate addition efforts and a five-year nitrate addition assessment report will be prepared and provided to NYSDEC for review and comment prior to being finalized. The first five-year nitrate addition assessment report is scheduled to be submitted after the 2018 nitrate applications are completed.

Any significant proposed changes to the nitrate addition program including proposed changes to lake monitoring associated with nitrate addition will be subject to review and approval by NYSDEC prior to implementing those changes.

#### 9.0 REFERENCES

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# FIGURES





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