
ONONDAGA LAKE TECHNICAL SUPPORT DOCUMENT FOR NITRATE ADDITION

Prepared For:

Honeywell

301 Plainfield Road, Suite 330
Syracuse, NY 13212

Prepared By:

PARSONS

301 Plainfield Road, Suite 350
Syracuse, NY 13212

and



JUNE 2014

TABLE OF CONTENTS

	<u>PAGE</u>
ACRONYMS	ii
GLOSSARY OF TERMS	ii
EXECUTIVE SUMMARY	1
1.0 INTRODUCTION	2
2.0 BACKGROUND	3
2.1 Description	3
2.2 Advancements Following the 2005 ROD.....	6
3.0 NITRATE ADDITION PILOT TEST RESULTS	7
4.0 DISCUSSION AND CONCLUSIONS	13
4.1 Nitrate Addition.....	13
4.2 Oxygenation	15
4.3 Conclusions	16
5.0 REFERENCES	17

LIST OF FIGURES

- Figure 1 Onondaga Lake Bathymetry and Pilot Test Locations for Nitrate Addition
- Figure 2 Schematic Representation of Typical Summertime Thermal Stratification in Onondaga Lake
- Figure 3 Annual Maximum Mass of Methylmercury (MeHg) in Grams from 1992 through 2013 in the Hypolimnion of Onondaga Lake
- Figure 4 Annual Maximum Volume-Weighted Soluble Reactive Phosphorus Concentrations from 2006 through 2013 in the Hypolimnion of Onondaga Lake
- Figure 5 Total Mercury and Methylmercury Concentrations from 2008 through 2013 in Zooplankton from Onondaga Lake
- Figure 6 Nitrite and Total Ammonia Concentrations in the Hypolimnion of Onondaga Lake Before and During the Nitrate Addition Pilot Test
- Figure 7 Water Temperature, Dissolved Oxygen and pH in the Hypolimnion of Onondaga Lake Before and During the Nitrate Addition Pilot Test
- Figure 8 Dissolved Gas Percent Saturations in the Hypolimnion of Onondaga Lake

ACRONYMS

DO	Dissolved oxygen
ESD	Explanation of Significant Differences
mg/kg	Milligram per kilogram
mg/L	Milligram per liter
ng/L	Nanogram per liter which is 0.000001 mg/L
NH ₃ -N	Ammonia-nitrogen
NO ₂ -N	Nitrite-nitrogen
NO ₃ -N	Nitrate-nitrogen
NYSDEC (or DEC)	New York State Department of Environmental Conservation
ROD	Record of Decision
SMU	Sediment Management Unit
SU	Syracuse University
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.

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 by wind and waves.

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 in the hypolimnion than in the epilimnion.

Metalimnion – water layers located in the vertical dimension between epilimnion and hypolimnion waters and characterized by a steep temperature change.

Methylmercury - An organic form of mercury, which 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.

Metro – the Metropolitan Syracuse Wastewater Treatment Plant located on the south shore of Onondaga Lake which is owned and operated by Onondaga County. This treatment plant typically treats 80 million gallons of wastewater each day and provides on average 80 percent of the inflow of nitrate to Onondaga Lake.

EXECUTIVE SUMMARY

This Technical Support Document explains how nitrate addition has been proven to be effective and implementable in deep waters of Onondaga Lake. A three-year nitrate addition pilot test was successfully completed in the lake in 2013. The purpose of adding nitrate or oxygen is to inhibit release of methylmercury from sediment in the deep portions of the lake, and thus reduce methylmercury concentrations in aquatic organisms, including fish. 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.

New scientific and engineering insights have been developed that pertain to the oxygenation pilot study portion of the remedy for Onondaga Lake specified in the 2005 Record of Decision. The 2007 Consent Decree Statement of Work specified a study of nitrate addition and, if nitrate addition was found to be effective and appropriate, it would be implemented in lieu of oxygenation.

Results of in-lake and laboratory tests followed by a three-year lake-wide pilot test demonstrate that nitrate can be effectively added to the deep waters of Onondaga Lake. Methylmercury concentrations in the lake water were significantly reduced during the pilot test. Lower methylmercury concentrations in lake water have resulted in lower methylmercury concentrations in zooplankton, which in turn has resulted in lower exposure of fish to methylmercury given methylmercury accumulates as it moves up the food chain from zooplankton to other aquatic organisms that consume zooplankton. These reductions in methylmercury exposures from the water column and through the food chain are anticipated over time to result in lower concentrations of methylmercury in fish in Onondaga Lake which would reduce potential risk to humans who consume the fish.

Adding nitrate is protective of human health and the environment, and is more implementable than adding oxygen. Furthermore, adding nitrate to deep waters effectively builds on the benefit provided since 2004 by the Metropolitan Syracuse Wastewater Treatment Plant converting ammonia to nitrate in treated effluent it discharges to the lake. Therefore, full-scale implementation of nitrate addition is recommended.

1.0 INTRODUCTION

This Technical Support Document explains how nitrate addition has been proven to be effective and implementable in Onondaga Lake. A three-year nitrate addition pilot test was successfully completed in the lake in 2013.

The New York State Department of Environmental Conservation (NYSDEC or DEC) and the United States Environmental Protection Agency (USEPA) issued a Record of Decision (ROD) in July 2005 which selected a remedy for the Onondaga Lake Bottom Subsite of the Onondaga Lake Superfund Site (Site). One element of the selected remedy was to perform a pilot study of oxygenation to reduce formation of methylmercury in deep water areas of the lake while preserving the normal cycle of lake stratification. The ROD specifies that if supported by a pilot study, full-scale implementation of oxygenation would follow.

Subsequent to the ROD in 2005, new insights for controlling methylmercury concentrations in lake waters emerged, and the potential effectiveness of nitrate addition was identified as an alternative to oxygenation by Upstate Freshwater Institute (UFI) and Syracuse University (SU). As a result, the 2007 Statement of Work attached to the Consent Decree between the State of New York and Honeywell International Inc. (Honeywell) specified the following:

“Honeywell shall conduct a study (which may include the performance of a nitrification pilot study as determined by DEC) to determine if nitrification would effectively reduce the formation of methyl mercury in the water column while preserving the normal cycle of stratification within the lake. If DEC determines that nitrification is effective and appropriate based upon the results of this study, this will be documented in an Explanation of Significant Difference (ESD), and Honeywell shall be required to implement a nitrification program in lieu of oxygenation.”

Consistent with the Statement of Work, Honeywell completed a successful, lake-wide three year pilot study of nitrate addition. The pilot study achieved significant reductions in methylmercury release from sediment in the deeper, stratified waters of Onondaga Lake resulting in lower lake water methylmercury concentrations while preserving the lake’s normal cycle of stratification. Lower methylmercury concentrations in lake water have resulted in lower methylmercury concentrations in zooplankton, which in turn has resulted in lower exposure of fish to methylmercury given methylmercury accumulates as it moves up the food chain from zooplankton to other aquatic organisms that consume zooplankton. These reductions in methylmercury exposures from the water column and through the food chain are anticipated over time to result in lower concentrations of methylmercury in fish in Onondaga Lake which would reduce potential risk to humans who consume the fish. Information and results from tests and other evaluations support full-scale implementation of nitrate addition in Onondaga Lake as summarized in this Technical Support Document.

2.0 BACKGROUND

2.1 Description

Methylmercury, the organic form of mercury found in aquatic systems, bioaccumulates in aquatic food webs and can adversely affect fish and wildlife that consume fish when concentrations are high. Methylmercury is the most bioavailable and toxic form of mercury found in lakes. Mercury is present in profundal surface sediments (those underlying the hypolimnion) of Onondaga Lake albeit at lower concentrations than in sediments closer to shore that are being dredged and/or capped. Methylmercury produced in profundal sediments of Onondaga Lake diffuses into the hypolimnion in the absence of oxygen and nitrate. Phytoplankton actively uptake methylmercury from the water column and represent the primary entry point for mercury into aquatic food webs (Pickhardt and Fisher, 2007). As a result, the methylmercury concentration in the water is considered a key factor in determining the concentration of mercury in biota (Rolfhus et. al., 2011).

Methylmercury production is a naturally occurring process by which inorganic mercury is transformed to methylmercury by anaerobic bacteria (in the absence of oxygen and nitrate). Sulfate-reducing bacteria are the principal methylators of inorganic mercury (Benoit et al., 2003), though production of methylmercury has also been attributed to iron-reducers (Kerin et al., 2006). Anaerobic sediments in thermally stratified lakes are particularly active zones for methylation of inorganic mercury and can be an important source of methylmercury to the water column during summer anoxia and fall turnover (Wollenberg and Peters, 2009). Production of methylmercury in lake sediments is promoted by anaerobic conditions and the supply of inorganic mercury, sulfate, and the portion of organic carbon prone to biochemical transformations.

Each year, typically from May until October, waters in Onondaga Lake where depths exceed 30 ft. (Figure 1) are thermally stratified. Warmer upper waters overlay the colder and denser lower waters. Warmer, upper waters are called the epilimnion, while cooler, deeper waters are called the hypolimnion, and the intervening water layers characterized by a steep temperature change are called the metalimnion (Figure 2). The hypolimnion is isolated from sources of dissolved oxygen and nitrate during the stratified period of the year. If nitrate is not added to the hypolimnion, depletion of oxygen and nitrate in the hypolimnion results in anaerobic conditions (absence of both oxygen and nitrate). Anaerobic hypolimnetic waters are common in relatively shallow productive stratifying lakes such as Onondaga Lake.

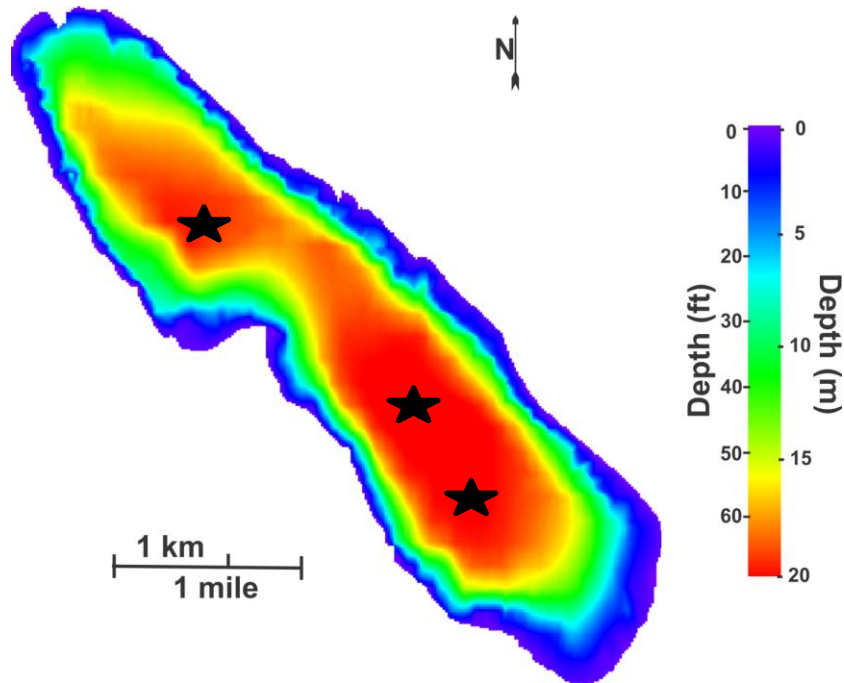
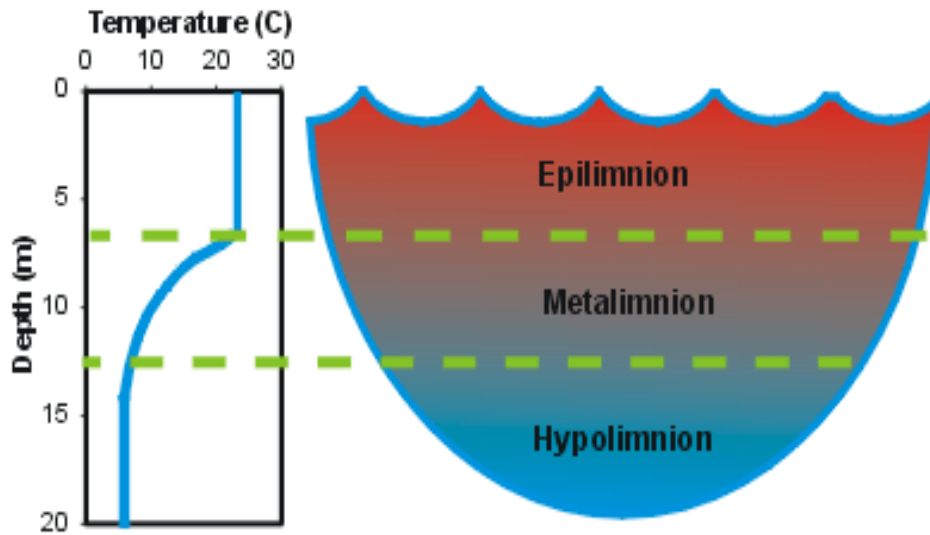


Figure 1 Onondaga Lake Bathymetry and Pilot Test Locations (★) for Nitrate Addition



Notes:

1. C is degrees Centigrade (or Celsius). 10 degrees C is 50 degrees Fahrenheit (F), and 20 degrees C is 68 degrees F.
2. Depth is in meters (m). 1 meter is 3.28 feet or 1.09 yards.

Figure 2 Schematic Representation of Typical Summertime Thermal Stratification in Onondaga Lake

When lake waters become vertically mixed at fall turnover in mid-to-late October, methylmercury accumulated in the hypolimnion during summer months mixes throughout the water column and can then become available to bioaccumulate in other aquatic life including fish. Methylmercury concentrations in zooplankton have been observed to increase during the period of fall turnover. Sediments in the deeper, stratified portion of Onondaga Lake are referred to as Sediment Management Unit 8 (SMU 8). A remedial action objective from the 2005 ROD is to eliminate or reduce releases of mercury from SMU 8 sediments to the extent practicable.

Zooplankton are a sensitive indicator of changes in methylmercury availability in the water column due to their short life span (i.e., weeks), limited range of movement, and position near the base of the aquatic food chain. Fish, in contrast, are expected to have a less direct response to changes in methylmercury in the water column with slower responses to changes, since fish have a relatively long life span (e.g., several species will live 10 to 20 years or more), are more mobile than zooplankton (the larger species range over the entire lake and into the Seneca River system), occupy positions near the top of the food chain, and are exposed to other portions of the food chain (e.g., benthic macroinvertebrates and food sources transported into the lake system from wetlands and upland areas). Zooplankton were monitored during each year of the nitrate addition pilot test. Also, both NYSDEC and Honeywell conduct adult sport fish monitoring for total mercury each summer, so effects of nitrate addition on fish are being monitored from year to year.

Wastewater treatment upgrades in 2004 at the Metropolitan Syracuse Wastewater Treatment Plant (Metro), which is owned and operated by Onondaga County, resulted in higher levels of nitrate discharge and a 2-fold increase in nitrate concentrations in the lake at the onset of stratification in May. Higher nitrate concentrations have contributed to major reductions in accumulation of methylmercury in hypolimnetic waters during summer stratification (Figure 3; see also Todorova et. al., 2009 and Matthews et. al., 2013). Methylmercury data were not collected from 1993 through 1999 and from 2001 through 2005. Adding nitrate directly to the hypolimnion from 2011 through 2013 further reduced methylmercury surface water concentrations in the hypolimnion.

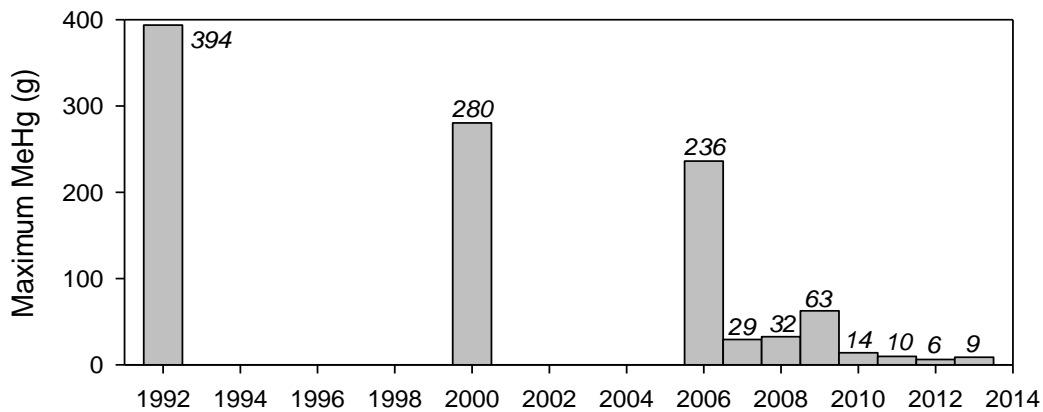


Figure 3 Annual Maximum Mass of Methylmercury (MeHg) in Grams from 1992 through 2013 in the Hypolimnion of Onondaga Lake

Additional wastewater treatment upgrades at Metro in 2005 to remove phosphorus resulted in marked reductions in phosphorus loading to Onondaga Lake and commensurate reductions in primary production and demand for oxygen and nitrate in the lake’s hypolimnion. Less demand for oxygen and nitrate leads to less release of methylmercury from lake sediments.

2.2 Advancements Following the 2005 ROD

In 2005, Upstate Freshwater Institute and Syracuse University (UFI and SU) identified the benefits to mercury cycling resulting from nitrification treatment (conversion of ammonia to nitrate via bacteria) and improved phosphorus removal implemented by Onondaga County at Metro. The potential benefits of augmenting the hypolimnetic nitrate pool were presented to NYSDEC and Honeywell in the fall of 2005. In 2006, a feasibility analysis was prepared by UFI and SU that documented that addition of nitrate to the hypolimnion of Onondaga Lake during summer stratification could meet the objectives specified in the ROD associated with oxygenation (UFI and SU, 2007 and 2008).

In 2007 and 2008, multiple in-lake dye tracer tests and laboratory evaluations with lake sediment were conducted on behalf of Honeywell to better understand hypolimnetic mixing processes and sediment-water interactions affecting methylmercury release. These efforts, and subsequent efforts by Honeywell related to nitrate addition, were completed implementing work scopes approved in advance by NYSDEC. The dye tracer tests (UFI, 2009) provided a basis for quantifying horizontal dispersion of substances like dissolved nitrate within the hypolimnion of Onondaga Lake. A number of laboratory experiments examined relevant interactions between lake waters and SMU 8 sediment (Exponent et. al., 2011). Flow-through microcosm chambers and intact sediment cores were used to investigate the effects of nitrate on methylmercury production and found that nitrate-nitrogen concentrations of 0.3 to 1.0 milligram per liter decreased the flux of methylmercury from Onondaga Lake sediments by 65 percent relative to anaerobic controls.

A successful in-lake nitrate application field trial was conducted which applied results from the in-lake dye tracer tests and laboratory evaluations with lake sediment. The field trial consisted of two continuous, six-hour applications of nitrate (Parsons and UFI, 2010). The purpose of the nitrate application field trial was to demonstrate that a widely-available calcium nitrate solution could be effectively added and mixed with lake-bottom waters in a manner that retains the nitrate at the target depth to counteract nitrate depletion below critical levels that result in release of methylmercury. The nitrate application field trial also provided additional information about horizontal dispersion of nitrate as a follow-up to the 2008 dye tracer tests. Monitoring results that were part of the field trial confirmed that nitrate was successfully delivered to the target depth and that the nitrate remained within the target depth zone. Results from the nitrate application field trial also significantly increased understanding of the range of dispersion that is encountered in the hypolimnion of Onondaga Lake.

3.0 NITRATE ADDITION PILOT TEST RESULTS

In-lake evaluations described in Section 2 above were followed in 2011, 2012 and 2013 by a successful three-year pilot test of nitrate addition documented in three annual reports (Parsons and UFI, 2012; Parsons and UFI, 2013; and Parsons and UFI, 2014). Work during each year of the nitrate addition pilot test was conducted across the entire hypolimnion of Onondaga Lake. The pilot test consisted of applying nitrate on 29 to 40 days as warranted during the summers of 2011, 2012 and 2013 and included detailed vertical monitoring of nitrate in the lake at up to 34 locations, robotic buoy monitoring at the South Deep location (located approximately 300 ft. from the southernmost pilot test nitrate application location (Figure 1), and laboratory analyses for multiple parameters. The work plan for each year of the nitrate addition pilot test was approved by NYSDEC prior to starting nitrate applications (Parsons and UFI, 2011; 2012 and 2013). Concentrations of trace metals were measured in the nitrate solution prior to the start of the pilot test and found to be acceptable as presented in the work plan for 2011.

Each of the three years of the nitrate addition pilot test consisted of daily applications of a diluted calcium nitrate solution (nitrate) to the bottom waters. The applications of nitrate were conducted between June 30 and October 10. Equipment and procedures used to apply nitrate were virtually the same for each of the three pilot test years. A self-propelled barge measuring approximately 40 ft. long and 24 ft. wide was used to conduct each of the nitrate applications. The barge is designed to dilute liquid nitrate with epilimnetic lake water to achieve neutral buoyancy at the target water depth. The resulting solution was then pumped through flexible hosing to between 7 ft. and 17 ft. (2 and 5 meters) above the lake bottom at water depths between approximately 42 ft. and 55 ft. (13 and 17 meters). The target dose for each daily application was typically 4,800 gallons of nitrate (2.3 metric tons of nitrate-nitrogen). The dose could be easily controlled and modified to meet target nitrate levels in the lake water. The added nitrate was able to spread laterally throughout the entire deep water area of the lake by natural forces as determined with extensive lake monitoring. Throughout each of the three pilot test years, nitrate was added to the lake at one of three lake locations during each day of application (see Figure 1).

In order for the nitrate solution to remain in the lower hypolimnion following release to the lake, the solution needs to be diluted to the density of the hypolimnetic water with less dense

epilimnetic water before being pumped to the lower hypolimnion. The actual flow rate of nitrate added to the lake was determined prior to each day of application based on available water quality monitoring results. The pilot test field crew adjusted flow rates of the nitrate solution to maintain a suitable dilution ratio that provided a diluted nitrate solution that was neutrally-buoyant and thereby able to spread laterally near the lake bottom.

Lake conditions were monitored between late May and late November during each of the three pilot test years. Data collected as part of the nitrate addition monitoring program were used to guide rates and locations for subsequent applications of nitrate, to track ongoing spreading of nitrate within the hypolimnion, to verify that there were no negative impacts to water quality, and to assess nitrate addition as a means of abating methylmercury accumulation.

An important component of the nitrate addition pilot test was near-real-time detailed spatial monitoring of the nitrate pool in the hypolimnion measured to assess the transport and fate of the added nitrate and guide subsequent additions. A three-dimensional representation of the distribution of nitrate was obtained during nitrate addition the same day measurements were conducted. Sulfide concentrations were also monitored in all three dimensions within the hypolimnion to indicate reducing conditions where methylation could occur and thereby identify the potential for occurrences and sources of methylmercury. In addition, ferrous iron concentrations were monitored within the hypolimnion at South Deep to provide supplementary information on the oxidation-reduction status of the lower waters.

In addition to near real-time monitoring, robotic monitoring was conducted over the April to November time interval at a location in the southern portion of the lake to assess dynamics of density stratification, dissolved oxygen resources, and an array of auxiliary limnological conditions at least daily for every one meter of water depth.

Concentrations of total mercury and methylmercury in the water column and in zooplankton were also monitored. During the first year of the pilot test (2011), total mercury and methylmercury were monitored at two locations, the South Deep and North Deep locations, as frequently as weekly, and total mercury and methylmercury were also monitored at 10 other locations in the water column five times from late June to mid-October of 2011 at a water depth 3 ft. above the lake bottom. Results from the first year of the pilot test (2011) showed that monitoring only at the South Deep location sufficiently describes water and zooplankton mercury concentrations throughout the deep portion of Onondaga Lake. As a result, mercury monitoring in 2012 and 2013 focused on the South Deep location.

The nitrate addition pilot test in Onondaga Lake was very successful. The pilot test achieved the objective of maintaining nitrate concentrations across the entire lower hypolimnion of the lake at concentrations sufficient to inhibit release of methylmercury from lake sediment (i.e., a target nitrate concentration of 1.0 milligram per liter as nitrogen). Adding nitrate reduced methylmercury concentrations in hypolimnion waters during all three years of the pilot test (Figure 3). Adding nitrate also reduced concentrations of soluble reactive phosphorus in the hypolimnion during all three years of the pilot test (Figure 4).

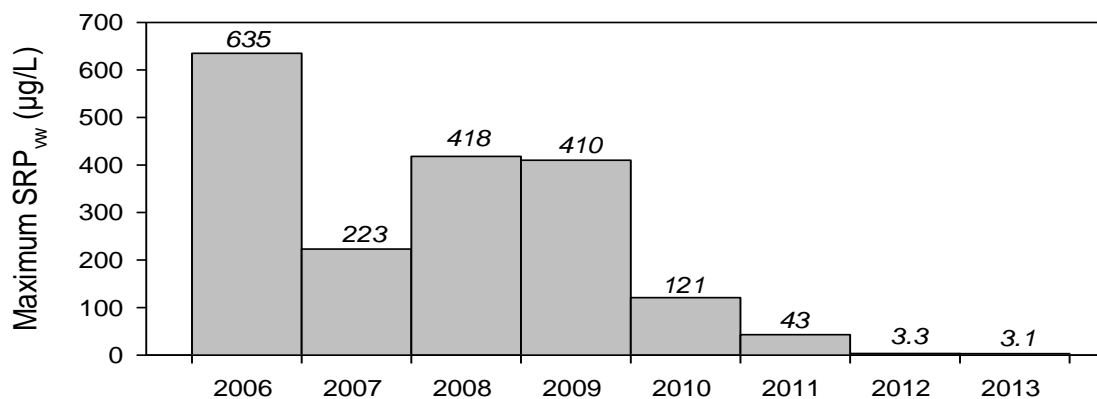
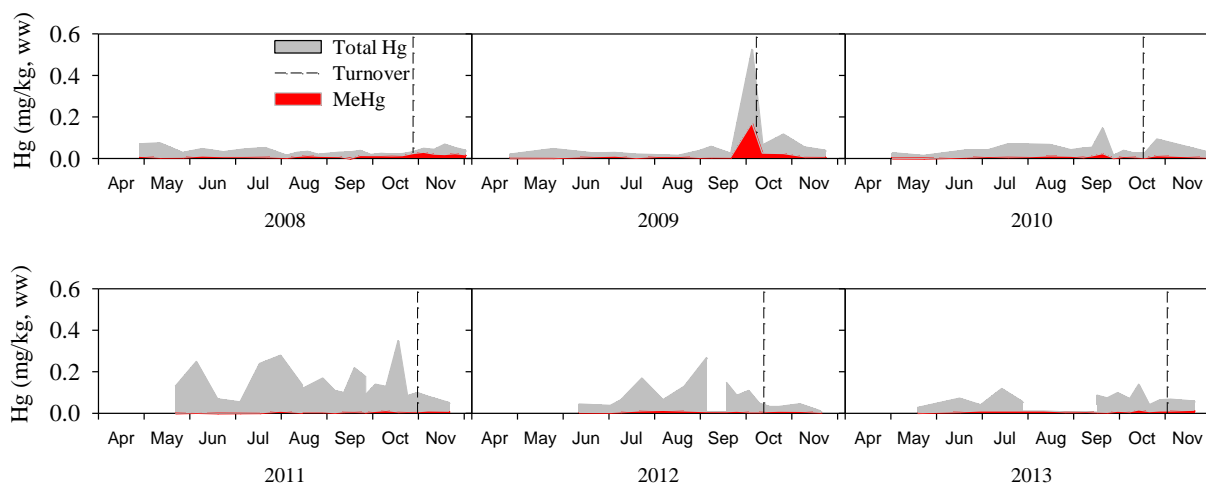


Figure 4 Annual Maximum Volume-Weighted Soluble Reactive Phosphorus Concentrations from 2006 through 2013 in the Hypolimnion of Onondaga Lake

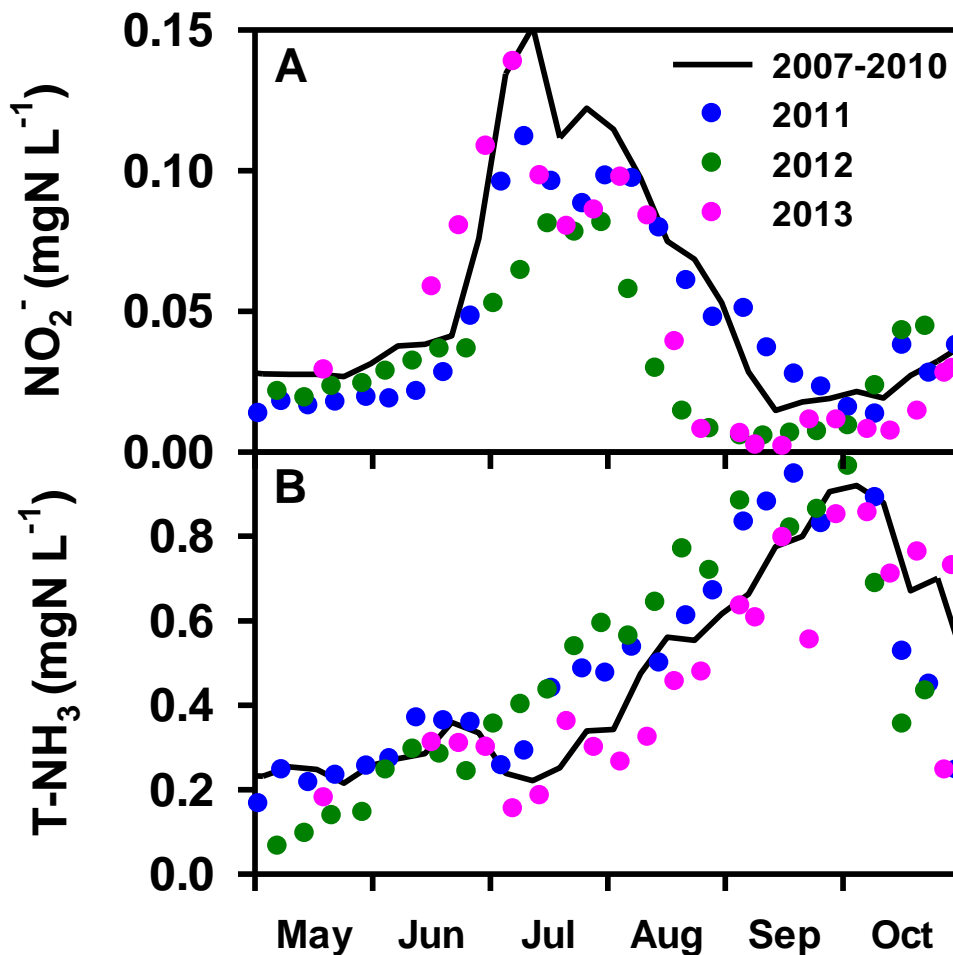
The combination of nitrification treatment of wastewater at Metro and nitrate added as a result of the pilot test resulted in zooplankton methylmercury concentrations that were very low during the nitrate addition pilot test (Figure 5). Peak concentrations of zooplankton methylmercury in Onondaga Lake from 2008 through 2013 were as follows (in milligrams per kilogram on a wet weight basis): 0.028 in 2008, 0.17 in 2009, 0.023 in 2010, 0.013 in 2011, 0.014 in 2012 and 0.016 in 2013. Zooplankton methylmercury concentrations have not significantly increased annually during fall turnover since 2009. Lower zooplankton methylmercury concentrations are expected to gradually reduce levels of total mercury in fish given methylmercury bioaccumulates as it moves up the food chain to larger forms of aquatic life.



Note: Total mercury is in gray shading. Methylmercury is in red shading. Units for total mercury and methylmercury per kilogram on a wet-weight basis (ww).

Figure 5 Total Mercury and Methylmercury Concentrations from 2008 through 2013 in Zooplankton from Onondaga Lake

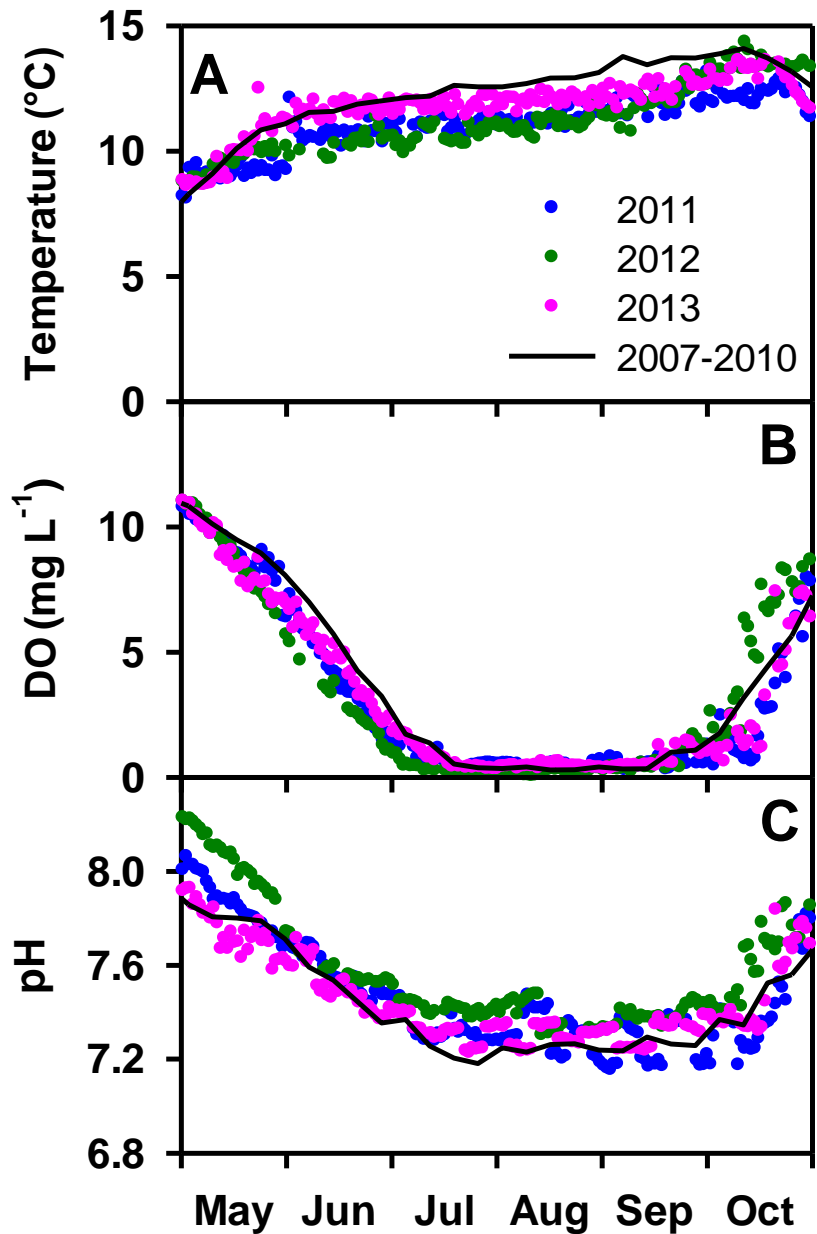
Adverse impacts on water quality from adding nitrate were not observed during the pilot test. Concentrations of nitrite (NO_2^-) and ammonia (NH_3) in the hypolimnion were in general the same or lower during the nitrate addition pilot test compared to the years 2007 through 2010 prior to adding nitrate (Figure 6). The statewide water quality standard for nitrite was not exceeded in the lake's epilimnion between 2007 and 2010 or during the pilot test. Exceedances of the water quality standard for nitrite in the lake's hypolimnion during the pilot test were less than a factor of two above the standard (0.10 mg/L as nitrogen). Average concentrations of nitrite were generally higher in the hypolimnion in years before the pilot test (2010 and earlier) than in years during the test. Contemporary concentrations of nitrite and ammonia in Onondaga Lake are much lower than historic levels. Through the early 2000s annual maximum concentrations of nitrite and total ammonia in the epilimnion routinely exceeded 0.2 mg/L and 2.0 mg/L, respectively as nitrogen (Effler et al. 2010). Treatment upgrades at Metro in 1999 and 2004 and pretreatment of pharmaceutical waste beginning in 1999 have resulted in reduced loadings of nitrite and ammonia to the lake.



Note: Concentrations of both nitrite and ammonia are presented as nitrogen (N). Values plotted are volume-weighted averages for the Onondaga lake hypolimnion measured at the South Deep location.

Figure 6 Nitrite (NO₂) and Total Ammonia (T-NH₃) Concentrations in the Hypolimnion of Onondaga Lake Before and During the Nitrate Addition Pilot Test

Water temperatures, dissolved oxygen concentrations, and pH in the hypolimnion of Onondaga Lake were approximately the same in 2007 through 2010 prior to the nitrate addition pilot test as during the pilot test (Figure 7).



Note: Water temperatures are in degrees Centigrade (C), dissolved oxygen concentrations are in milligrams per liter (mg/L), and pH is in standard units. Values plotted are volume-weighted averages for the Onondaga Lake hypolimnion measured at the South Deep location.

Figure 7 Water Temperature, Dissolved Oxygen (DO) and pH in the Hypolimnion of Onondaga Lake Before and During the Nitrate Addition Pilot Test

4.0 DISCUSSION AND CONCLUSIONS

4.1 Nitrate Addition

Nitrate addition has been proven to be effective and implementable and presents numerous advantages in comparison to oxygenation. Disadvantages of oxygenation are presented in Section 4.2. Nitrate addition as described in this support document merits full-scale implementation. Nitrate was provided throughout the lower hypolimnion in 2011 through 2013 thereby significantly reducing release of methylmercury and release of phosphorus from sediments in the deeper, stratified portion of the lake (Parsons and UFI, 2014). Reducing the release of methylmercury from sediment in turn helps to reduce zooplankton methylmercury concentrations in the lake which over time is anticipated to reduce mercury concentrations in fish.

Full-scale nitrate addition can be conducted using a barge-based application consistent with the applications successfully completed during the pilot test. However, even with the effectiveness of barged-based applications of nitrate, alternative methods for nitrate addition may be evaluated and implemented in the future.

Nitrate addition is sufficiently flexible that even unlikely extreme future scenarios with very low nitrate levels in lake waters during the spring season would be manageable. For example, in the unlikely event that Metro treatment of ammonia to nitrate would go offline or in the unlikely event that the lake would not mix vertically in early Spring prior to summer stratification, then less nitrate would be available in the hypolimnion. However, sufficient quantities of nitrate could be added to the lake at a more rapid pace if needed to sufficiently address these conditions.

Applying nitrate to Onondaga Lake does not result in any potentially significant adverse effects on water quality or growth of algae in the lake. Effects of adding nitrate on water quality are discussed in Section 3. Adding nitrate does not affect algal productivity in Onondaga Lake, because algal productivity is controlled by phosphorus inputs to the lake rather than by nitrogen inputs. The nitrate solution is most often used as an agricultural fertilizer and has been used as such for many years with no known effects on human health or biota. Monitoring data confirm that algal biomass did not increase during the years of the nitrate addition pilot test and that summertime algal blooms have not occurred since 2007 (UFI et al. 2014). Concentrations of nitrate in Onondaga Lake will be monitored in future years as nitrate is added in order to ensure a proper amount of nitrate is applied.

Monitoring during the three-year nitrate addition pilot test also addressed other potential impacts discussed in the 2007 feasibility analysis (UFI and SU, 2007). Average nitrate-nitrogen concentrations in the hypolimnion remained on average less than 2 milligrams per liter which is well below the 10 milligrams per liter concentration at which long-term exposure may adversely affect sensitive freshwater species (Camargo et. al., 2005). Ammonia toxicity is generally not a noteworthy concern in deeper waters in stratified lakes, because concentrations of the toxic fraction are low at typical values of pH and temperature in lake waters (Matthews et. al., 2000). Adding nitrate also did not lead to significant changes in pH of the hypolimnion or deposition of solids to the Onondaga Lake hypolimnion. Water temperatures in the hypolimnion were 2 to 4 degrees Fahrenheit lower during the pilot test compared to the years 2007 through 2010 prior to

the pilot test (Figure 7), which indicates that mixing and transport between hypolimnion and epilimnion waters does not increase due to nitrate addition. During the nitrate addition pilot test, concentrations of nitrate-nitrogen in the hypolimnion at fall turnover ranged from 0 to 1 milligram per liter higher than in the years without nitrate addition which is less than 10 percent of the prevailing summertime (June through September) mass of nitrate carried by the Seneca River which receives the outflow from Onondaga Lake. Nitrate loading is not a concern with respect to primary production in downstream ecosystems (Seneca River, Oswego River, Lake Ontario), because algal growth in these systems is limited by phosphorus.

No adverse impacts on the benthic community and fish were observed during the nitrate addition pilot test. Nitrate addition is not believed to result in any significant physical disturbance to surface sediments whereas oxygenation would more likely result in disturbance of surface sediments thereby potentially reducing the rate of natural recovery and potentially increasing the transport of mercury from the sediments to the water column.

Adding nitrate to the hypolimnion also did not result in significant increases in dissolved gases during the pilot test (see Figure 8). The ultimate fate of nitrate added to the lake is transformation to nitrogen gas based on supporting studies conducted prior to the pilot test as well as the dissolved gas measurement data collected during the pilot test. In addition, elevated levels of nitrogen gas in the deep hypolimnion measured after Metro upgrades prior to and during the pilot test confirm nitrogen gas as the final product of nitrate utilization at the sediment-water interface. Although there may have been minor increases in dissolved nitrogen gas in the hypolimnion during the pilot test, total dissolved gas (TDG) measurements indicate that dissolved gas levels have been relatively constant at about 90 to 100 percent of saturation in the epilimnion during times of elevated N₂ gas. TDG measurements of over 110 percent of saturation in the epilimnion were observed prior to nitrate addition during times of extremely high [130 to 160 percent of saturation] oxygen levels due to high rates of photosynthesis prior to the onset of elevated nitrogen gas levels.

July - September Average Hypolimnetic Saturation (South Deep)

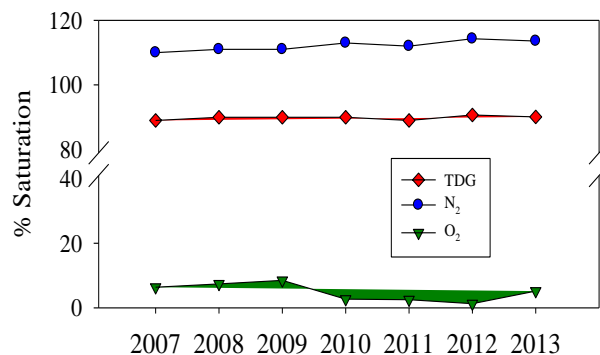


Figure 8 Dissolved Gas Percent Saturations in the Hypolimnion of Onondaga Lake

No adverse impacts to fish are evident in Onondaga Lake from dissolved gases given supersaturation conditions did not exist during the pilot test. As discussed in the 2007 feasibility analysis of nitrate addition (UFI and SU, 2007), elevated total dissolved gas concentrations can be of concern in aquatic ecosystems because of the potential for dissolved gas supersaturation and gas bubble trauma in aquatic organisms, particularly fish. Dissolved gas supersaturation can produce a variety of physiological effects that are harmful or fatal to fish and other aquatic organisms. The US Environmental Protection Agency has published TDG water quality guidelines which recommend a maximum TDG pressure of 110 percent of local atmospheric pressure (USEPA 1986). This recommendation is because fish can usually tolerate supersaturated water of less than 110 percent of saturation near the surface of the water. At a water depth of 3.3 feet (1 meter), most fish can tolerate a total gas pressure of 120 percent of saturation with tolerance increasing about 10 percent for each additional meter of water depth.

The need to add nitrate in the future is expected to decline gradually on an average annual basis. The need for continued nitrate addition will be evaluated annually based on prior year results, the lake's fluctuating seasonal hydrologic and nitrate inputs, and other factors. Improved phosphorus removal from Metro discharges since 2005 is 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 with inflows will reduce total mercury concentrations in SMU 8 surface sediments.

4.2 Oxygenation

The need for extensive infrastructure and the potential for increased colonization of SMU 8 sediment by organisms are disadvantages of adding oxygen compared to adding nitrate to the hypolimnion of Onondaga Lake.

Oxygenation remains unproven, potentially not effective and would likely result in more adverse impacts than nitrate addition for the type of application needed in Onondaga Lake to prevent release of methylmercury from SMU 8 sediment. While oxygenation has been used in lakes and rivers to improve water quality and eliminate fish kills, it has not yet been used specifically to address mercury release from sediment. A large scale, long-term pilot test would be needed to assess whether the entire footprint of the hypolimnion could be effectively oxygenated and to observe impacts of oxygenation on water quality and sediment dynamics.

Oxygenation would require significantly more in-lake infrastructure compared to nitrate addition. Oxygen would likely be delivered as a gas rather than as a liquid. Infrastructure for oxygenation would include in-water equipment, onshore evaporators or oxygen-generation units, and possibly high-voltage electrical service.

Oxygenation could potentially be implemented using a number of methods. The specific method evaluated as part of the Onondaga Lake Feasibility Study (Parsons et. al., 2004) is based on down-flow contact oxygenation implemented using a Speece Cone. Three to four cones would be needed to mix oxygen gas with oxygen-depleted water inside a contact chamber. This system would draw water into a chamber, dissolve oxygen into lake water, and provide oxygenated water at the same water depth. Each Speece Cone would be approximately 12 ft. in diameter and 20 ft.

tall. Oxygen delivery and power lines would run from the shoreline into the lake to the Speece Cones. Access to the lake bottom (e.g., anchoring of boats) would be restricted in the vicinity of underwater infrastructure.

A significant operational advantage for nitrate addition over oxygenation is that the nitrate solution has a specific gravity of 1.5 allowing the operator the ability to control the density of the diluted nitrate so the nitrate can remain close to the lake bottom and spread laterally across the deeper, stratified portion of the lake. It may not be feasible to apply oxygenation in a way that would result in highest dissolved oxygen concentrations in the deepest areas of the lake, where oxygen would be most beneficial.

Oxygenation could directly affect biological productivity in the deeper, stratified portion of the lake by promoting colonization by organisms within the sediments (Liboriussen et. al., 2009) which could increase vertical mixing of sediments and thereby adversely reduce the rate of ongoing natural recovery (Boudreau, 1997 as applied in the final design – Anchor QEA, 2012). The extent of colonization in SMU 8 sediment would likely be greater in an oxygenated hypolimnion than in the same hypolimnion undergoing nitrate addition. Burrowing activities of macroinvertebrates, for example, would greatly enhance sediment mixing and thus bring previously buried mercury closer to the sediment-water interface which would create a potential for increased methylmercury uptake by biota. Sampling for benthic macroinvertebrates during 2010 and 2012 indicate numbers may be increasing in shallower portions of SMU 8. An assessment of profundal zone benthic macroinvertebrates will continue in 2014 as part of the ongoing monitoring of natural recovery in SMU 8.

Adding oxygen to the hypolimnion of Onondaga Lake has the potential to increase turbulence and mixing between the epilimnion and hypolimnion and warm hypolimnion waters. These conditions could potentially reduce the duration of time the lake is stratified each summer. Operation of a Speece Cone in Camanche Reservoir in California resulted in an increase in the bottom temperature of the hypolimnion of 3 degrees Fahrenheit (Beutel and Horne, 1999).

Speece Cones have been installed in the United States at two locations comparable to Onondaga Lake. In 1994, a Speece Cone was installed in Camanche Reservoir in California. In 2009, a Speece Cone was installed in Marston Reservoir near Denver, Colorado (Dominick and DiNatale, 2009). Installation costs for a single Speece cone at these two locations exceeded comparable equipment costs for the nitrate addition pilot test completed in Onondaga Lake, and three or four Speece cones would likely be needed to add sufficient oxygen to Onondaga Lake. Annual costs for energy, labor and materials would also be higher for adding oxygen compared to nitrate largely due to energy requirements for generating oxygen.

4.3 Conclusions

Adding nitrate to deep waters in Onondaga Lake during summer months provides a significant environmental benefit to the lake by effectively inhibiting releases of methylmercury from lake sediments without adverse effects. This benefit was demonstrated by a three-year nitrate addition pilot study completed in 2013. Adding nitrate is protective of human health and the environment and complies with federal and state requirements that are applicable or relevant and

appropriate. Furthermore, adding nitrate to deep waters effectively builds on the benefit provided since 2004 by the conversion of ammonia in wastewater to nitrate at Metro. The alternative to adding nitrate would be to add oxygen after conducting an oxygenation pilot study. Oxygen addition would most likely not be as effective in Onondaga Lake as nitrate addition and would bring with it questions such as the suitability of adding extensive infrastructure in the lake. Therefore, full-scale addition of nitrate to Onondaga Lake is recommended in lieu of implementing an oxygenation pilot study.

A work scope for future nitrate addition will be submitted as an operations and monitoring plan for agency approval. This operations and monitoring plan will be submitted consistent with the nitrate addition Explanation of Significant Differences (ESD) being prepared by NYSDEC and USEPA.

Long-term monitoring will continue to be performed in Onondaga Lake to assess progress toward meeting the goals specified in the ROD, as well as to continue to confirm that nitrate addition does not result in adverse impacts on the environment.

5.0 REFERENCES

- Anchor QEA, 2012. *Onondaga Lake Capping, Dredging, Habitat and Profundal Zone (SMU 8) Final Design, Appendix M – MNR Modeling*. Prepared for Honeywell. Reviewed by Parsons and Exponent. February 2012.
- Benoit, J., Gilmour, C., Heyes, A., Mason, R., Miller, C., 2003. *Geochemical and Biological Controls over Methylmercury Production and Degradation in Aquatic Ecosystems*. In: Cai, Y., Brouds, O. (Ed.). Biogeochemistry of Environmentally Important Trace Elements, Symposium Series 835. American Chemical Society, pp. 262-297.
- Beutel, M. and A.Horne, 1999. *A Review of the Effects of Hypolimnetic Oxygenation on Lake and Reservoir Water Quality*. Lake and Reservoir Management, 15(4):285:297.
- Boudreau, B., 1997. Diagenetic Models and Their Implementation: Modeling Transport Reactions in Aquatic Sediments. New York: Springer.
- Camargo, J., A. Alonso and A. Salamanca. 2005. *Nitrate Toxicity to Aquatic Animals: A Review with New data for Freshwater Invertebrates*. Chemosphere 58:1255-1267.
- Dominick, S. and K. DiNatale, 2009. *Mile-High Decisions: Denver*. Lakeline. Fall 2009.
- Effler, S.W., O'Donnell, S. M., Prestigiacomo, A.R., O'Donnell, D.M., Gelda, R.K., Matthews, D.A., 2010. *The Effect of Municipal Wastewater Effluent on Nitrogen Levels in Onondaga Lake, a 36-Year Record*. Water Environment Research 82, 3-19.
- Exponent, Michigan Technological University, UFI and SU, 2011. *Data Report: Sediment Incubations and Supporting Studies for Onondaga Lake Sediment Management Unit (SMU) 8*. Prepared for Honeywell. July 2011.

- Kerin, E.J., Gilmour, C.C., Roden, E., Suzuki, M.T., Coates, J.D., Mason, R.P. 2006. *Mercury Methylation by Dissimilatory Iron-Reducing Bacteria*. Appl. Environ. Microbiol. 72, 7919-7921.
- Liboriussen, L., Søndergaard, M., Jeppesen, E., Thorsgaard, I., Grünfeld, S., Jakobsen, T.S., Hansen, K. 2009. *Effects of Hypolimnetic Oxygenation on Water Quality: Results from Five Danish Lakes*. Hydrobiologia 625, 157-172.
- Matthews, D. A., S. W. Effler and C. M. Matthews (Brooks). 2000. *Ammonia and toxicity criteria in polluted Onondaga Lake, New York*. Water Environment Research 72:731-741.
- Matthews, D.A., et. al., 2013. *Whole-Lake Nitrate Addition for Control of Methylmercury in Mercury-Contaminated Onondaga Lake, NY*. Environmental Research, 125, pages 52-60.
- New York State Department of Environmental Conservation and United States Environmental Protection Agency Region 2. 2005. *Record of Decision. Onondaga Lake Bottom Subsite of the Onondaga Lake Superfund Site*. July 2005.
- Parsons, Anchor Environmental, and Exponent. 2004. *Onondaga Lake Feasibility Study Report*. Onondaga County, NY. Three volumes. Prepared for Honeywell. Draft Final (final version). November 2004.
- Parsons and UFI. 2010. *Report for the Nitrate Application Field Trial in the Hypolimnion of Onondaga Lake*. Prepared for Honeywell. March 2010.
- Parsons and UFI. 2011, 2012 and 2013. *Work Plan for Pilot Test to Add Nitrate to the Hypolimnion of Onondaga Lake (2011) and Addendum 1 (2012) and Addendum 2 (2013)*. Prepared for Honeywell. March 2011, May 2012 and June 2013.
- Parsons and UFI, 2012. *Report for the First Year of the Nitrate Addition Pilot Test (2011) in the Hypolimnion of Onondaga Lake*. Prepared for Honeywell. August 2012.
- Parsons and UFI, 2013. *Report for the Second Year of the Nitrate Addition Pilot Test (2012) in the Hypolimnion of Onondaga Lake*. Prepared for Honeywell. September 2013.
- Parsons and UFI, 2014. *Report for the Third of Three Years of the Nitrate Addition Pilot Test (2013) in the Hypolimnion of Onondaga Lake*. Prepared for Honeywell. June 2014.
- Pickhardt, P.C., Fisher, N.S., 2007. *Organic Material: Accumulation of Inorganic and Methylmercury by Freshwater Phytoplankton in Two Contrasting Water Bodies*. Environ. Sci. Technol. 41, 125-131.
- Rolfhus, K.R., Hall, B.D., Monson, B.A., Paterson, M.J., Jeremiason, J.D., 2011. *Assessment of Mercury Bioaccumulation Within the Pelagic Food Web of Lakes in the Western Great Lakes Region*. Ecotoxicology 20, 1520-1529.
- Todorova, S.G., Driscoll, C.T., Matthews, D.A., Effler, S.W., Hines, M.E., Henry, E.A., 2009. *Evidence for Regulation of Monomethyl mercury by nitrate in a seasonally stratified, eutrophic lake*. Environ. Sci. Technol. 43, 6572-6578.

- United States District Court, Northern District of New York. 2007. State of New York and Denise M. Sheehan against Honeywell International, Inc. Consent Decree Between the State of New York and Honeywell International, Inc. Senior Judge Scullin. Dated October 11, 2006. Filed January 4, 2007.
- UFI. 2009. *Report on the 2008 Dye Tracer Study to Evaluate Transport and Mixing in the Hypolimnion of Onondaga Lake*. Prepared for Honeywell. July 2009.
- UFI and SU. 2007. *Preliminary Feasibility Analysis for Control of Methylmercury Production in the Lower Waters of Onondaga Lake Through Nitrate Addition*. A report prepared for Honeywell by Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Center for Environmental Systems Engineering, Syracuse, NY.
- UFI and SU, 2008. *Interpretive Report Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake: 2006 Study*. Prepared for Honeywell. April 2008.
- UFI, Anchor QEA, Onondaga County Department of Water Environment Protection, Rudstam, L., and Walker, W., 2014. *Onondaga Lake Ambient Monitoring Program 2012 Annual Report*. February 2014.
- US Environmental Protection Agency, 1986. *Quality Criteria for Water*. Washington, DC. Office of Water Regulations and Standards. EPA 440/5-86-001. May 1986,
- Wollenberg, J.L., Peters, S.C., 2009. *Mercury Emission from a Temperate Lake during Autumn Turnover*. Sci. Total Environ. 407, 2909-2918.