Preliminary Feasibility Analysis for Control of Methylmercury Production in the Lower Waters of Onondaga Lake Through Nitrate Addition

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Table of Contents

Executive Summary

The New York State Department of Health has posted fish consumption advisories for Onondaga Lake because of contamination in fish by chemicals of concern including mercury (Hg). Exposure of humans and wildlife to methylmercury (MeHg) largely occurs through fish consumption. This exposure is a health concern because MeHg is a neurotoxin that strongly bioaccumulates in aquatic food webs. The deep water sediments of Onondaga Lake are a source of MeHg to the water column of the lake during the June to October interval when the lower layers of the lake are anoxic. Production of MeHg in anoxic portions of the water column may also contribute to accumulations of MeHg in the hypolimnion, which are observed annually. In-lake production of MeHg represents a potentially important pathway for bioaccumulation of Hg in the food web of the lake. Therefore, evaluating methods to control MeHg production in the lake is an integral component of a larger program designed to remediate Hg contamination in this ecosystem.

Sulfate-reducing bacteria (SRB) are the dominant methylators of inorganic Hg in freshwater sediments. The activity of SRB, and consequently the production of MeHg, is stimulated by sulfate (SO_4^{2-}) and labile organic matter. Onondaga Lake is culturally eutrophic and naturally enriched with sulfate. These characteristics promote high rates of sulfate-reduction in the lake. Sulfate reduction is a bacterially mediated oxidation-reduction (redox) reaction involved in the terminal decomposition of organic matter. Oxygen-reduction and nitrate-reduction are alternate, energetically favorable decomposition pathways that are common in lake ecosystems. The well-established hierarchy of redox processes suggests that SRB activity in lake sediments and related internal production of MeHg might be inhibited by maintenance of adequate concentrations of alternate energetically favorable electron acceptors, such as oxygen (O_2) and/or nitrate (NO_3^-). No direct evidence for the inhibition of Hg methylation by NO_3^- or any other electron acceptor is available at the field scale. However, laboratory studies have demonstrated the potential for control of MeHg production by addition of terminal electron acceptors, including NO_3^-.

The commencement of year-round nitrification at the Metropolitan Syracuse Waste Water Treatment Facility (Metro) in 2004 caused NO_3^- concentrations in Onondaga Lake at spring turnover to increase by approximately 50% over historic levels. As a result, the interval of NO_3^- reduction in the hypolimnion was extended by about 50 days compared to earlier years. In-lake monitoring in 2004 and 2005 established that the extended interval of NO_3^- reduction was accompanied by a delay in the onset of sulfide and MeHg accumulation. Major accumulations of sulfide and MeHg in the hypolimnion were not observed until September when the NO_3^- pool was largely depleted. These findings suggest that the presence of NO_3^- as an alternate electron acceptor may have abated SO_4^{2-} reduction and associated MeHg production in the sediments. Preliminary assessments of data collected as part of a more intensive monitoring in 2006 continue to support this mechanism as a regulator of MeHg production and transport to the hypolimnion.

The observations from 2004 and 2005 suggest that major additional decreases in MeHg production might be attained by maintenance of adequate NO_3^- concentrations in the hypolimnion until fall turnover. Under current conditions this would require substantial augmentation of the hypolimnetic NO_3^- pool during the July to October interval. However, it is reasonable to expect that the magnitude of NO_3^- amendments would decrease in the future associated with recent reductions in primary production, cleanup of Hg sources to the lake, and burial of Hg in the sediments. Nitrate addition has been used as a water quality management technique in a number of lakes, primarily as a method to control phosphorus release from sediments. Various chemical forms of NO_3^- are suitable for treatment of lake sediments, including calcium nitrate ($Ca(NO_3)_2$), sodium nitrate ($NaNO_3$), and potassium nitrate (KNO_3). Calcium nitrate is a widely available form of NO_3^- that has been used extensively to treat lake sediments.

Preliminary calculations suggest that NO_3^- addition to the hypolimnion at a rate of approximately 1000 kg NO_3^- -N/day during the July to October interval would be required to maintain NO_3^- concentrations >1 mgN/L at the sediment-water interface and abate the activity of SRB and related MeHg production. This corresponds to an application rate of about 7540 L/day for a concentrated $Ca(NO_3)_2$ solution. Year-to-year variations in the NO_3^- addition required to abate SO_4^{2-} reduction would result from interannual differences in organic carbon deposition, runoff, and the duration of stratification. Data collected during 2006 will help refine these estimates and provide information on the associated decrease in MeHg production that might be expected from the proposed treatment.

Application of the concentrated solution to the hypolimnion of the lake could be made from either a boat-based or shore-based delivery system. A boat-based delivery system would have several advantages, including the ability to carefully control the total rate of NO_3^- addition and its vertical and horizontal distribution. In either case, the NO_3^- salt solution would require dilution of approximately 300:1 in order to attain an appropriate density prior to release into the lake. The necessary dilution could be achieved by mixing with ambient lake water and release through a multi-port diffuser.

A preliminary analysis was conducted to evaluate the potential impacts associated with the addition of NO_3^- salts to the hypolimnion of Onondaga Lake. This analysis indicates that NO_3^- addition would not result in noteworthy negative water quality impacts in Onondaga Lake or downstream ecosystems. However, the concentrations of several constituents should be tracked prior to and during a proposed NO_3^- addition, including nitrite (NO_2^-), total ammonia (T-NH_3), nitrogen gas (N_2), and total dissolved gas (TDG). Because a NO_3^- addition program would maintain an anoxic hypolimnion, it is anticipated that exposure of aquatic organisms to Hg contaminated sediments would be limited. Addition of $Ca(NO_3)_2$ would likely cause a small increase in calcite ($CaCO_3$) deposition and contribute in a small but positive way to burial of Hg contaminated sediments. This preliminary analysis suggests that hypolimnetic NO_3^- addition holds promise as a method of abating MeHg production in Onondaga Lake with minimal negative environmental effects.

Scientific Justification for the Application of Nitrate to Control Methylmercury Production

Background/Problem Statement

Mercury (Hg) contamination of the water column and sediments of aquatic ecosystems raises concerns related to biological exposure, including potential health effects in humans and wildlife caused by consumption of contaminated fish (Clarkson 1990, 1998). Methylmercury (MeHg) is the form of primary concern because it is a neurotoxin that strongly bioaccumulates in food webs. External loads of Hg to aquatic ecosystems occur largely in inorganic forms, while MeHg concentrations reflect the net effect of *in situ* methylation and demethylation processes (Benoit et al. 2003). The anoxic sediments of lakes have been found to be particularly active locations for MeHg production (Henry et al. 1995, Pak and Bartha 1998). Production of MeHg has also been observed in anoxic hypolimnia (Watras et al. 1995, Regnell et al. 1997). Processes that can influence MeHg concentrations in lake sediments include *in situ* methylation and demethylation (Pak and Bartha 1998), activity of sulfate-reducing bacteria (Gilmour et al. 1992), and HgS precipitation by methylating bacteria (Benoit et al. 1999).

Sulfate-reducing bacteria (SRB) predominately facilitate the methylation of inorganic Hg in freshwater sediments (Benoit et al. 2003). The activity of SRB, and consequently the production of MeHg, is stimulated by sulfate in freshwater sediments (Benoit et al. 2003). Sulfate (SO_4^{2-}) reduction is a bacterially mediated oxidation-reduction (redox) reaction involved in the decomposition of organic matter. Sulfate reducing bacteria (SRB) use SO_4^{2-} as the terminal electron acceptor during the oxidation of organic matter and produce hydrogen sulfide (H_2S), (eqn. 1; Westrich and Berner 1984)

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (1)$$

where CH_2O is a generic representation for organic matter. Two moles of organic carbon (with an oxidation state of zero) are stabilized and one mole of H_2S is produced per mole of SO_4^{2-} reduced. Bisulfide (HS^-) is the dominant form of sulfide at the slightly alkaline pH levels (7.0-7.5) found in the hypolimnion of Onondaga Lake (although with a pK_{a1}=7.0, significant concentrations of H_2S are also evident). Sulfate reduction is the major anaerobic decomposition pathway in marine systems (Westrich and Berner 1984), but it is usually a secondary pathway in productive freshwaters because concentrations of SO_4^{2-} are typically low (Ingvorsen et al. 1981, Smith and Klug 1981). A SO_4^{2-} concentration of 0.2 mmol/L (~ 19.2 mg/L; e.g., higher than found in most lakes) has been reported to be non-limiting to SO_4^{2-} reduction (Winfrey and Zeikus 1977). Early production of HS^- may be immobilized via precipitation with metals (e.g., FeS; Davison 1993), but subsequent production of this soluble constituent, greater than the molar concentration of metals, accumulates in sediment pore water and in the hypolimnion. The vast majority of SO_4^{2-} reduction is localized in the upper sediments, where the process can be supported by hypolimnetic concentrations (e.g., diffusion into sediments) of this electron acceptor, though the process has been documented in anoxic hypolimnia (Ingvorsen and Brock 1982).

The other terminal decomposition processes that are important in freshwater systems are aerobic respiration, nitrate reduction, manganese reduction, iron reduction, and methanogenesis. A sequence of organic matter degradation processes in sediments is generally upheld in time and space (vertically), according to the free energy yields of various electron acceptors. Thermodynamic calculations establish that energy yields decrease progressively in the order $O_2 > NO_3^- > Mn^{4+} > Fe^{3+} > SO_4^{2-} > CO_2$ (Stumm and Morgan 1996). Accordingly, sulfate reduction proceeds in the absence of energetically favorable electron acceptors such as O_2, NO_3^-, Mn^{4+} and Fe^{3+}. In addition, sulfate reduction and the other decomposition pathways are affected by the availability of labile organic substrate, and are thus inextricably linked to the level of primary production and the flux of organic matter to the sediments.

Internal production of MeHg in lakes can cause increases in hypolimnetic MeHg during intervals of anoxia (Bloom and Effler 1990, Sharpe 2004) and represents an important pathway for biological exposure and contamination. Thus, decreased internal production of MeHg is an important rehabilitation goal for Hg-polluted lakes. The redox sequence described above suggests that SRB activity in lake sediments and related internal loading of MeHg to the water column might be inhibited or blocked by maintenance of adequate concentrations of alternate energetically favorable electron acceptors. Although O_2, NO_3^-, Mn^{4+} and Fe^{3+} are all viable candidates to block sulfate reduction from a thermodynamic perspective, their feasibility and performance are expected to vary widely as a function of key ecosystem characteristics, including water chemistry, primary production, and the structure of biological communities. In addition, the choice of the electron acceptor should be consistent with the rehabilitation goals for the impacted ecosystem.

The purpose of this report is to provide background information to help evaluate the concept of nitrate addition for control of MeHg production in Onondaga Lake, New York. The overarching objectives of this report are to preliminarily evaluate the feasibility and potential impacts of controlling MeHg production in the lower waters of the lake through nitrate addition. An abbreviated retrospective analysis of redox conditions in Onondaga Lake is presented based on a long-term (1978 – 2005) monitoring program. Insights from this analysis are used to evaluate management alternatives for the control of MeHg production. Water column results are presented from the summer of 2005, which provide preliminary support for the concept of nitrate addition to abate sulfate reduction and MeHg production. Note under support from Honeywell, a detailed analysis of redox chemistry and Hg dynamics was conducted during the field season of 2006. These data will greatly inform the interactions of NO_3^- supply and HS^- and MeHg accumulation in the hypolimnion of Onondaga Lake. The historic usage of nitrate addition as a management alternative for lakes is reviewed and the feasibility of its use in Onondaga Lake is assessed. In addition, potential impacts of nitrate addition on the physical, chemical and biological status of the lake are preliminarily discussed.

System Description

Onondaga Lake

Onondaga Lake (lat. 43º 06′ 54″, long. 76º 14′ 34″) is an alkaline, hard-water, stratifying ecosystem located in metropolitan Syracuse, NY (Figure 1). The lake has a surface area of 12.0 km^2, a volume of 131 x 10^6 m^3, and a maximum depth of 20 m. The lake is naturally enriched in SO_4^{2-} (~ 1.6 mmol/L at spring turnover), associated with gypsum deposits in the watershed (Effler 1996). A population of approximately 450,000 people presently resides in the lake's watershed of 642 km^2, located almost entirely within Onondaga County. The lake flushes rapidly, an average of approximately 4 times per year (Effler 1996). This characteristic is particularly important with respect to tracking the effects of rehabilitation efforts, because the water column of the lake responds rapidly to changes in external loading (Doerr et al. 1994, Effler et al. 2001a). Water exits the lake at its northern end, via a navigable channel, and enters the Seneca River (Figure 1). This promotes migrations of fish to and from the lake, and establishes pathways between various local lakes, including Lake Ontario (Figure 1).

Early European development of the area was predicated on the rendering of salt (NaCl) from springs along the shores of the lake (Effler and Matthews 2003). These salt springs supported an active salt recovery industry and led to the development of railroads, the Erie Canal, and growth of additional industry. Over the past 100 years, Onondaga Lake has received industrial and municipal wastewater discharges that have affected the quality of water, sediment, and biota. Industrial discharges included mercury released from two mercury cell chlor-alkali facilities operated by predecessors of Honeywell. Both plants had ceased operation by 1988. Municipal waste has been discharged to the surface waters of the lake at its southern end by the Metropolitan Syracuse Wastewater Treatment Plant (Metro, operated by Onondaga County; Figure 1) since the 1920s. Metro presently serves about 300,000 residents of Onondaga County, as well as a number of industries. The hydrologic contribution of this facility to the lake is 20% of the total inflow on an annual basis, and is the largest single source of water in August of most years (Effler 1996). Metro is also the dominant source of nitrogen (N) and P to the lake.

On June 23, 1989, Onondaga Lake was added to the New York State Registry of Inactive Hazardous Waste disposal sites. On December 16, 1994, Onondaga Lake and areas upland of the lake that contribute or have contributed contamination to the lake system were added to the US Environmental Protection Agency’s (USEPA’s) National Priorities List (NPL). The lake has been the subject of a comprehensive remedial investigation and feasibility study, conducted by Honeywell under the direction of NYSDEC and USEPA. In 2005, NYSDEC issued a Record of Decision (ROD) that documented NYSDEC's and EPA's selection of a remedy for Onondaga Lake (NYSDEC 2005). With respect to Metro, Onondaga County signed an Amended Consent Judgment (ACJ) in 1998 that detailed a rehabilitation program for water quality issues associated with discharge of municipal wastewater. Comprehensive rehabilitation efforts for the lake guided by the ROD and ACJ, and development of a major tourist and entertainment venue on its shores, are presently underway.

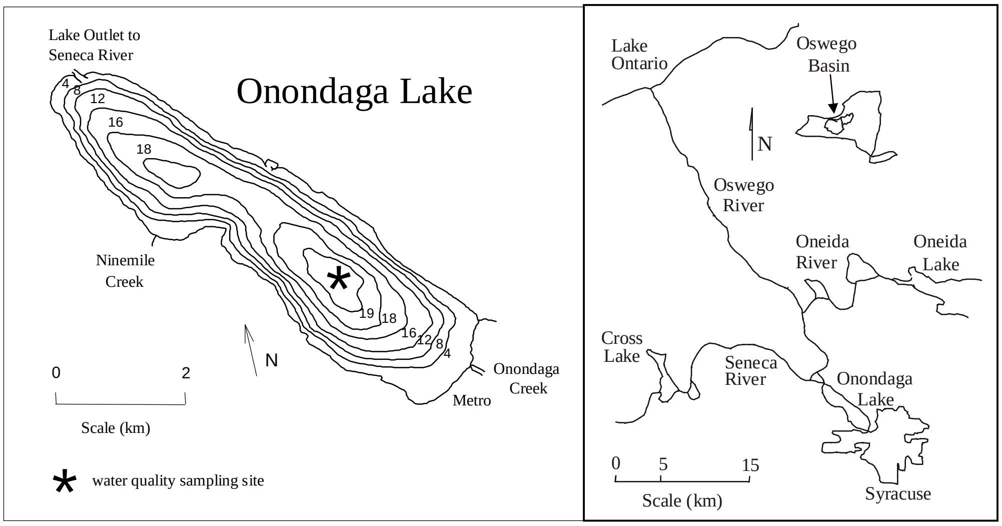

Figure 1. Onondaga Lake with long-term monitoring site, Metro Waste Water Treatment Plant, outlet to Seneca River, and location within the Oswego Basin and New York.

Current Rehabilitation Efforts

The ROD (NYSDEC 2005) adopts a hypolimnetic oxygenation pilot study as a potentially applicable means of reducing the formation of methylmercury in the water column. Oxygenation is intended to: (1) reduce Hg methylation in the hypolimnion and reduce concentrations of dissolved Hg; (2) reduce the flux of methyl Hg from profundal sediments; and (3) thereby result in decreased concentrations of Hg in fish tissue (NYSDEC 2005). There is no precedent for the use of hypolimnetic oxygenation to reduce MeHg production in the scientific literature, though Beutel and Horne (1999) speculated that maintenance of oxic conditions may help decrease Hg contamination in lake biota by reducing sediment release. Hypolimnetic aeration/mixing has recently been tested as a method to reduce MeHg concentrations in the water column of Almaden Lake, California, with positive preliminary results (John Nolan, personal communication). The ROD calls for the conduct of oxygenation "pilot studies". Addition of NO_3^- to the hypolimnion will also be evaluated as an alternate method to reduce internal MeHg production (State of New York 2006).

The ACJ is guiding the rehabilitation program for the water quality problems of the lake associated with domestic waste. The program, to be executed by Onondaga County, consists of three stages, extending over a 15 year period (1998 - 2012), at an estimated cost of $380 million. It calls for continued discharge of Metro's effluent to the southern end of the lake, but with reduced concentrations of total ammonia (T-NH_3) and total P (TP). The first stage limited T-NH_3 and TP concentrations in the Metro effluent to 1997 levels. The aeration system for biological treatment of Metro was upgraded in 1998. Stage 2 required the Metro effluent T-NH_3 concentration be reduced to 1.65 and 3.3 mgN/L for the June-to-October and November-to-May intervals, respectively, starting in May 2004. Additionally, the effluent TP was to be reduced to approximately 0.12 mg/L by April 2007 (~ 4.5 -fold reduction from 1997 levels; operation started in spring 2004). Stage 3 requires that T-NH_3 be reduced to 1.0 and 2.0 mgN/L for the two intervals, and that TP be reduced to 0.02 mg/L, by December 2012. These effluent limits were developed as part of two Total Maximum Daily Load (TMDL) analyses that had goals of eliminating in-lake violations of the ammonia standard(s) (NYSDEC 1998a) and not exceeding a summer average epilimnetic TP concentration of 20 µg/L (NYSDEC 1998b). The long-term approach implicit in the ACJ for recovery of the oxygen resources of the lake is to reduce phytoplankton primary production and associated deposition of particulate organic matter into the hypolimnion through reductions in external P loading.

Implications of Management Initiatives for Sulfate Reduction and other Redox Processes

A number of the management initiatives directed at the rehabilitation of Onondaga Lake have implications for redox processes, including sulfate reduction. For example, upgraded treatment of nitrogen and phosphorus at Metro affects the availability of electron acceptors and the deposition of labile organic carbon to the sediments. The achievement of year-round nitrification at Metro has substantially increased in-lake concentrations of NO_3^- and decreased concentrations of T-NH_3. The profound effects of increased NO_3^- concentrations on redox conditions in the hypolimnion, including the stimulation of NO_3^- reduction and inhibition of sulfate reduction, are presented subsequently in the retrospective analysis. Recent improvements in phosphorus treatment have resulted in lower levels of primary production (Effler et al. 2006). An associated decrease in the flux of organic matter to the sediments and lower rates of decomposition are a reasonable expectation.

Monitoring Specifications for Historic Data Set

The long-term monitoring program that supported this analysis has been described previously in several related retrospective analyses (Effler 1996, Matthews and Effler 2006a, 2006b, Matthews et al. 2005, 2006). Detailed descriptions of laboratory methods and data analyses are provided in those contributions. All data presented here were collected from a long-term monitoring site in the southern basin near the maximum depth of Onondaga Lake (19.5 m; Figure 1). This site is generally representative of lake-wide conditions (Effler 1996). Sampling was usually conducted weekly over the April to October interval from 1978 to 2005. Samples were collected at depth intervals of 1 or 2 m. Daily vertical profiles of DO and chlorophyll **a** (fluorescence) were made with calibrated probes from a robotic monitoring platform (RUSS, Apprise Technologies) over the 2000 to 2005 interval.

Retrospective Analysis of Onondaga Lake – Redox Processes

Value of Retrospective Analyses

The rates and relative importance of decomposition processes in aquatic sediments are determined by the availability of labile organic substrates and electron acceptors (Capone and Kiene 1988). However, large changes in organic carbon deposition and availability of electron acceptors are rarely encountered in natural ecosystems. Therefore, insights into the effects of variations in these factors have come primarily from laboratory experiments (e.g., Kelly and

Chynoweth 1981), mesocosm experiments (e.g., Jones and Simon 1980) and cross-site studies (e.g., Kelly et al. 1988). Schindler (1998) has demonstrated that experiments conducted at less than ecosystem scales may often fail to accurately reflect whole-lake responses. Although whole-lake experiments allow for assessments of response to large perturbations at the appropriate spatial and temporal scales (Schindler 1998, Kitchell and Carpenter 1993), opportunities to conduct experiments at these scales are rare. Retrospective analyses of long-term data sets for lakes undergoing either degradation or rehabilitation provide opportunities to expand our understanding of lake response to perturbation (e.g., Lehman 1988). In addition, insights gained from retrospective analyses of long-term data sets can be used to guide future management initiatives.

The retrospective analysis presented here focuses on long-term trends in redox constituents and related drivers. Assessments of management alternatives for the abatement of MeHg production should be informed by an understanding of the redox processes that regulate the cycling of Hg. The system-specific information presented in this retrospective analysis provides a scientific foundation for management decisions related to the reduction of MeHg concentrations in the hypolimnion of Onondaga Lake.

Conceptual Model of Decomposition Processes in Onondaga Lake

As indicated above, sulfate reduction is regulated primarily by the availability of SO_4^{2-}, labile organic matter, and energetically favorable electron acceptors (e.g., O_2, NO_3^-). Thus, management initiatives directed at inhibiting the activity of SRB must consider the major pathways involved in the production and decomposition of organic matter and the interactions amongst the various decomposition processes. The vertical stratification of redox processes according to their energy yields is the basis for the classical model of biogeochemical cycling in aquatic sediments (Lovley and Klug 1986, Capone and Kiene 1988, DiToro 2001).

A generalized conceptual model of the major decomposition processes in Onondaga Lake sediments is presented here (Figure 2), which includes important drivers and metabolic pathways. The operation of aerobic respiration, denitrification and sulfate reduction in the surficial sediments and methanogenesis in the deeper sediments is consistent with thermodynamic considerations and pore water measurements from other ecosystems (e.g., Urban et al. 1997, Van Den Berg et al. 2000). The external electron acceptors, O_2, NO_3^-, and SO_4^{2-} are relatively soluble and tend to diffuse into the upper sediments (Figure 2) where they are utilized in the oxidation of recently deposited organic matter or reduced chemical species. Gelda et al. (1995) estimated that >70% of SOD in Onondaga Lake was associated with the oxidation of reduced chemical species. Methanogenesis predominates in the deeper sediments beyond the diffusive limits of external electron acceptors (Matthews et al. 2005). This model forms the conceptual foundation for the retrospective analysis of redox processes in Onondaga Lake and supports the development of the strategy to abate sulfate reduction through the addition of an alternate electron acceptor such as NO_3^-.

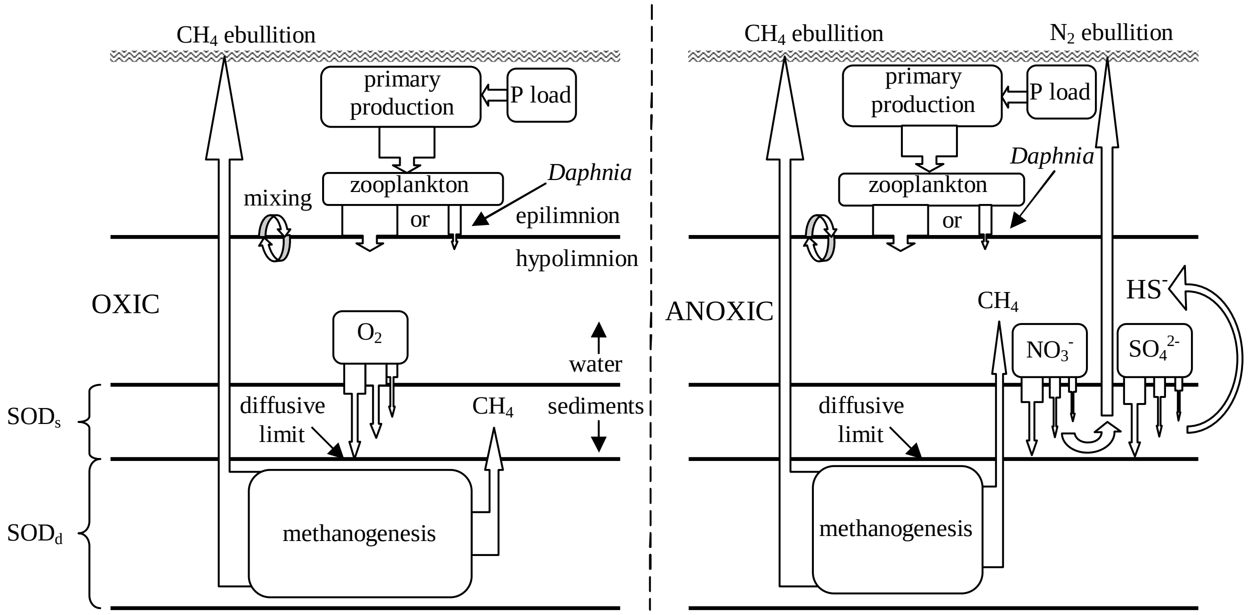

Figure 2. Conceptual models of processes of decomposition in oxic and anoxic hypolimnion and sediments, with epilimnetic drivers, metabolic pathways and byproducts identified.

Progression of Redox Processes and Consistency with Thermodynamics

Vertical profiles of key redox constituents are presented for spring (Figure 3a), mid-summer (Figure 3b and c), late summer (Figure 3d and e), and the beginning of fall turnover (Figure 3f) for 1990. The patterns depicted here have been recurring (Effler et al. 1988, Brooks and Effler 1990, Addess and Effler 1996). Concentrations of NO_3^- and T-NH_3 were both extraordinarily high throughout the water column at spring turnover (~ 1.5 mg N/L in 1990, Figure 3a). The reduced byproducts of anaerobic metabolism, CH_4 and HS^-, were absent during this oxygenated interval, and in oxygenated layers throughout the year. By mid-summer the hypolimnion of the lake was anoxic (Matthews and Effler 2006a, 2006b) and the NO_3^- pool had been consumed (Figure 3b and c). Marked progressive increases of T-NH_3 with depth within the hypolimnion (Figure 3b) reflect production as a byproduct of both aerobic and anaerobic metabolism. This vertical pattern was recurring for the byproducts of the various metabolic pathways (Figure 3b-e), reflecting the localization of these decomposition processes within the sediments (or at the sediment-water interface) in combination with limited mixing within the hypolimnion (Effler et al. 1988, Addess and Effler 1996).

The operation of methanogenesis and SO_4^{2-} reduction was clearly manifested by mid-summer of 1990 through the presence of CH_4 and, at somewhat lower concentrations, HS^- (Figure 3c). The continued operation of these decomposition processes through summer stratification has been manifested annually through progressive increases in CH_4, HS^-, and T-NH_3 within the hypolimnion, which in 1990 reached their highest levels in mid-September (Figure 3d and e). By the onset of fall turnover CH_4 and HS^- are eliminated from the water column as a result of the rapid oxidation of these constituents (Effler et al. 1988, Addess and

Effler 1996, Gelda and Auer 1996). The fate of the other potential source of oxygen demand, T-NH_3, has varied amongst years. The major reduction in T-NH_3 and increase in NO_3^- with the onset of turnover (Figure 3d and f) in 1990 reflected the operation of in-lake nitrification in that year, and the exertion of the associated oxygen demand, as substantiated by Gelda et al. (2000) through application of validated nitrogen and oxygen models.

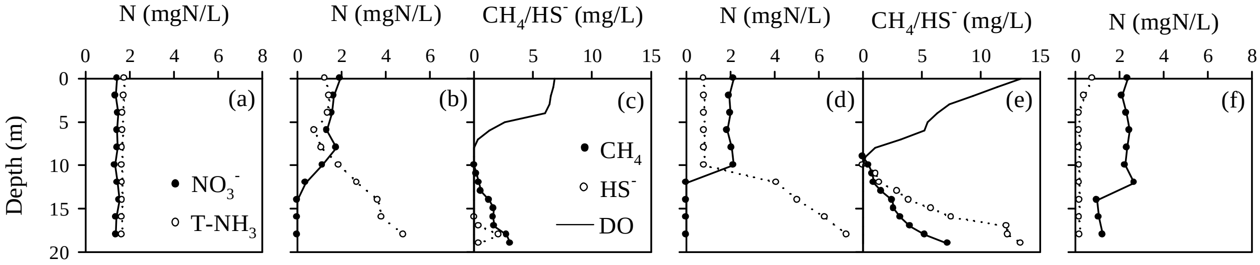

Figure 3. Vertical profiles of redox constituents on selected days in Onondaga Lake in 1990: (a) NO_3^- and T-NH_3, 19 April, (b) NO_3^- and T-NH_3, 25 July, (c) DO, CH_4, and HS^-, 25 July, (d) NO_3^- and T-NH_3, 18 September, (e) DO, CH_4, and HS^-, 18 September, and (f) NO_3^- and T-NH_3, 22 October. CH_4 and HS^- values are presented as mgC/L and mgS^{2-}/L, respectively.

Vertical profiles of electron acceptors and decomposition byproducts from similar dates in 2004 depict substantial shifts from earlier years (Figure 4). The concentration of NO_3^- at spring turnover (2.2 mgN/L; Figure 4a) was 57% higher in 2004 than in 1990 (1.4 mgN/L; Figure 3a). In contrast, the spring turnover concentration of T-NH_3 in 2004 (0.4 mgN/L; Figure 4a) was approximately 4-fold lower than in 1990 (1.7 mgN/L; Figure 3a). The principal driver of these marked changes in the nitrogen speciation of the lake was the operation of year-round nitrification at Metro. As a consequence of higher NO_3^- concentrations during spring turnover and a similar rate of depletion of the larger hypolimnetic NO_3^- pool (subsequently), levels of NO_3^- in the hypolimnion were markedly higher in July 2004 than in July 1990 (Figure 3b and 4b). By early October of 2004, however, the hypolimnetic pool of NO_3^- had been almost entirely consumed via the denitrification process (Figure 4d). Complete fall turnover was attained by 1 November, resulting in vertically uniform concentrations of NO_3^- and T-NH_3 (Figure 4f).

Hypolimnetic concentrations of CH_4 were somewhat lower in 2004 (Figure 4c and e) than in 1990 (Figure 3c and e). This change is attributable to a systematic long-term decrease in methanogenesis that followed an abrupt reduction in organic carbon deposition in 1987 (Effler et al. 2001, Matthews et al. 2005). A more conspicuous decrease was observed for HS^- concentrations (Figure 3e and 4e). The maximum volume-weighted hypolimnetic concentrations of HS^- were 4.6 mgS^{2-}/L and 2.1 mgS^{2-}/L in 1990 and 2004, respectively. The marked decrease in HS^- production in 2004 was apparently caused by inhibition of SO_4^{2-} reduction by the higher NO_3^- concentrations and the energetically favorable denitrification process.

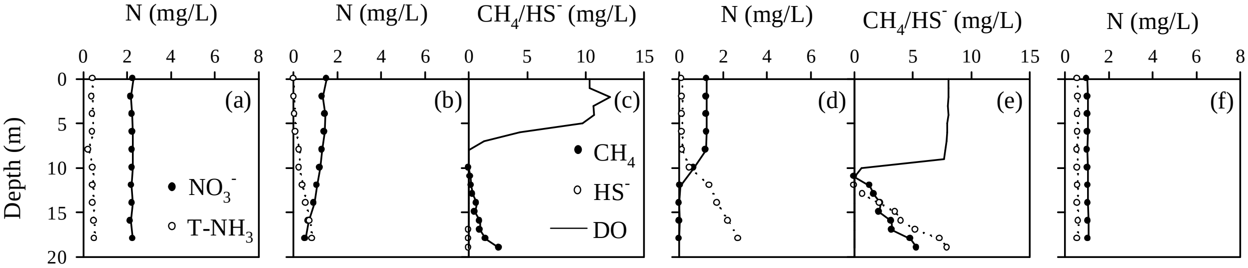

Figure 4. Vertical profiles of redox constituents on selected days in Onondaga Lake in 2004: (a) NO$_3^-$ and T-NH$_3$, 19 April, (b) NO$_3^-$ and T-NH$_3$, 26 July, (c) DO, CH$_4$, and HS$^-$, 26 July, (d) NO$_3^-$ and T-NH$_3$, 4 October, (e) DO, CH$_4$, and HS$^-$, 4 October, and (f) NO$_3^-$ and T-NH$_3$, 1 November. CH$_4$ and HS$^-$ values are presented as mgC/L and mgS^{2-}/L, respectively.

Seasonal patterns of the hypolimnetic pools for either the electron acceptor (Figure 5a and b) or the reduced byproduct (Figure 5c and d) of the four most important decomposition pathways of in Onondaga Lake, along with T-NH$_3$ (Figure 5e), are presented for two years to depict the sequence of processes and contrast conditions for these years. The selected years depict substantial differences in certain conditions that reflect changes in anthropogenic drivers. The pool sizes were calculated from vertical profiles of each constituent and hypsographic data for the lake (Effler 1996), adopting 10.5 m as the upper bound of the hypolimnion (Matthews and Effler 2006a, 2006b, Matthews et al. 2005), and normalizing by the area of this layer. A nearly linear decrease in the hypolimnetic mass of DO is observed in Onondaga Lake (Figure 5a, Matthews and Effler 2006a) and many other lakes (Wetzel and Likens 2000). Following adjustments for vertical mixing-based inputs from the epilimnion, the slope represents an estimate of the areal hypolimnetic oxygen deficit (AHOD; Matthews and Effler 2006a). The AHOD values were similar for 1990 and 2004 (Figure 5a). The DO depletion is localized at the sediment-water interface (i.e., associated with the exertion of sediment oxygen demand (SOD; Matthews and Effler 2006a). SOD can be partitioned into two components, a near-surface component (SOD$_s$) associated with decomposition of recently deposited (e.g., the same year) organic matter, and the other associated with decomposition in deeper deposits (SOD$_d$; e.g., older and more recalcitrant, Figure 2; SOD = SOD$_s$ + SOD$_d$; DiToro 2001, Matthews and Effler 2006a). Both components of SOD are exerted primarily through the oxidation of reduced byproducts of anaerobic decomposition (Gelda et al. 1995). Anoxia was first established in the bottom waters in late May and occurred throughout the hypolimnion by late June in these two years (Figure 5a).

Depletion of NO$_3^-$ (Figure 5b) and accumulations of the three metabolic byproducts (Figure 5c-e) have also proceeded at approximately linear rates within the hypolimnion (Matthews et al. 2006). A higher depletion rate for NO$_3^-$ was observed in July and August of 2004 following the establishment of anoxia in the hypolimnion. The initial pool size of NO$_3^-$ was approximately 50% higher in April 2004 (Figure 5b), reflecting the establishment of year-round nitrification treatment at Metro. Despite the large difference in initial concentrations of NO$_3^-$, similar depletion rates were observed for the two years. As a result the NO$_3^-$ pool persisted (denitrification proceeded) about 50 days longer in 2004 than 1990. Low levels of HS^- and CH_4 were present in the lower waters soon after the development of anoxic conditions, which occurred by late June of both 1990 and 2004 (Figure 5a, c, d). The CH_4 pool increased immediately and progressively following the onset of hypolimnetic anoxia (Figure 5d), while substantial accumulations of HS^- were delayed by about 30 days in 1990 and more than 60 days in 2004 (Figure 5c). The onset of substantial SO_4^{2-} reduction was shifted later in 2004 because of the initially larger pool of NO_3^-, resulting in a maximum pool of HS^- that was 2-fold smaller in 2004 than in 1990. Differences in the timing of the peak pool sizes for both HS^- (Figure 5c) and CH_4 (Figure 5d) between the two years (mid-September versus late September) reflect the effects of interannual differences in the mixing/stratification regime (i.e., meteorology; Owens and Effler 1989).

The timing of accumulations of CH_4 (Figure 5d) has been superficially inconsistent with thermodynamic constraints, as methanogenesis appears to have proceeded concurrently with NO_3^- reduction (Figure 5b) and substantially before the onset of SO_4^{2-} reduction (Figure 5c). The explanation, which retains thermodynamic consistency, is that CH_4 is produced at subsurface sediment depths below which the favored electron acceptors, DO, NO_3^-, and SO_4^{2-}, can reach through diffusion from the overlying water column (Figure 2, Matthews et al. 2006). This hypothesis is supported by a sediment pore water CH_4 profile (with the corresponding overlying water column profile) collected in 1995 (Figure 6). The linear decrease from a maximum at about 12 cm up towards the sediment-water interface is a manifestation of regulation by the diffusion process (Lovely and Klug 1986). Accordingly, the substrates for methanogenesis are older and more recalcitrant (Matthews et al. 2005). Thus the rate of this process should be expected to be relatively insensitive to seasonal variations in the downward flux of organic material from the productive layers. It is reasonable to assume that the upward flux of CH_4 is largely responsible for SOD_d (Figure 2). Despite similar timing for the onset of CH_4 accumulations for the two years, the rate was 70% higher in 1990 than in 2004 (Figure 5d). Assuming the upward flux of CH_4 via the sediment pore waters is essentially equal to the CH_4 accumulation rate (Gelda et al. 1995), adjusted for vertical mixing (Matthews et al. 2005), the nearly equal AHOD values for the two years suggest a compensating higher rate of deposition of organic matter in 2004, at least during the interval of aerobic decomposition.

Although systematic increases in the T-NH_3 pool were observed in the hypolimnion in both years, features of the patterns differed dramatically (Figure 5e). The much lower initial pool size of 2004 was a result of effective nitrification treatment at Metro over the proceeding winter months (i.e., lower effluent T-NH_3 concentrations, consistent with the ACJ). Progressive increases in the hypolimnetic pool commenced with the establishment of stratification in 1990, but were not clearly manifested until late June in 2004 (Figure 5e). The maximum pool size for T-NH_3 in 1990 was approximately 3-fold larger than in 2004, associated with the initially higher content in April and the higher accumulation rate.

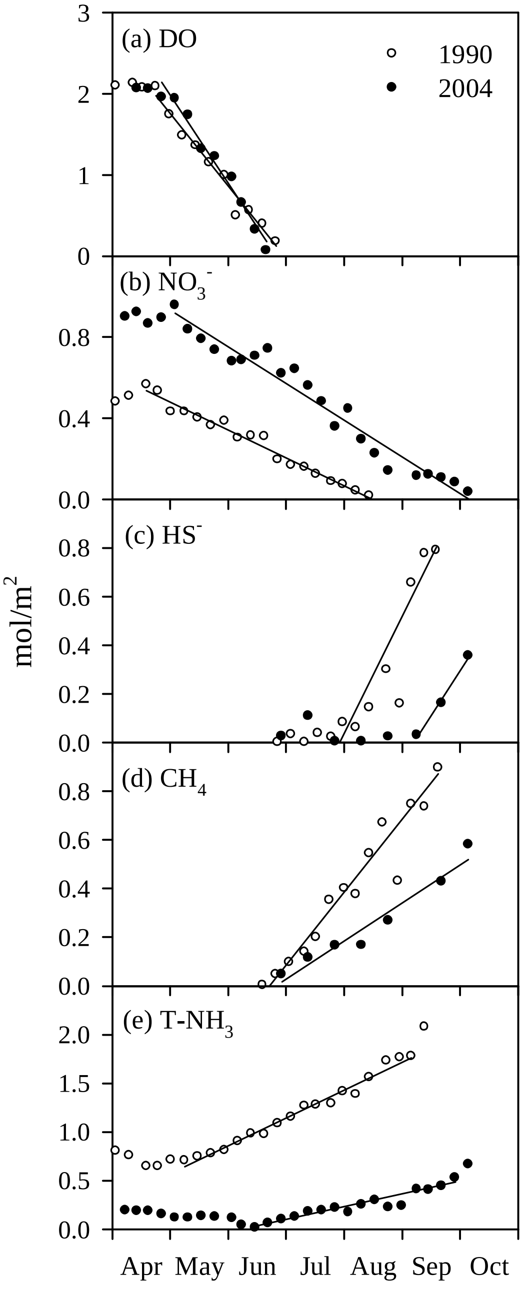

Figure 5. Depletion and accumulation rates of redox constituents in the hypolimnion of Onondaga Lake in 1990 and 2004: (a) DO (b) NO_3^-, (c) HS^-, (d) CH_4, and (e) T-NH_3 (modified from Matthews et al. 2006).

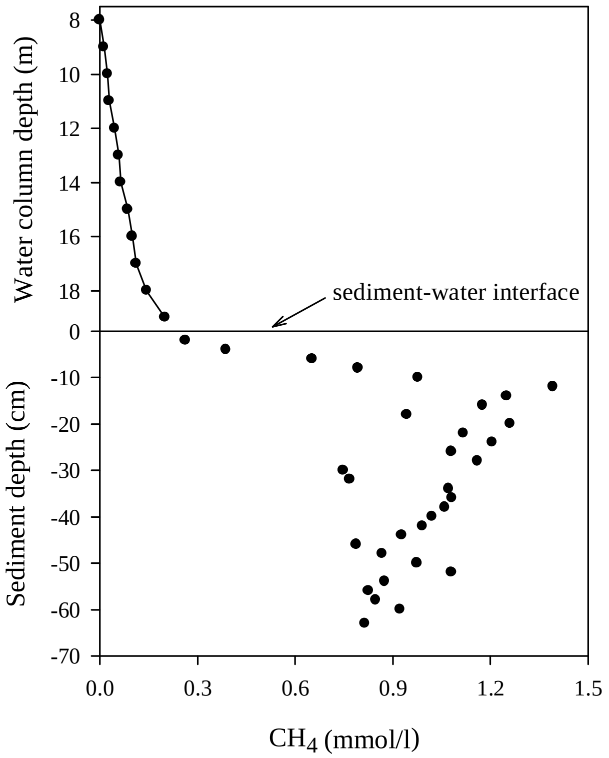

Figure 6. A single CH_4 profile extending from the water column into the sediments of Onondaga Lake for 10 August, 1995 (From Matthews et al 2005).

The consistency between the hypolimnetic accumulations of oxygen-demanding reduced byproducts of decomposition processes and the subsequent DO depletion during the approach to fall turnover is depicted for 1990 and 2004 (Figure 7). The oxygen demand at the peak of the accumulations, partitioned according to HS^-, CH_4 and T-NH_3, is compared to the mass of the DO deficit at the time of its minimum concentration (subtracted from saturation values throughout oxygenated layers). Though this analysis is imperfect because it fails to accommodate other time varying sinks and sources of DO, it serves to demonstrate that the observed DO depletions in these two years were generally consistent with the antecedent oxygen debts represented by the hypolimnetic accumulations of these reduced substances. Each of the three oxygen debt components was smaller in 2004 than in 1990 (Figure 7). The total potential debt was 53% lower in 2004, and the rapidly exerted component (CH_4 plus HS^-) was 40% lower. The observed oxygen deficit in 2004 was also lower (24%) than in 1990 (Figure 7). These changes are not proportional because factors not accommodated in this simple budget analysis may differ from year to year. For example, the DO_{min} resulting from a given mass of oxygen demanding reduced species will vary as a result of antecedent DO concentrations and the rate of entrainment of anoxic layers.

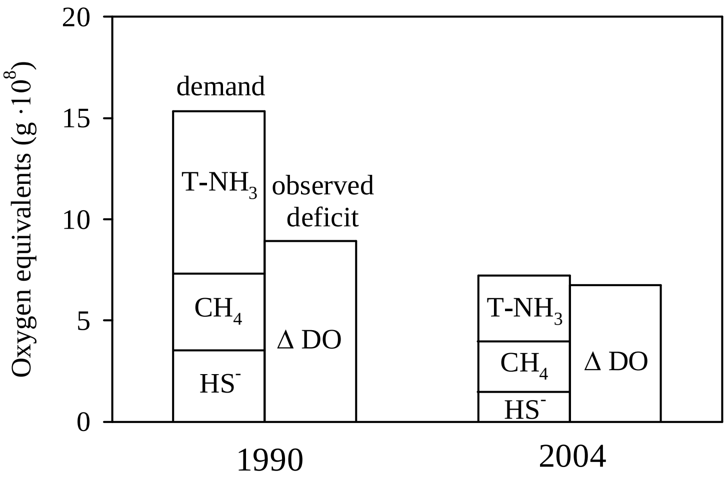

Figure 7. Comparison of DO demand associated with hypolimnetic accumulations of metabolism byproducts and subsequent DO deficits of the upper waters of Onondaga Lake, 1990 and 2004.

Central Role of High Sulfate Levels in Onondaga Lake

The geologic setting of Onondaga Lake dictates the naturally high SO_4^{2-} concentrations (Perkins and Romanowicz 1996). The high rate of SO_4^{2-} reduction observed in the lake has implications for the cycling of iron, phosphorus, and mercury. Stauffer (1987) used the term “sulfuretum” to describe hypolimnia in which the rate of sulfide production over summer exceeds the rate of supply of iron from the drainage basin and sediments. Under these conditions much of the iron in pelagic sediments is immobilized as insoluble FeS, which through diagenesis is converted to FeS_2. Precipitation of FeS minerals can control hypolimnetic concentrations of either iron II or sulfide, depending on the relative abundance of the reactants (Davison 1993). These ferrous iron – sulfide interactions have important implications for the release of metals (e.g., copper, lead, zinc) and phosphorous from lake sediments (Caraco et al. 1989, Wetzel 2001). Under oxidizing conditions Fe(III) forms an effective barrier to the transport of PO_4^{3-} from the sediment through the formation of $FePO_4$ and/or surface adsorption of PO_4^{3-} to Fe oxy-hydroxides. When the upper sediments become anoxic, Fe(III) is reduced to soluble Fe(II) and PO_4^{3-} is released to the water column. Sediment release of PO_4^{3-} is exacerbated in sulfide-rich systems through the precipitation of FeS, which reduces the supply of Fe(III) available to immobilize PO_4^{3-}. Recognition of this process has resulted in the suggestion of artificial sulfide enrichment as a lake fertilization technique (Hasler and Einsele 1948).

Sediment P release in Onondaga Lake appears to be regulated primarily by Ca-PO_4 minerals rather than by Fe-PO_4 interactions (Driscoll et al. 1993). This alternate mechanism for sediment P release is promoted by high water column concentrations of Ca^{2+}, high rates of $CaCO_3$ deposition, and low Fe concentrations due to formation of FeS. Driscoll et al. (1993) demonstrated that decreases in water column Ca^{2+} concentrations or pH may enhance the P supply from the sediments. Thus, efforts to control P release in Onondaga Lake through common methods, such as maintenance of oxic conditions at the sediment-water interface, may not be successful in this ecosystem.

The combination of high sulfate concentrations, abundant organic carbon, and a pool of available inorganic Hg create favorable conditions for MeHg production in Onondaga Lake. In addition, sulfide concentrations affect the speciation and cycling of Hg, including the production of MeHg (Benoit et al. 1999). Only small, uncharged Hg complexes (e.g., HgS, $Hg(HS)_2$) that can diffuse passively across bacterial cell membranes are believed to be available for methylation (Benoit et al. 1999). Because S^{2-} is an important ligand for Hg(II) in anoxic environments, S^{2-} concentrations may affect sediment Hg^{2+} chemistry and the potential for methylation (Benoit et al. 1999, Mehrotra et al. 2003). This mechanism is consistent with the inverse relationship between sulfide and MeHg that has been observed in estuarine (Compeau and Bartha 1983, 1987) and freshwater sediments (Winfrey and Rudd 1990, Gilmour et al. 1998).

Preliminary Support for Methylmercury Benefits from Nitrate –2005

Background

Production of MeHg in freshwater lake ecosystems is usually associated with anoxic conditions, as MeHg is primarily a result of the activity of SRB (Benoit et al. 2003). The eutrophic state of Onondaga Lake, together with elevated levels of sulfate, results in favorable conditions for establishment of sulfate-reducing communities during summer months. The activity of SRB in the lake is regulated by the flux of organic matter to the sediments, the availability of oxygen or other terminal electron acceptors for oxidation of organic matter, and the duration of thermal stratification.

In the summer and fall of 2005 (July through November) samples were collected weekly from four depths (9, 12, 15 and 18m) in the hypolimnion of Onondaga Lake as a preliminary effort to examine the response of in-lake MeHg production to increases in nitrate loading associated with year-round nitrification at Metro. Water samples were analyzed for total Hg (THg) and MeHg concentrations following EPA Methods 1631 (USEPA 2002) and 1630 (USEPA 2001), respectively. Laboratory quality control samples were run with each analytical batch to assure system performance. Laboratory procedures for analysis of THg were carried out in a class 1000 clean room. Sample preparation was performed in class 100 clean workspace.

Samples were collected using a continuous flow system custom-built at UFI. The system consisted of a vinyl hose attached to a submersible pump. Blank field samples were taken at the beginning and the end of the field season, to assure no contamination of Hg occurred during sample collection. Additional blank samples were analyzed with each sampling batch. Sampling protocol generally followed the clean hands-dirty hands procedure as described in EPA Method 1669 (USEPA 1996). Deviations from the sampling procedure described in EPA 1669 included: (1) the use of a metal boat rather than fiberglass; (2) no special apparel (e.g., Tyvek suits) was used to collect samples; and (3) the use of non-approved collection materials. Note the boat remained on the lake during the entire field season.

Auxiliary water chemistry samples were taken two days prior to sample collection for Hg analyses for the first 6 weeks of the study. Subsequently all samples were collected on the same day. The dynamics of THg and MeHg in the hypolimnion for 2005 were compared to previous observations reported for 1992 (TAMS 2002) and 2000 (Sharpe 2004). Inorganic Hg (In Hg) is calculated as the difference between THg and MeHg.

Mercury Patterns

Vertical profiles of THg and MeHg for the lower layers of the lake for each of the sampling days are presented (Figure 8a - r). Concentrations of THg ranged from about 1 to 20 ng/L. The vertical and temporal patterns were coupled to the dynamics of the thermal stratification regime. For example, vertical differences occurred when the lake was thermally stratified (Figure 8a - m). In contrast, more nearly vertically uniform patterns were observed over those same depths during fall turnover (Figure 8n - r), particularly for MeHg. Most of the structure in the THg patterns was associated with the MeHg component, as variations in MeHg explained 64% of the observed differences in THg ($r^2 = 0.64\%$, $p < 0.001$). Moreover, most of the THg in the bottom waters during stratification was in the form of MeHg. This strong relationship suggests the potential use of THg as a surrogate metric of MeHg in the lower anoxic stratified layers. This may be attractive because of the comparative simplicity of the THg method (Oxidation, Purge and Trap, and Cold Vapor Atomic Flourescence Spectrometry (CVAFS)). This technique, which is partially automated, features comparatively rapid "turn-around" of analytical results.

The vertical patterns of MeHg within the hypolimnion, which demonstrated increasing concentrations with the approach to the sediments, were consistent with seasonal release of this constituent from the sediments and the limited vertical mixing that prevails within the stratified layers of the hypolimnion (Owens and Effler 1996). This type of vertical pattern has been reported for a number of constituents in this lake (Effler 1996, Matthews et al. 2005) and others (Wetzel 2001) where pelagic sediments serve as a major source of these materials to the hypolimnion. In particular, hypolimnetic patterns of electron acceptors (depletions) and redox reaction byproducts (accumulations) demonstrate qualitatively similar vertical patterns (as illustrated above), which reflect localization of decomposition processes on and within the sediments. With the exception of the mid-hypolimnetic MeHg peak observed on October 3 (Figure 8j), the generally progressive increases with depth suggest water column production and mid-depth sediment production are not important sites for methylation. A more comprehensive monitoring program (e.g., increased vertical resolution) conducted in 2006 will provide more definitive evidence concerning the relative importance of various positions within the lake (e.g., pelagic sediments versus water column) for production of MeHg.

The extent to which changes in the redox conditions of the lake's hypolimnion, brought about by year-round nitrification at Metro, have influenced THg mobilization and MeHg production is depicted in terms of volume-weighted concentrations for the summer months of July, August and September, for the years 1992, 2000, and 2005 (Figure 9). Year-round nitrification was established at the facility starting in 2004. The corresponding hypolimnetic temporal patterns of HS^- are presented (Figure 9a) as a surrogate, albeit imperfect, metric of SRB activity. Progressive increases in the HS^- pool, an annual occurrence for the lake described above, is also manifested in this presentation format (Figure 9a). Conspicuous differences in SRB activity are indicated between 2005 and the two earlier years. HS^- was present in July in both 1992 and 2000, but absent in that month in 2005. Levels in August and September were decidedly lower in 2005 than in both of the two earlier years. This presentation indicates substantially lower levels of SO_4^{2-} reduction and SRB activity occurred in 2005 compared to both 1992 and 2000. This pattern is consistent with the larger initial NO_3^- pool in the hypolimnion at the onset of stratification in 2005 from year-round nitrification at Metro. The lower MeHg pool in 2005 and the temporal trend within that summer are generally consistent with the lower HS^- levels (Figure 9a and b). MeHg levels were lower in each of the three months in 2005 compared to the two earlier years. However, unexplained temporal irregularities in the MeHg pool were manifested in both of the earlier years; e.g., decrease in September in 1992, and decrease in August in 2000 (Figure 9b). Further, relatively low MeHg levels were observed in July of 2005 in the absence of HS^-. Overall, these HS^- and MeHg patterns support the position that blocking SRB activity through augmentation of the hypolimnetic NO_3^- pool may substantially abate production of MeHg. For example, additions of NO_3^- that would be adequate to eliminate hypolimnetic HS^- perhaps would limit production of MeHg to the level observed in July 2005 (Figure 9b). The origins and processes responsible for the low levels of MeHg observed in July 2005, in the apparent absence of HS^-, are under investigation.

An interesting and potentially noteworthy observation of this preliminary study is the supply of limited concentrations of MeHg to the hypolimnion during the period of active NO_3^- reduction but prior to the period of HS^- accumulation. There are potential mechanisms that may contribute to this phenomenon. First, it has been suggested that iron reducing bacteria can supply MeHg (Fleming et al. 2006). Iron reduction would occur following NO_3^- reduction but before SO_4^{2-} reduction. Second, initial methylation by SRB could be occurring in the sediments, but HS^- produced could be metabolized by either dissimilatory nitrate reduction to ammonia (DNRA) or the oxidation of HS^- by denitrifying bacteria. The mechanism(s) driving this phenomenon should be elucidated through future studies.

The causes of the changes in THg levels in the hypolimnion of the lake for these three years are less clear. Concentrations of THg in 1992 were decidedly higher than in both 2000 and 2005 (Figure 9c). These differences indicate substantially higher inorganic Hg concentrations in 1992. Levels of THg in July and August of 2005 were substantially lower than in 1992 and 2000. However, the THg hypolimnetic concentration for 2005 was somewhat higher than reported for that month by Sharpe (2004) for 2000. We anticipate that detailed observations for 2006 will help clarify these patterns.

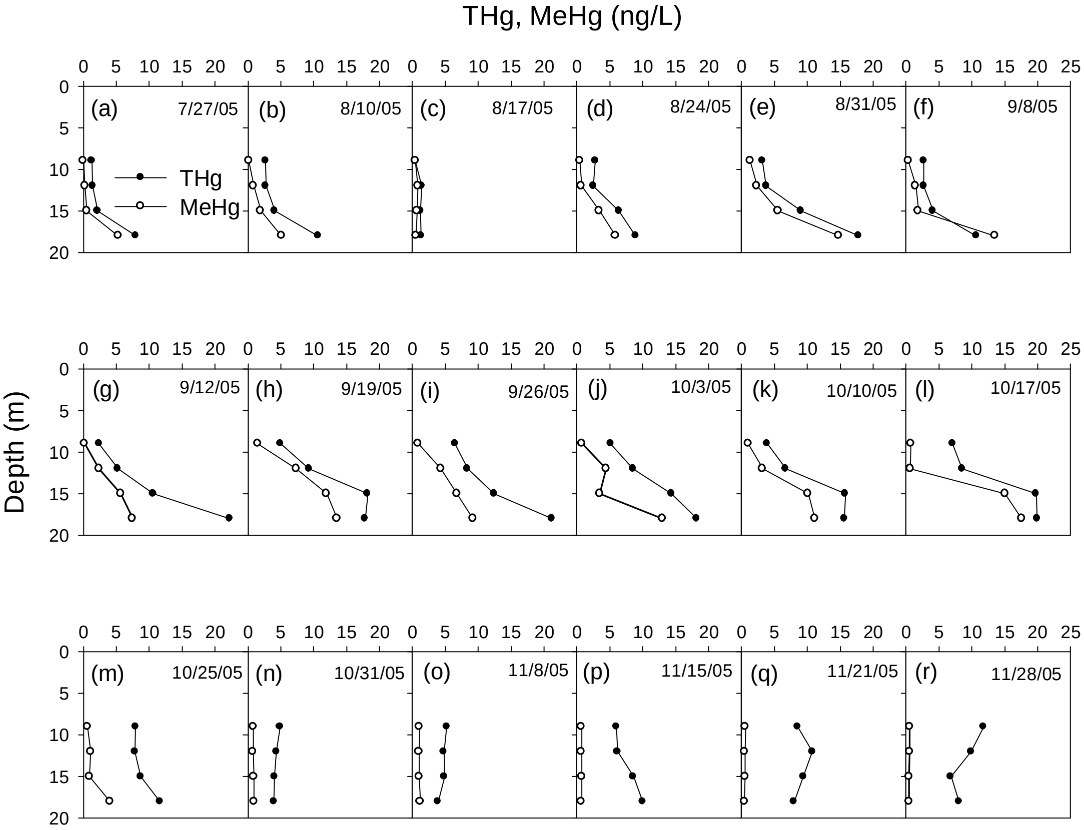

Figure 8. Vertical profiles of THg and MeHg from approximately weekly sampling of Onondaga Lake during the late July to late November interval of 2005.

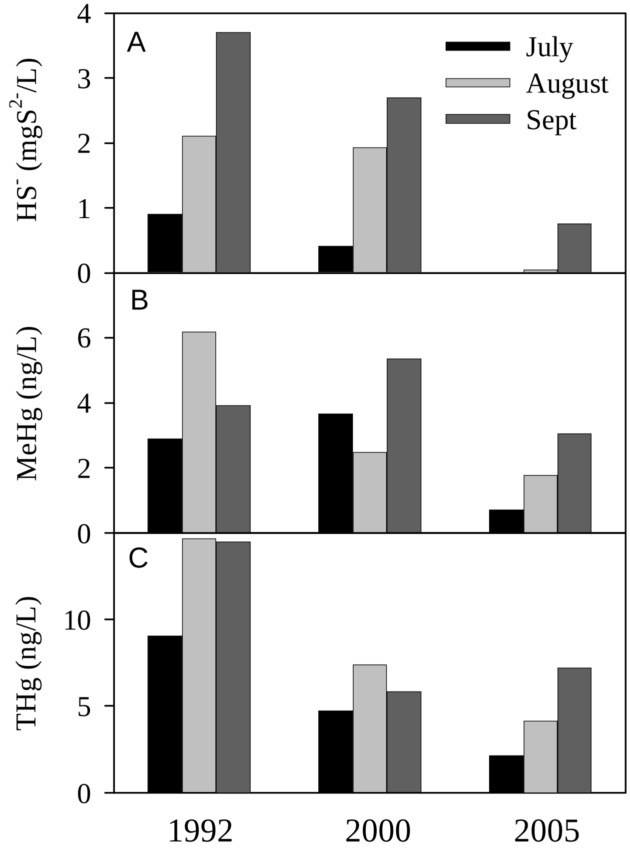

Figure 9. Average monthly volume-weighted concentrations for the hypolimnion of Onondaga Lake in 1992, 2000 and 2005: (a) HS^-, (b) MeHg, and (c) THg.

Nitrate Addition as a Management Alternative

Description of Historic Usage – Methods, Results, and Costs

The addition of NO_3^-, in the form of $Ca(NO_3)_2$, as a treatment to prevent or abate P release from pelagic sediments within anoxic hypolimnia was developed and tested by Ripl and coworkers (Ripl 1976, 1981, Ripl and Lindmark 1978). This lake restoration technique, known as the "Riplox Method" (Ripl 1976), has been applied by others (Willenbring et al. 1984, Foy 1986). These investigators reported increased denitrification, increased binding of interstitial P with ferric hydroxide complexes, and thereby lower release rates of P. Losses of added NO_3^- were reported to be almost entirely in the form of N_2 gas. Nitrate is used as the electron acceptor in the oxidation of organic matter, and its liquid form readily penetrates into the sediment (Cooke et al. 2005).

A sediment injection procedure applied to Lake Lillesjön, Sweden resulted in the oxidation of the upper 15 to 20 cm of anaerobic lake sediment (Ripl 1976). However, of greater interest to the Onondaga Lake site is that SO_4^{2-} reduction is supposedly prevented (Cooke et al. 2005). Lasting reductions in SOD were reported at one application site 8 years later (Ripl 1976). In contrast, Riplox treatment of eutrophic Lake Trekanten, Sweden resulted in a temporary decrease in sediment P release, but no permanent improvement in the oxygen and phosphorus status of the hypolimnion was observed (Lindgren 1986). A similar NO_3^- injection technique (Limnofix In-Situ Sediment Treatment Technology (LIST)) has been used by Golder Associates to treat organic contamination and the release of nutrients and sulfide in aquatic sediments (Golder Associates 2003). The LIST treatment has resulted in substantial reductions (> 80%) in sulfide production in bench, pilot, and full-scale applications (Golder Associates 2003).

The potential benefits of a more passive (i.e., no injection) treatment with NO_3^- have been identified previously (Stewart et al. 1982, Cooke et al. 2005). For example, deep-water discharge of NO_3^--rich effluents has been suggested as a management strategy to promote organic matter decomposition and increase sediment binding of P (Cooke et al. 2005). Søndergaard et al. (2000) added NO_3^- [as $Ca(NO_3)_2$] to the hypolimnion of Lake Lyng, Denmark over a 2-year period to study the impact on sediment P release and to evaluate the potential of hypolimnetic NO_3^- dosing as a lake restoration method. Additions of $Ca(NO_3)_2$ were made to the hypolimnion during summer stratification as a series of small doses to avoid high NO_3^- concentrations. Dissolved $Ca(NO_3)_2$ was added to the hypolimnion of Lake Lyng in the first study year and granules (2 to 4 mm diameter) in the second year. Additions of 8 to 10 gN/m^2 resulted in NO_3^- concentrations above the sediment-water interface of approximately 0.5 to 2.0 mgN/L. Both treatments resulted in marked reductions in the accumulation of P in the hypolimnion. However, addition in the dissolved form resulted in higher NO_3^- and lower P concentrations than application of granules, which penetrated into the loose sediments. In addition, lower accumulation of HS^- in the hypolimnion was noted in years with $Ca(NO_3)_2$ treatment. Hypolimnetic ammonium concentrations in Lake Lyng were higher in years with $Ca(NO_3)_2$ addition, which may suggest that NO_3^- addition enhanced overall decomposition of organic matter or that a portion of the added NO_3^- was channeled through the dissimilatory nitrate reduction to ammonia (DNRA) pathway (discussed below). This pattern is in contrast with the results of Ripl and Lindmark (1978) who observed that $Ca(NO_3)_2$ addition resulted in lower ammonium concentrations in the sediment pore water of Lake Lillesjön.

Nitrate addition has been applied as a lake management technique in a number of lakes and in various physical and chemical forms. Depox®, a recently developed compound, consisting of Fe(III) and NO_3^-, was tested in enclosures and under laboratory conditions as a method to control sediment P release (Wauer et al. 2005). In addition to nearly eliminating P release, the Depox® treatment significantly reduced SO_4^{2-} reduction and methanogenesis in the laboratory. In enclosure experiments the treatment had no significant effect on SO_4^{2-} reduction or methanogenesis. A similar iron-nitrate combination ($FeCl_3$ and $Ca(NO_3)_2$) was applied to the shallow urban Lake ‘Alte Donau’, Austria, which resulted in marked improvements in the trophic state indicators TP, Chl and transparency (Dokulil et al. 2000). Iron-calcium nitrate pellets showed promise for reducing P release in bench scale experiments (Na and Park 2004). Nitrate addition has been applied as a lake management technique in Long Lake, Minnesota (Willenbring et al. 1984, Noon 1986), White Lough, Ireland (Foy 1986), Lake Biwa, Japan

(Murphy et al. 1999), and Hamilton Harbour, Canada (Murphy et al. 1995, Murphy et al. 1999). Costs of Riplox treatments at various sites are reviewed in Cooke et al. (2005). Costs ranged from \$179,000 to \$469,000 (both in 2002 U.S. dollars). However, costs for these one-time sediment treatments are of limited value for the Onondaga Lake situation because NO_3^- addition would be required on a nearly continuous basis during the summer months.

Alternate Pathways of Nitrate Consumption and Mechanisms for Inhibition of SRB Activity and Associated MeHg Production

Denitrification is generally assumed to be the major process for NO_3^- consumption in aquatic sediments (Wetzel 2001). According to the classical model of biogeochemical cycling in aquatic sediments (Figure 2) NO_3^- is reduced to N_2 by denitrifying bacteria, which can outcompete SRB for electron donors in the presence of non-limiting concentrations of NO_3^-. Thus, the primary mechanism for the inhibition of SRB by NO_3^- addition is a shift in electron flow from SRB to denitrifying bacteria. A biochemically and taxonomically diverse group of bacteria are capable of denitrification (Knowles 1982). The availability of electrons in organic carbon compounds is an important factor controlling the activity of heterotrophic denitrifying bacteria (Knowles 1982, Seitzinger 1988). However, reduced inorganic compounds can also serve as electron donors in denitrification. *Thiobacillus denitrificans* is a widely distributed obligate chemolithoautotrophic bacterium that couples denitrification to the oxidation of reduced sulfur compounds (e.g., $S_2O_3^{2-}$, H_2S, S, FeS, FeS_2; Bisogni and Driscoll 1977, Beller et al. 2006). Autotrophic denitrifiers use inorganic carbon compounds (e.g., CO_2, HCO_3^-) as their carbon source and do not require an external organic carbon source. Mechanisms in addition to canonical denitrification have been identified for the consumption of NO_3^- and inhibition of SRB that merit consideration in the assessment of a NO_3^- addition program.

Dissimilatory nitrate reduction to ammonia (DNRA), in which NH_4^+ replaces N_2 as the nitrogenous product of NO_3^- reduction, has recently been identified as an important sink for NO_3^- in organic-rich marine and freshwater sediments (Brunet and Garcia-Gil 1996, Bonin et al. 1998, An and Gardner 2002). In highly reducing environments sulfides rather than organic substrates can serve as electron donors for DNRA (Dannenberg et al. 1992, An and Gardner 2002). Sulfide concentrations appear to play an important role in determining the dominant pathway of NO_3^- reduction. At low HS^- concentrations, NO_3^- is reduced mostly via denitrification whereas at higher HS^- concentrations there is a shift to DNRA and incomplete denitrification (Brunet and Garcia-Gil 1996, Senga et al. 2006). The presence of HS^- has been observed to enhance the production of N_2O, NO_2^- and NH_4^+ in lake sediments with concomitant oxidation of S^{2-} to S^0 (Brunet and Garcia-Gil 1996, Senga et al. 2006). Brunet and Garcia-Gil (1996) reported that DNRA accounted for up to 30% of the total NO_3^- reduction in freshwater sediments amended with $Ca(NO_3)_2$ and H_2S. Isotope tracer experiments conducted on sediments from eutrophic Lake Baldegg, Switzerland showed that $< 5\%$ of the consumed NO_3^- was reduced to NH_4^+ (Mengis et al. 1997).

Although the importance of autotrophic denitrification and DNRA as sinks for NO_3^- in Onondaga Lake is currently unknown, the observation that NO_3^- and HS^- do not co-occur in the water column (e.g., Figure 3 and 4) suggests the possibility of NO_3^- reduction coupled to oxidation of sulfide. In addition, recent observations of a turbid layer in the vicinity of the NO_3^-

/HS^- interface (UFI, unpublished data) may indicate the presence of a bacterial population, possibly performing autotrophic denitrification or DNRA. Tracer studies using ^{15}N (e.g., Nielsen 1992, Mengis et al. 1997) could be performed on Onondaga Lake sediments to elucidate important mechanisms and determine the fate of NO_3^- in this ecosystem. Vertically detailed sediment pore water measurements would allow for quantification of these and other important redox reactions in the sediments.

Ammonia oxidation coupled to nitrate/nitrite reduction (anammox) has recently been discovered as an important alternate pathway of N_2 production in anaerobic marine sediments (Thamdrup and Dalsgaard 2002). The relative importance of anammox and denitrification appears to be regulated by the availability of their reduced substrates, NO_2^- concentrations, and the sediment organic content (Dalsgaard and Thamdrup 2002, Thamdrup and Dalsgaard 2002, Trimmer et al. 2003). The importance of the bacterially mediated anammox reaction in Onondaga Lake is unknown, but it should be recognized as an additional potential sink for NO_3^-.

Nitrate can also serve as an electron acceptor in the oxidation of Fe(II) to Fe(III) (Senn and Hemond 2002), which is unlikely to be a major loss pathway for NO_3^- in Onondaga Lake due to its low iron concentrations (Figures 3 and 4). However, anaerobic oxidation of Fe(II) does have implications for MeHg production through its effects on Hg speciation. Production of MeHg is dependent on the concentration of uncharged Hg complexes (e.g., HgS, $Hg(HS)_2$) as well as the growth of SRB. The activity of S^{2-} and the potential for formation of bioavailable Hg complexes may be regulated by the formation of FeS. Mehrotra et al. (2003) reported that addition of high concentrations of Fe(II) (10^{-2} M) to sulfide-rich model wetland sediments resulted in a 70% decrease in MeHg production. Warner et al. (2003) found that Hg methylation in wetland sediment slurries was suppressed under iron-reducing conditions, but the controlling mechanism could not be determined from the available data. Two potential mechanisms for the suppression of Hg methylation were identified: (1) lower bioavailability of Hg as a result of sorption to iron(III) oxides; or (2) the inability of SRB to effectively compete for substrates with iron-reducers.

Mechanisms in addition to competition for electron donors have been proposed to explain the inhibition of SRB by NO_3^-. Jenneman et al. (1986) attributed the prolonged inhibition of SRB in dilute sewage sludge amended with 59 mM NO_3^- and 30 mM SO_4^{2-} to an increase in redox potential by accumulation of denitrification byproducts (e.g., N_2O, NO). In the presence of oxidized nitrogen species redox potentials remain above the upper limit for SO_4^{2-} reduction. In addition, sulfate reduction may be suppressed by certain nitrate reduction byproducts (e.g., N_2O, NO, NO_2^-) that can have toxic effects on SRB (Greene et al. 2003, Jenneman et al. 1986).

Inhibition of Mercury Methylation by Iron and Nitrate Amendments

We have found no direct evidence for the inhibition of Hg methylation by NO_3^- or any other electron acceptor at the field scale. However, results from laboratory studies have demonstrated the potential for control of MeHg production by addition of terminal electron acceptors, including NO_3^-. Much of the research on the effects of terminal electron acceptors on MeHg production has focused on wetland ecosystems under Mn-reducing and more commonly Fe-reducing conditions (Mehrotra et al. 2003, Warner et al. 2003, Bonzongo and Gomez 2004, Mehrotra and Sedlak 2005). In laboratory experiments conducted on wetland and riverine anoxic freshwater sediments, the net rate of Hg methylation was substantially lower at sites where Fe(III)-reduction was the dominant terminal electron accepting process rather than SO_4^{2-} reduction (Warner et al. 2003). Similarly, Mehrotra and Sedlak (2005) reported that addition of 30 mM Fe(II) decreased net Hg methylation by a factor of 2.1 to 6.6 relative to that of unamended controls. However, recent research performed on sediments from Clear Lake, California has indicated that Fe(III)-reducing bacteria are likely methylators of Hg (Fleming et al. 2006).

The effects of NO_3^- addition on MeHg production have not been researched as thoroughly as iron, possibly because NO_3^- concentrations are typically low in sulfate-reducing aquatic sediments (Senga et al. 2006). However, laboratory experiments have been conducted that support the concept of NO_3^- addition to abate MeHg production. For example, Steffan et al. (1988) found that NO_3^- concentrations of 5.6 mgN/L and greater resulted in near complete inhibition of methylation. In the same study, methylation was not inhibited by NO_3^- at a concentration of 0.42 mgN/L. Gilmour et al. (1998) investigated the effects of various amendments (including NO_3^-) on Hg methylation. The results indicated that Hg methylation was inhibited significantly by the addition of 1.4 mgN/L NO_3^-, a finding that was not discussed by the authors. In fact, NO_3^- inhibited methylation almost as completely as molybdate (MoO_4), a specific microbial inhibitor of SRB. Similar results were found in laboratory methylation/demethylation experiments conducted by Mark Hines of the University of Massachusetts at Lowell. The addition of 1 mM NO_3^- resulted in a 96% decrease in Hg methylation (unpublished data). Demethylation rates were not significantly changed by the NO_3^- addition, but the pathway of MeHg degradation was shifted from 50% oxidative/50% reductive to 100% oxidative. Nitrate amendments (2 mM) were also associated with a shift from reductive to oxidative demethylation in Florida Everglades peat sediment (Marvin-DiPasquale and Oremland 1998). In the same study, NO_3^- addition appeared to cause an overall decrease in demethylation in two of the four amendment experiments.

Feasibility Analysis

Target Areas, Time Intervals and Concentrations

Detailed vertical profiles indicate that sediments overlain by NO_3^- depleted water layers are active areas of SO_4^{2-} reduction (Figures 3 and 4) and an important source of MeHg to the water column of Onondaga Lake during summer stratification (Figure 8). In 2004 and 2005 substantial NO_3^- depletion was limited to water depths below 10 m (e.g., Figure 4d). Thus, the primary target area for NO_3^- addition is the volume of water below 10 m, which has an upper surface area of 6.98×10^6 m^2 and a volume of 4.02×10^7 m^3 in Onondaga Lake. The time interval of NO_3^- application is predicated on abating SO_4^{2-} reduction, which commenced in late August to early September in 2004 and 2005 (Figure 10). Accumulation of HS^- in the bottom waters was observed only when volume-weighted NO_3^- concentrations in the hypolimnion were below 0.5 mgN/L (Figure 10). Detailed vertical profiles indicate that HS^- and NO_3^- did not co-occur at the same depth (e.g., Figures 3 and 4). However, as a margin of safety, and in an effort to promote diffusion of NO_3^- into the sediments, we have adopted a minimum NO_3^-

concentration of 1.0 mgN/L as a target for the sediment-water interface. In 2004 NO_3^- concentrations < 1.0 mgN/L were observed in portions of the hypolimnion from 12 July to 1 November, an interval of 112 days. Fall turnover, which typically occurs in mid-October, was unusually late in 2004, resulting in an extended interval of NO_3^- depletion. Nitrate concentrations < 1.0 mgN/L were observed from 27 July to 17 October of 2005, a period of 82 days. It is expected that both the volume of water requiring NO_3^- addition and the duration of application will vary from year-to-year as a result of variations in meteorological forcing conditions (e.g., wind, runoff), performance of the nitrification process at Metro, and organic matter deposition to the hypolimnion. Therefore, a longer treatment interval of 120 days (July through October) has been adopted for purposes of preliminary design.

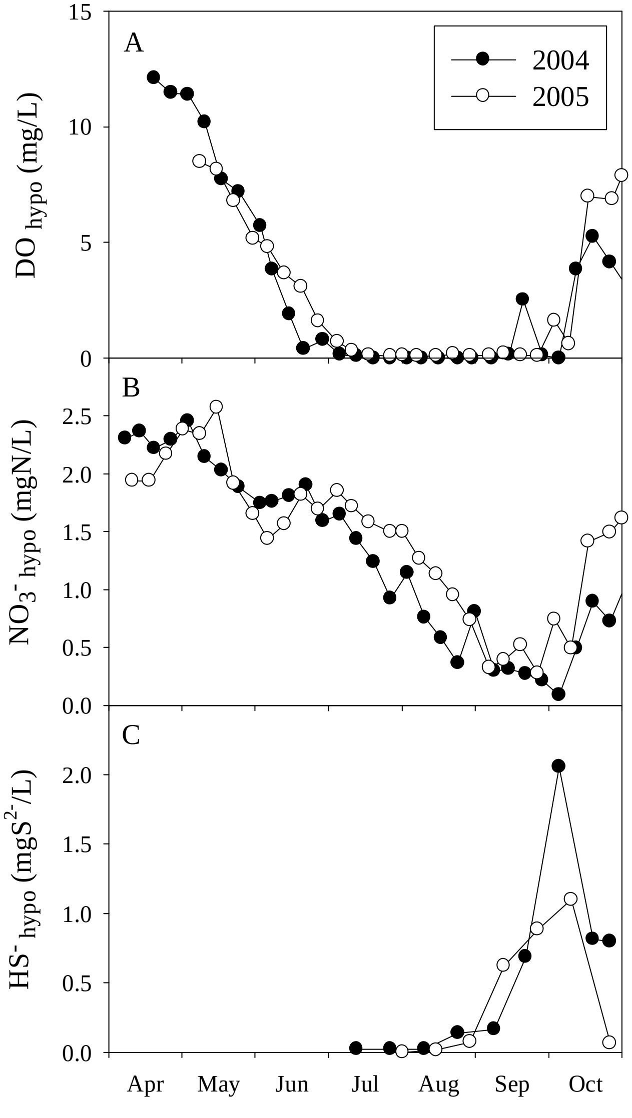

Figure 10. Comparison of time series of volume-weighted hypolimnetic concentrations in Onondaga Lake for 2004 and 2005: (a) DO, (b) NO_3^-, and (c) HS^-.

Passive NO_3^- Addition Versus Sediment Treatment

Addition of NO_3^- to the hypolimnion of Onondaga Lake is expected to reduce SO_4^{2-} reduction and the production of HS^- and MeHg through the promotion of denitrification in the upper sediments. The use of NO_3^- to inhibit the activity of SRB and the accompanying methylation of Hg requires that the supply of electron acceptor is sufficient to oxidize organic matter that would otherwise be decomposed through the SO_4^{2-} reduction pathway while satisfying all other sinks of NO_3^-. Various methods to supply NO_3^- to the surficial sediments exist, including sediment treatment, passive addition via wastewater effluent, and hypolimnetic addition in either liquid or solid forms. The Riplox (Ripl 1976) and Limnofix (Golder Associates 2003) sediment treatment processes achieve oxidation of organic matter through injection of $Ca(NO_3^-)_2$ into the sediments. The aggressive nature of these injection alternatives creates the potential for negative consequences associated with the disturbance and transport of contaminated sediments. Given the level of sediment contamination in Onondaga Lake, the sediment disturbance associated with the injection procedure it would not appear to be an acceptable alternative (NYSDEC 2004).

Although it was not intended to inhibit SO_4^{2-} reduction, the improvement in ammonia treatment at Metro has provided an opportunity to observe the effects of passive NO_3^- addition on SO_4^{2-} reduction and MeHg production. Water column measurements revealed that the higher NO_3^- concentrations observed in 2004 and 2005 did indeed reduce HS^- accumulation and MeHg production (Figures 5 and 9). Substantial accumulations of HS^- and MeHg were observed only after depletion of NO_3^- from hypolimnetic layers. Further additions of NO_3^- to the hypolimnion could be made as necessary to further diminish or eliminate SO_4^{2-} reduction, probably with substantially less added turbulence than sediment treatment. Further, it is likely that it can be easily implemented on an "as needed" basis, guided by monitoring of the hypolimnetic NO_3^- pool. Perhaps the most compelling support for such an approach is that it represents the *continuation and extension* of an ongoing management action, manifested in the high NO_3^- concentration of the effluent presently being discharged to the lake from Metro. A full-scale pilot study of this management alternative has been effectively underway since the establishment of year-round nitrification treatment in 2004. Benefits with respect to reductions in SO_4^{2-} reduction and HS^- production are already being observed, as reported here, and additional improvements are expected as improved P treatment at Metro decreases primary production and the deposition of labile organic matter to the sediments.

Chemical and Physical Forms of Nitrate

Nitrate and dissolved molecular N_2 are the most abundant forms of inorganic nitrogen in most fresh waters. Concentrations of NO_3^- range from undetectable levels to elevated levels (e.g., > 5 mgN/L) in unpolluted fresh waters and are subject to substantial seasonal and spatial variations (Wetzel 2001). Nitrate salts (e.g., $Ca(NO_3)_2$, KNO_3, $NaNO_3$) are highly soluble in cold water and widely used as agricultural fertilizers. Physical, chemical, and toxicological properties of three solid forms and one liquid form of NO_3^- are summarized in Table 1. Product information sheets, technical data sheets and MSDS are available from Yara North America (http://www.yara.us/en/products/safety_data_sheets/index.html). The chemical products listed in

Table 1 are available locally at the Tully Ag Center, located in Tully, NY, approximately 15 minutes south of Syracuse.

Table 1. Physical, chemical, and toxicological properties of $Ca(NO_3)_2$, KNO_3, and $NaNO_3$. Product information and costs provided by Tully Ag Center, Tully, NY (August 2006).

Properties	**$Ca(NO_3)_2$**	**$Ca(NO_3)_2$**	**KNO_3**	**$NaNO_3$**
Physical state	liquid	solid (hygroscopic)	solid	solid
Color	clear	white/off-white	white	white
Grain size	-	80% from 1 to 2 mm	94% less than 0.43 mm	87% from 0.85 to 2.36 mm
Odor	odorless	odorless	odorless	odorless
pH	5 to 7	-	6 to 9	-
Percent NO_3^- - N	8.5	14.5	13.8	16.0
Specific gravity	1.48	1.12	2.109	2.257
Bulk density	12.3 lbs/gal	70 lbs./cu. ft.	80 lbs./cu. ft.	79 lbs./cu. ft.
Solubility (at 20°C)	-	2.64 lb/gal	2.64 lb/gal	7.34 lb/gal
Toxic effects on humans	None	none	none	none

With respect to effectiveness in abating SO_4^{2-} reduction, there is no *a priori* basis to favor any of the three solid forms ($Ca(NO_3)_2$, KNO_3, $NaNO_3$). Sodium nitrate has been shown to effectively inhibit sulfide production in sewage sludge, pond sediment, and oil field brines (Jenneman et al. 1986). Londry and Suflita (1999) found that $Ca(NO_3)_2$, KNO_3, and $NaNO_3$ were equally effective in curtailing sulfide formation in sludge associated with an oily waste stream. However, $Ca(NO_3)_2$ has been applied more frequently than the other forms in lake ecosystems. Calcium nitrate is an attractive option because of the high background concentrations of Ca^{2+} in Onondaga Lake (~150 mg/L, Effler 1996) and the potential to reduce phosphorus in the water column through the formation of Ca-P minerals (Driscoll et al. 1993). In addition, formation and deposition of $CaCO_3$ is expected to contribute in a small but positive way to higher sediment burial rates and the monitored natural recovery approach (see *Hypolimnetic Chemistry, Sedimentation, and Cation Concentrations*). Sodium concentrations are also very high in Onondaga Lake (~250 mg/L, Effler 1996), and much higher than concentrations of potassium (~5 mg/L, Effler 1996).

All of these chemicals are oxidants and harmful if swallowed. In addition, they can cause irritation to the eyes, skin and respiratory system. These products are non-flammable, but all sources of ignition (spark or flame) should be avoided. The creation of dust when handling solid forms should be avoided. Personal protective equipment used during handling and deployment of these chemicals should be selected based on the physical form (liquid or solid), the task being performed, and assessment of the risks involved. Protective equipment may include safety eyewear, chemical-resistant gloves, and boots. These chemicals are not considered to be toxic for humans and they do not show any bioaccumulation phenomena. However, toxic effects have been documented for mammals and fish at high concentrations (see Data Sheets at http://www.yara.us/en/products/safety_data_sheets/index.html). These chemicals would be deployed at a rate that would maintain in-lake concentrations orders of magnitude below levels shown to produce toxic effects. NO_3^- additions would be directed to anoxic layers, providing further protection to aquatic fauna.

The choice between a liquid or solid form of NO_3^- should be based on both scientific and practical considerations. The Lake Lyng experience suggests that a liquid application may provide better performance through superior distribution of NO_3^- in the sediment (Søndergaard et al. 2000). Burial of pellets at depth within the sediment is a concern, particularly in the unconsolidated profundal sediments of Onondaga Lake. Nitrate salts are highly soluble in cold water (Table 1), so solid forms could be dissolved prior to distribution in the hypolimnion. However, application of NO_3^- purchased in a liquid form (e.g., $Ca(NO_3)_2 \cdot 4H_2O$, Table 1) would eliminate the need for dissolving solid material prior to deployment. The high specific gravity of the liquid form would cause it to sink to the sediment (related deployment issues are addressed subsequently), which is the primary target area for proposed NO_3^- amendments.

Nitrate Doses and Duration of Application

The estimated rate of NO_3^- addition is based on observed rates of depletion in the hypolimnion of Onondaga Lake during 2004 and 2005. In both 2004 and 2005, maximum rates of NO_3^- depletion were observed during the June to early September interval, following the loss of oxygen from the hypolimnion (Figure 10b). The maximum NO_3^- consumption rates observed in 2004 (119 mgN/m^2-d from June 14 to August 23) and 2005 (140 mgN/m^2-d from July 5 to September 6) and the higher rate adopted for preliminary planning purposes (150 mgN/m^2-d) are high relative to those reported for lake sediments in reviews by Knowles (1982) and Seitzinger (1988). When multiplied by the hypolimnetic surface area of 6.98×10^6 m^2 and adjusted for vertical mixing inputs (5%; Matthews et al. 2006), the areal depletion rate of 150 mgN/m^2-d translates to an application rate of 1050 kg NO_3^- -N/d. This rate should be considered a preliminary estimate, which has value for evaluating the feasibility and environmental impact of a NO_3^- addition program.

Knowles (1982) reported denitrification rates on the order of 100 mgN/m^2-d in relatively NO_3^- rich eutrophic freshwater ecosystems. Seitzinger (1988) reviewed rates of denitrification in lake sediments and found values ranging from 0.5 to 40 mgN/m^2-d. Much lower denitrification rates (0.05 to 0.45 mgN/m^2-d) have been observed in the anaerobic hypolimnetic waters of lakes (Seitzinger 1988). The higher rates reported for river sediments (up to 81 mgN/m^2-d, Seitzinger 1988) may be attributable to higher temperatures, which support higher metabolic rates, and smaller diffusive boundary layers caused by higher levels of turbulent diffusion. The higher rates reported in these reviews are from ecosystems that receive substantial amounts of nutrient input. An extreme value of 500 mgN/m^2-d was reported for sediments from Bryup Langsø, Denmark under extremely high NO_3^- concentrations (> 5 mgN/L, Andersen 1977). Nitrate consumption rates in aquatic sediments are strongly impacted by the availability of NO_3^-, as indicated by the observed linear dependence of denitrification on NO_3^- concentrations in the overlying water (Jensen et al. 1994, Johnson et al. 2000). In an investigation of denitrification in six Danish lakes, Andersen (1977) found that the relationship between NO_3^- consumption and NO_3^- concentrations in the overlying water was well described by Michealis-Menten kinetics.

Given its high rates of primary production and deposition of organic matter to the sediments and high NO_3^- concentrations, it is not surprising that NO_3^- consumption rates are relatively high in Onondaga Lake.

Estimated costs for the chemical products, transportation to Onondaga Lake, and onsite storage are provided by Tully Ag Center and listed in Table 2. Preliminary annual costs (2006 estimates) are based on a treatment interval of 120 days and an application rate of 1050 kg NO_3^--N/day. A trailer equipped for efficient onsite delivery of the product is included in these costs. Chemical costs, including transportation and storage, range from about \$484,000 for $NaNO_3$ to \$826,000 for KNO_3 (Table 2). The estimated annual cost for the liquid $Ca(NO_3)_2$ alternative is approximately \$588,000. Transportation and storage costs (\$0.03 per pound of product) are higher for the liquid form because of its greater weight.

Table 2. Estimated product, transportation and storage costs for $Ca(NO_3)_2$, KNO_3, and $NaNO_3$. Costs provided by Tully Ag Center, Tully, NY.

Properties	**$Ca(NO_3)_2$ liquid**	**$Ca(NO_3)_2$ solid**	**KNO_3 solid**	**$NaNO_3$ solid**
Cost per lb	\$0.15	\$0.28	\$0.38	\$0.25
Cost per kg NO_3^--N	\$3.87	\$4.25	\$6.07	\$3.43
Annual product cost[1]	\$490,000	\$536,000	\$765,000	\$432,000
Transportation and storage[2]	\$98,000	\$57,000	\$61,000	\$52,000
Total annual product cost[3]	\$588,000	\$593,000	\$826,000	\$484,000

[1] annual cost based on 120 day application period at 1050 kg NO_3^--N/day
[2] transportation and onsite storage cost is \$0.03 per pound of product
[3] includes transportation and onsite storage

Scenarios – According to Historic Observations and Selected Future Cases

Systematic Changes and Perturbation

If, as expected, reduced phosphorus loading from Metro results in lower levels of primary production, reduced deposition of organic carbon, and lower SOD, the need for NO_3^- addition may be reduced or eliminated in the future. Reasonable expectations for the trajectory of these changes could be determined through the development and testing of a quantitative framework to simulate the relationship between the rate of organic carbon deposition and NO_3^- demand, including magnitude and timing features. In addition, ongoing and future efforts to reduce Hg loading to the lake may significantly reduce MeHg production in the hypolimnion and thereby eliminate the need for additional electron acceptors to inhibit SO_4^{2-} reduction. A NO_3^- addition program could be easily modified in response to future changes that may decrease the quantity necessary to abate SO_4^{2-} reduction and associated MeHg production. For example, NO_3^- addition could be reduced through shortening the application interval or decreasing the rate of application.

The ultimate goal for a NO_3^- addition program, or any program designed to abate MeHg production through the addition of an electron acceptor, is that one day it will become unnecessary. Because of the minimal infrastructure requirements for NO_3^- addition, such a program could be easily terminated. When the addition of NO_3^- is no longer required, the vessel used for NO_3^- application can be removed from the lake without the need for removal of additional infrastructure.

A NO_3^- addition program would also have the flexibility required to address the unexpected scenario of increased demand for electron acceptors brought about by increased primary production and deposition of organic matter. Abbreviated or incomplete spring turnover continues to occur on an irregular basis (Effler and Matthews 2003). In the absence of spring turnover the hypolimnion is not fully replenished with O_2 and NO_3^-, and a larger quantity of NO_3^- may be required to abate SO_4^{2-} reduction. In these cases additional NO_3^- could be supplied to the hypolimnion by increasing the application interval and/or the rate of application. The estimates of NO_3^- addition presented here include margins of safety in both the duration and rate of application, which may cover contingencies including increased sediment demand and reduced availability of electron acceptors.

Variations in Spring Turnover NO_3^- Concentrations

Natural variations in runoff can cause in-lake concentrations of NO_3^-, and other constituents that emanate primarily from Metro, to vary from year-to-year. This is described as a "dilution" effect (Matthews et al. 2000), similar to that observed and reported for streams and rivers downstream of localized continuous inputs such as wastewater discharges (Johnson 1979, Manczak and Florczyk 1971). This effect is particularly important for spring turnover (e.g., just before onset of stratification) conditions in Onondaga Lake, as this influences the NO_3^- pool size available to support decomposition processes in the hypolimnion. A dilution effect has been reported earlier for spring turnover T-NH_3 concentrations in the lake, before year-round nitrification was implemented (Matthews et al. 2000, Gelda and Effler 2003).

A modeling analysis was conducted to predict the variability in the spring turnover NO_3^- concentration in Onondaga Lake to be expected associated with natural variations in runoff. The analysis takes advantage of the long-term tributary flow record (since 1971) for the contributing streams (Effler 1996). These historic observations are inherently representative for the system (Gelda et al. 2001). Further, the long-term record provides an opportunity to represent NO_3^- predictions in a probabilistic format (Owens et al. 1998, Gelda et al. 2001).

A quasi-dynamic, mass balance model was developed to simulate NO_3^- concentration in Onondaga Lake at spring turnover. The model simulations begin on November 1 and end on April 1, during which the lake can be assumed to be completely mixed with respect to NO_3^- concentration. It was also assumed that no reactions involving NO_3^- take place in the lake during this period. The assumption is supported by: (1) the seasonally low temperatures that slow reaction rates, including photosynthesis, and (2) the availability of T-NH_3^- during the interval of interest that is preferentially used by phytoplankton. The governing equation then can be written as:

$$V\frac{dc}{dt} = Q_M c_M + Q_T c_T - (Q_M + Q_T) \cdot c \tag{2}$$

where, V = lake volume, m^3; c = in-lake NO_3^- at spring turnover, mgN/L; t = time, d; Q_M = Metro flow, m^3/d; c_M = Metro NO_3^-, mgN/L; Q_T = tributary flow, m^3/d; and c_T = tributary NO_3^-, mgN/L. Q_M, c_M, and c_T were assumed to be at steady-state (i.e., not varied during the simulation period). Eq. (2) was solved numerically using Euler's integration method (Chapra and Canale 1988) with a time step of 1 d and an initial concentration of 1.25 mgN/L (unpublished UFI data; average for 2004-2006) of NO_3^- in the lake at fall turnover (November 1). In addition, the following values of various parameters were adopted: $V = 131 \times 10^6$ m^3; Q_M = 68 MGD; c_M = 11 mgN/L (November-April average for 2004-2006); and c_T = 0.6 mgN/L (Effler 1996). Daily average Q_T was available from USGS for 1971-2005. Thus, the model was used to predict spring turnover NO_3^- concentration in the lake for the flow regimes of 1972-2005 (34 years).

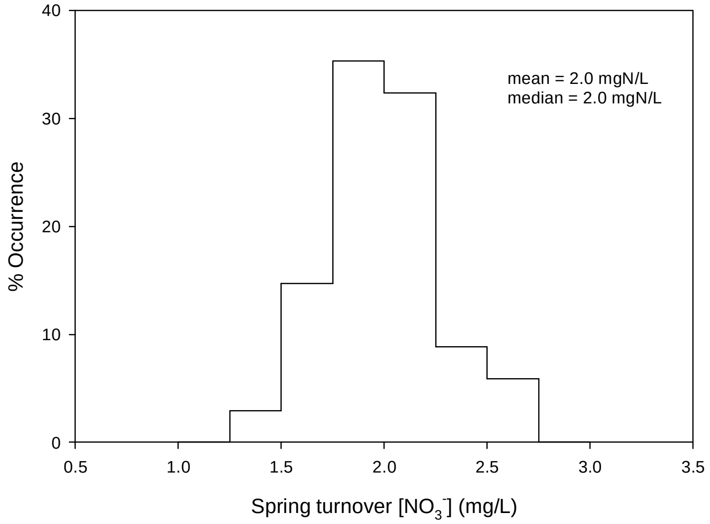

Figure 11. Predicted distribution of the NO_3^- concentration in Onondaga Lake at spring turnover, formed by accommodating the observed variability in antecedent tributary flow rates for the 1972 - 2005 period (n = 34 years).

The distribution of spring turnover NO_3^- concentrations for 34 years of observed hydrologic conditions is presented in Figure 11. The distribution has a normal character with essentially equivalent mean and median values of 2.0 mgN/L. The consistency of observations since implementation of year-round nitrification (NO_3^- concentrations of 2.3, 2.0, and 2.1 mgN/L, in 2004, 2005 and 2006, respectively) supports the representativeness of the predictions. Nearly 70% of the predicted values were in the range 1.75 to 2.25 mgN/L, and about 90% of the predictions fell in the broader range of 1.5 to 2.5 mgN/L. Clearly, substantial variations in the hypolimnetic NO_3^- pool at the onset of stratification will occur. This variability will dictate coupled variations in the onset of NO_3^- treatment. For example, high runoff levels during the antecedent interval from fall turnover of the preceding year through spring turnover of the following year will cause a relatively low NO_3^- concentration at the onset of stratification (e.g., < 2.0 mgN/L), that will require earlier initiation of NO_3^- treatment. Effective and timely monitoring will be necessary to appropriately adjust to this variability in the initial NO_3^- pool, and to maintain the target hypolimnetic NO_3^- concentration.

Deployment/Treatment

Solid Form

Deployment of solid phase NO_3^- could be accomplished through direct application of granules to the surface of the lake or by pumping of pre-dissolved solids to the hypolimnion. Direct application of solids to the surface of the lake has at least two potentially serious disadvantages. First, a portion of the solid phase chemical may dissolve in the upper layers of the lake before reaching the sediments. Second, solids may penetrate the sediments and become coated with sedimentary material, resulting in delayed or incomplete release of NO_3^- to the interstitial water. Further, the observations of Søndergaard et al. (2000) during application of $Ca(CO_3)_2$ to Lake Lyng suggest that solid phase deployment may not be the optimal application technique (see p. 36 of this report).

Alternatively, NO_3^- in solid form could be dissolved with lake water in an onboard mixing container and pumped to the hypolimnion through a multi-port pipe positioned parallel to the lake bottom and perpendicular to the path of the deployment vessel. Onboard measurements of salinity and temperature of the NO_3^- solution would allow for real-time calculations of density, which would provide valuable information regarding transport of the chemical addition. The rate and locations of NO_3^- amendments would be guided by in-lake monitoring of NO_3^-, HS^- and Hg (see Monitoring Issues below). The additional handling required to dissolve solid form NO_3^- either onshore or onboard the deployment vessel may be viewed as undesirable. This additional handling of the NO_3^- product could be avoided through treatment with a solution form NO_3^-, which is described below.

Amendments of NO_3^- to the lake could be made from multiple fixed sites or from a boat. Preliminary application of a two dimensional hydrodynamic model suggests that deployment from a single location would result in uneven spatial distribution of NO_3^- in the bottom waters of the lake. Deployment from a boat would provide the mobility necessary to focus NO_3^- additions in specific areas and depths as guided by information from in-lake monitoring. This approach would allow for efficient use of NO_3^- while providing the ability to address specifically areas of more intense NO_3^- depletion. In addition, the presence of multiple deployment platforms in the lake during the summer months might be considered aesthetically undesirable.

Application of Nitrate in a Dissolved Form

A manufactured solution of $Ca(NO_3)_2$ was selected for use in this preliminary analysis. The product is Calcinit CN-8 solution, manufactured by Yara North America, Inc. of Tampa, FL. This is an extremely concentrated solution or brine; the manufacturer states that $Ca(NO_3)_2$ will begin to precipitate if the solution temperature falls below 35^oF. Other relevant characteristics are presented in Table 1. With a goal of providing 0.95 MT nitrate as N per day to the hypolimnion during treatment, the corresponding application rate of CN-8 solution is 7540 liter/day.

If this concentrated brine were to be discharged in an undiluted form into the lake, its high density would cause the liquid to rapidly sink and collect in low spots on the lake bottom where it would likely be resistant to ambient mixing processes. As a result, a significant amount of dilution would be required as a part of any injection system. There are two general methods to achieve dilution: mixing of the brine with ambient lake water in a mixing tank prior to release into the lake, and release of the brine at high velocity into the lake through the ports of a multi-port diffuser. Of course, a system that uses both of these methods of dilution may be employed.

Calculations of various mixtures of CN-8 solution and ambient lake water were made in order to identify the magnitude of mixing that would be required to meet certain objectives. In these calculations, the equation of state (relationship between temperature, dissolved solids concentration and density) of Effler et al. (1986) was used. This equation of state is specific to the mix of ions found in Onondaga Lake, but does not specifically consider the addition of $Ca(NO_3)_2$. However, the resulting error is likely to be small, especially at the relatively large dilutions that are described below. Nonetheless it is recommended that an equation of state that considers the ionic composition of both the lake and the CN-8 solution be developed for future use.

In order to determine the amount of dilution that would be required to reduce the density of the $Ca(NO_3)_2$ solution to reasonable levels, a calculation was conducted to determine the dilution of the concentrated brine with ambient lake water that would be required in order to produce a mixture having a density equal to that of the lake at a depth of 18 meters. This calculation was based on vertical profiles of temperature and salinity observed in the water column of the lake in 2006, and does not attempt to consider the effect that such a discharge would have on altering lake temperature and salinity. The resulting dilution varies in time and is relatively large (Figure 12), with an average value of roughly 300 for the July-September interval. Concentrations of NO_3^- that would be attained as a function of dilution are presented in Figure 13.

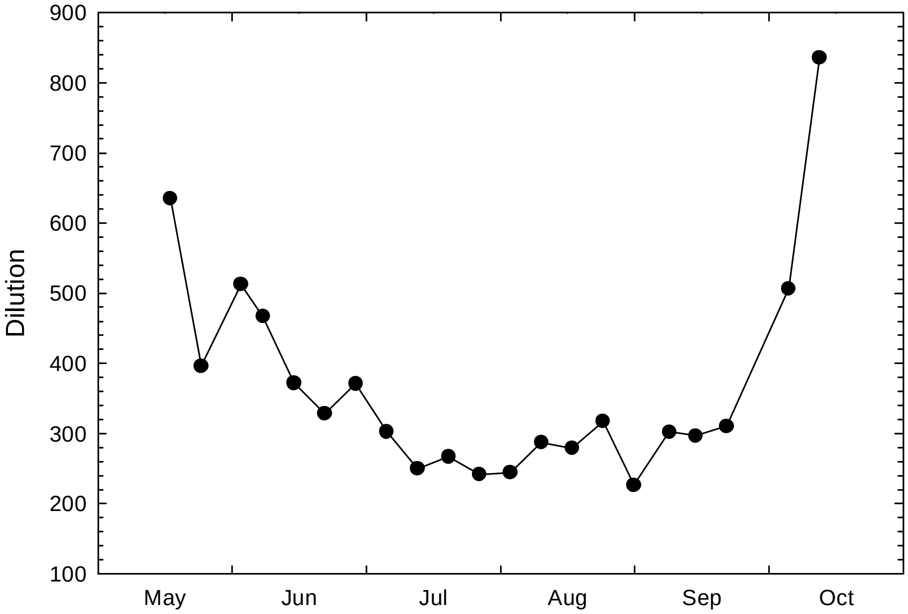

Figure 12. Volumetric dilution required to reduce the density of CN-8 solution to that of the bottom waters (18m depth) of Onondaga Lake, based on 2006 lake conditions.

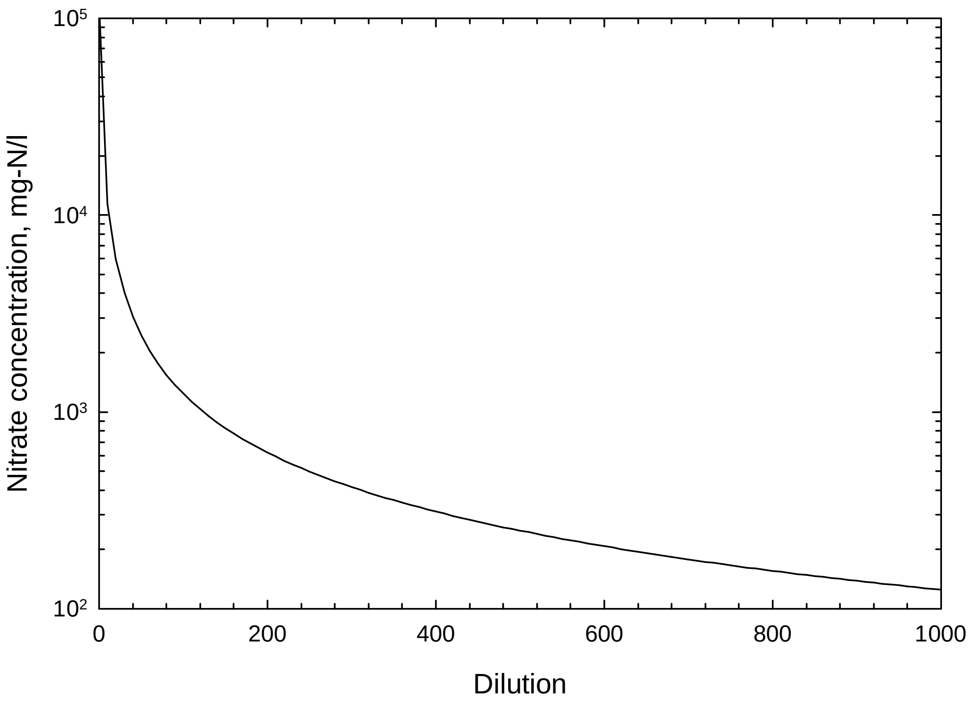

Figure 13. Nitrate concentration (mg-N/liter) of CN-8 solution diluted with Onondaga Lake water.

As described below, there is good reason for utilizing a dilution that is somewhat less than that required to produce a mixture equal to that of the lake bottom waters. However, a dilution of roughly 300 puts some restrictions on methods that might be used to achieve it. First, multi-port diffusers operating in a practical range (quantified by the discharge velocity from the diffuser ports) can achieve a maximum dilution of roughly 100; for a diffuser mounted on a boat the maximum is more likely to be in the range of 20. As a result, a dilution of roughly 300 would likely require some dilution of the CN-8 solution with ambient lake water before release into the lake.

Providing the entire dilution of 300 in a rapid-mix tank before release would result in a release flow rate of 6300 liter/min or 0.10 m^3/sec (assuming a six hour application interval each day), a rather large flow rate. For the purposes of estimation in this preliminary analysis, it is assumed that a dilution of 30 would be achieved in a rapid-mix tank prior to release, and an additional 10:1 dilution would be achieved using a diffuser, resulting in a total dilution of 300.

There are two general methods by which the nitrate solution may be released into the lake, these being from a diffuser suspended downward from a boat or through diffuser(s) resting on the lake bottom at one or more locations. Both methods would involve a storage facility near the lake shoreline where deliveries of the concentrated solution would occur. For a boat-based method, this facility would be adjacent to a dock where the boat would tie up.

Features of a boat-based system would include:

1. on-boat storage tank for undiluted chemical

2. pump and associated piping to withdraw ambient lake water and convey it to a rapid-mix tank
3. rapid-mix tank with mechanical mixers
4. another pump to force the diluted chemical through the diffuser and into the lake
5. a diffuser system mounted to the boat, which may be raised up to allow docking in shallow water
6. instruments/sensors to measure chemical and water flow rate, and temperature and salinity/conductivity of the diluted mixture

Features of a shore-based system (as an alternative) would include:

1. intake structure to remove dilution water from the lake at one or more depths or locations
2. piping and pump to convey water to rapid-mix tank
3. rapid-mix tank and with mechanical mixers located on the shoreline
4. pump(s) and piping to convey diluted chemical to deepwater site(s) in the hypolimnion
5. one or more diffuser structure(s) resting on the lake bottom
6. instruments to measure chemical and water flow rate, and temperature and salinity/conductivity of the diluted mixture

A final recommendation or selection of one of these methods is not made here, as further analysis is required before such a selection can be made. This analysis would include considerations of capital cost, operation and maintenance cost, reliability, flexibility, aesthetics, safety, and effect on induced nitrate demand (described below). Cost estimates for the release method itself are not presented here. However, comments on other considerations are provided.

Perhaps the most significant advantage of a boat-based release system is the flexibility to move the diffuser around the lake during application, which would allow for changing the application pattern in response to observed conditions. This would allow for control over both the total rate of nitrate addition to the lake, and its vertical and horizontal distribution. The boat-based system would not rely on natural (ambient) mixing processes to distribute the chemical horizontally within the hypolimnion of the lake. Depending on the magnitude of horizontal mixing in the hypolimnion, the shore-based option may require multiple release locations in order to achieve a reasonably uniform horizontal distribution of nitrate. Unlike a shore-based system, all components of the release system would be visible and subject to daily inspection, which would decrease the chance of leakage or spill from the system.

Another significant advantage of the boat-based system is its effect on induced nitrate demand. In an analysis of induced oxygen demand associated with artificial aeration or oxygenation, Moore et al. (1996) identified four processes contributing to induced oxygen demand: (1) resuspension of sediment materials in the aerator outlet stream; (2) increased residence time of particulates in the water column; (3) increased oxygen demand related to removal of low oxygen inhibition; and (4) increased sediment oxygen demand related to velocity and turbulence effects. The third and fourth mechanisms are thought to be of importance for nitrate demand in Onondaga Lake. The third mechanism is accommodated through the use of the higher nitrate depletion rates observed when the hypolimnion is anoxic but nitrate levels remain high. The fourth mechanism is caused by increases in water motion and/or turbulence in the vicinity of the sediment-water interface associated with the chemical addition process. Beutel and Horne (1999) found that the magnitude of induced oxygen demand decreased with the level of turbulence generated by an oxygen addition strategy, with destratification, aeration, and oxygenation resulting in progressive decreases in induced motion and turbulence and corresponding reductions in induced oxygen demand. The boat-based nitrate application strategy would have the advantage that any water motion or turbulence caused by the release would exist for at most a few minutes at any particular location, with the boat moving around the lake.

The recent study by Higashino et al. (2004) gave a theoretical investigation of the effect of water motion above the sediment-water interface on SOD. It was found that the time period necessary for SOD to respond to changes in water motion (a sudden increase or decrease in motion) is on the order of minutes to hours. Given that the increase in motion or turbulence that would exist at a fixed location due to a boat-based diffuser passing by is no more than a few minutes, it may be concluded that the nitrate demand may not even respond to such a brief disturbance, and if it did respond the demand would just as quickly be reduced to ambient levels after the boat passes.

The distributed chemical release from the moving boat would result in a relatively uniform horizontal distribution of nitrate. The minimal agitation together with the uniform concentrations makes it unlikely that a significant induced nitrate demand would occur with a boat-based system. However, given the preliminary nature of this analysis, it is recommended that induced nitrate demand be further studied.

A boat-based system would have the disadvantage that nitrate application may not be possible under severely adverse weather conditions. A shore-based system could be operated continuously, rather than for some number of hours each day. Depending on the location of a diffuser relative to the lake bottom, increased water motion and turbulence may occur in the immediate vicinity of a diffuser.

Based on this preliminary, qualitative analysis, a boat-based system appears to be the preferred method of application. Considering the concepts and factors described above, the following preliminary recommendation is made for a release system. A rapid-mix tank on the boat would be operated to achieve a dilution of 30 of the CN-8 solution before release to the lake. Dilution water would probably be drawn from hypolimnetic depths rather than the epilimnion to avoid heating of the hypolimnion. The diluted chemical would then be released through a diffuser suspended from the boat in the upper hypolimnion (e.g. depth of 12 meters). The high-velocity discharge of diluted chemical through the diffuser ports would induce mixing. The resulting mixture would remain negatively buoyant and would sink to the bottom of the lake in the form of a turbulent plume. While sinking, additional buoyancy-induced mixing would occur. After sinking to the bottom, ambient mixing processes, largely associated with wind-driven internal waves or seiches in the hypolimnion, would provide for additional distribution of nitrate in the bottom waters of the lake. On sloping portions of the lake bottom, the nitrate-enriched water overlying the bottom would remain slightly negatively buoyant, and may tend to flow gently down the slope, leading to further spreading of the nitrate over the lake bottom.

The path followed by the moving boat would be guided by monitoring of in-lake conditions, but the following concepts would be in play. It is likely that the moving boat would spend a majority of its time in the deepest parts of the lake (depth > 15 m), where the greatest quantities of deposited organic material are likely to be found and where nitrate depletion per unit volume of water is highest. However, in late summer and early fall the boat would likely spend some time above the shallower parts of the hypolimnion (water depth between 10 and 15 meters) to directly apply nitrate to that portion of the lake bottom where nitrate depletion is occurring at that time. As the depth of the thermocline increases with the approach to fall turnover, NO_3^- additions would be targeted on the decreasing volume of the hypolimnion.

Monitoring Issues

General

There would be three components of an overall monitoring program to support a hypolimnetic NO_3^- augmentation program to abate mobilization of MeHg from the pelagic sediments of Onondaga Lake: (1) fixed frequency monitoring to assess electron acceptors, redox constituents, Hg species and related conditions; (2) three-dimensional specification of NO_3^- and HS^- levels in pelagic regions during periods of NO_3^- treatments; and (3) on-board measurements conducted during chemical addition to guide treatment. Each of these is described below. This monitoring would also serve to meet some of the broader monitoring needs for the site.

Fixed Frequency Monitoring to Assess Electron Acceptors, Redox Constituents, and Related Conditions

This component of the monitoring program would allow for assessment of (1) in-lake conditions to establish the need for NO_3^- treatment; (2) the efficacy of the application; (3) and important perturbations and systematic changes that may influence the treatment program. This portion of the monitoring program would have at least two elements, water column and deposition. A third element, pore water, could be added, contingent upon the demonstration of the value and utility of this information as determined by forthcoming studies. Water column monitoring would be conducted weekly over the April - October interval, and bi-weekly in November at the long-term (south deep) monitoring site (Figure 1), according to NELAC, EPA, ELAP, and NYSDEC specifications. Parameter listings, sampling depths, analytical methods for laboratory analyses and parameter justifications are summarized in Table 3. Robotic monitoring (probe specifications in Table 4) over the same seasonal interval and at the same site would 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 m) resolution.

Table 3: Specifications for water column monitoring program, laboratory analytes.

Parameter	**Method**	**Depth Interval (m)**	**Justification**
TP	SM 18-20 4500P-E	0, 2, 4 m	trophic state/organic carbon deposition
[x]Chl	EPA 445	2m	trophic state/organic carbon deposition
TSS	SM 18-20 2540 D	0, 4, 16 m	partitioning of contaminants, MNR
VSS	SM 18-20 2540 E	0, 4, 16 m	partitioning of contaminants, MNR
NO_3^-	EPA 353.2	[xx]1 m	redox constituent, N cycle
NO_2^-	EPA 353.2	2 m	N cycle
T-NH_3	EPA 350.1	2 m	redox constituent, N cycle
DOC	SM 18 5310 C	2 m	complexation potential
PIC/POC	SM 18-20 5310B	0, 4, 16 m	trophic state/organic carbon deposition
DIC	SM 18-20 5310B	2 m	redox constituent, $CaCO_3$ deposition
pH	SM 18-20 4500 HB	2 m	sulfide speciation, DIC closure, $CaCO_3$ deposition
Alkalinity	SM 18-20 2320B	2 m	DIC closure, $CaCO_3$ deposition
Fe^{2+}	Heaney and Davidson, 1977	[+]1 m	redox constituent, sulfide cycling
H_2S method 1	SM 18-20 4500 S^{2-} D	[+]1 m	redox constituent, Hg cycle
H_2S method 2	SM 18-20 4500 S^{2-} G	[+]1 m	redox constituent, Hg cycle
Dissolved gases (N_2, CO_2, CH_4)	Addess 1990	[+]1 m	redox constituents, toxicity issue
Cl^-	SM 18-20 4500-Cl C	1 m	conservative tracer
Ca^{2+}	SM 18-20 3111B	2, 10, 12, 14, 16, 18 m	cation of treatment chemical
Total Hg	EPA 1631E	2 m	Contaminant
MeHg[*]	EPA 1630	2 m	contaminant byproduct

[x] chlorophyll **a**

[xx] 2 m in oxic layers; 1 m interval in anoxic layers

[+] 1 m in anoxic depths

MNR – monitored natural recovery

DOC – dissolved organic carbon

PIC – particulate inorganic carbon

POC – particulate organic carbon

DIC – dissolved inorganic carbon

Table 4: Specification of probes for robotic monitoring at Onondaga Lake.

Parameter	**Probe (YSI[*])**	**Performance Accuracy/Resolution**	**Attribute/Value**
dissolved oxygen (DO)	6562	± 2% reading/0.1% saturation	redox, decomposition pathway
temperature (T)	6560	± 0.15 °C/0.01 °C	thermal stratification, mixing
specific conductance (SC)	6560	± 0.5% reading/1 μS	Tracer
pH	6565	± 0.2 units/0.01 units	chemical equilibria, sulfide species
fluorometric chl (Chl_f)	6025	± NA/0.1 μg/L Chl	metric of phytoplankton biomass
redox potential	6565	± 20 mV/ 0.1 mV	indicator of redox status
turbidity (Tn)	6136	± 2 NTU/0.1 NTU	vertical pattern of particles

[*] model number correspond to YSI instrumentation

Monitoring of the deposition of Hg, organic matter, inorganic carbon and related constituents would be conducted through the laboratory analysis of sediment trap collections. The trap configurations and handling protocols would follow those adopted in a long-term program conducted for the lake (Womble et al. 1996, Effler and Brooks 1998, Effler et al. 2001). The traps would be constructed of PVC with an aspect ratio of 6:1, deployed at depths of 10 and 17 m at south deep over the April-October interval, and collected weekly. The analytes included in the deposition element of the program and justifications are presented in Table 5.

Table 5: Specifications for sediment trap analytical program.

Parameter	**Method**	**Justification**
total particulate Hg	EPA 1631E	mercury cycling
TSS	SM 18-20 2540D	sediment deposition
VSS/FSS	SM 18-20 2540E	components of deposition,
POC	SM 18-20 5310B	deposition of POC
PIC	SM 18-20 5310B	components of deposition,
PN	EPA 440.0	deposition of N, N budget
Chl	EPA 445	deposition of phytoplankton

[x] scanning electron microscopy with automated X-ray microanalysis and image analyses (SAX), one of cluster weekly, all three monthly

Three-Dimensional Specification of NO_3^- and HS^- Levels in Pelagic Regions During Periods of NO_3^- Treatment

The addition of NO_3^- to the lake's hypolimnion to abate SRB activity would require detailed spatial resolution of the NO_3^- pool in those deep layers to assess the transport and fate of the added NO_3^- and guide subsequent treatment. A three-dimensional representation of the distribution of NO_3^- would need to be obtained over a short interval during the treatment.

Further, occurrences of HS^- within the hypolimnion over three dimensions would help to identify the potential for occurrences and sources of MeHg. These demands would be met with modern rapid profiling instrumentation, which includes In Situ Ultraviolet Spectrophotometry (ISUS) for measurements of NO_3^- and HS^- (Prestigiacomo et al. 2007).

No chemical manipulations are necessary with this technology. Instead, ISUS utilizes the characteristic absorption spectra of selected inorganic constituents within UV wavelengths and spectral deconvolution techniques to separate and quantify the concentrations of these constituents (Johnson and Coletti 2002). Validation of ISUS measurements is underway (Prestigiacomo et al. 2007) and will continue through the 2007 field season. The ISUS would provide well-resolved patterns of both NO_3^- and HS^- within a single day, which is consistent with the preliminary applications of the technology in 2006 (Prestigiacomo et al. 2007). Specifically, the individual profiles (together a "gridding") necessary to support this resolution (probably 20 to 30) can be collected in 2 to 3 hours, a shorter interval than the period for internal waves in this lake (Effler et al. 2004). Other sensors in the rapid profiling "package" (Table 6) would provide an invaluable limnological context of stratification, tracer(s) patterns, and turbidity (e.g., bacterial and other microbial constituents, resuspended sediments). The goal would be to provide viewer-friendly spatial patterns (e.g., contours) of the NO_3^-, HS^-, and other related characteristics within the same day of field measurements. These capabilities are being demonstrated in 2007. The specifics of such a program, including number of profiles in a gridding, and frequency of griddings, would emerge during an appropriate demonstration project of NO_3^- treatment.

On-Board Measurements Conducted During Chemical Addition

Three types of monitoring would be conducted on-board the vessel during the NO_3^- treatment: (1) measurements to assess the density of the treatment chemical and discharge solution; (2) measurements of volumetric flow rates of the treatment chemical and the discharge solution; and (3) measurements of the treatment track within the lake (positions). Density is a function of temperature (T) and salinity (S). Salinity would be assessed through the widely used surrogate specific conductance measurement, based on a "chemical-specific" empirical relationship. Densities of the chemical solution and the diluted form to be added to the lake would be calculated in near-real-time by an on-board computer to guide the details of treatment, including the extent of on-board dilution and depth(s) of discharge.

Measurements of flow rates of the treatment chemical, dilution water, and discharge solution would be measured with appropriately precise instrumentation and stored on a computer. Calculations would be conducted to demonstrate closure of a total flow budget (chemical solution volume plus dilution volume equals discharge volume) and use of the treatment chemical.

Demonstration of the treatment tracks would be available in real-time on-board based on GPS measurements that would be stored on a computer. The actual track would be compared to the goal track for the day in real-time for continuous visualization.

Table 6: Specifications for rapid profiling instrumentation

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

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

Impact Analysis

Introduction

This section of the report addresses potential environmental impacts associated with the addition of NO_3^- to the hypolimnion of Onondaga Lake. Chemical, biological, and chemical effects related to NO_3^- addition are evaluated, including (1) production of N_2 gas; (2) toxicity potential of N_2 gas; (3) toxicity potential of NO_3^-; (4) production and potential toxicity of byproducts of NO_3^- reduction; (5) impacts on hypolimnetic chemistry and deposition; (6) vertical transport issues; (7) constituent loading to downstream ecosystems; (8) introduction of trace contaminants; (9) impacts on primary production; and (10) impacts on the benthic community and bioturbation.

Nitrogen Gas Ebullition

High rates of gas ebullition can facilitate transport of sediment contaminants by gas bubbles (Adams et al. 1997, Fendinger et al. 1992) or through the generation of convective currents (Ohle 1958). Although direct measurements are lacking, it has been proposed that ebullition of methane gas in Onondaga Lake is an important mechanism for transferring total Hg associated with particles from the sediments across the sediment-water interface and into the water column (TAMS 2002). The principal nitrogenous byproduct of NO_3^- reduction is N_2 gas (i.e., complete denitrification). Denitrification of added NO_3^- will increase N_2 production, which could potentially cause higher rates of ebullition. Therefore, the potential contribution of enhanced denitrification to higher rates of ebullition is of interest because of potential impacts on the transport of Hg.

The formation of bubbles in water requires that the sum of the partial pressures of volatile species be in excess of the ambient hydrostatic pressure. In a system where the principal volatile species are CH_4, CO_2, H_2S, N_2, and H_2O itself, this condition can be expressed as (Morel and Hering 1993)

$$P_{\mathrm{CH4}} + P_{\mathrm{CO2}} + P_{\mathrm{H2S}} + P_{\mathrm{N2}} + P_{\mathrm{H2O}} > P_{\mathrm{z}} \tag{3}$$

where P_z is the hydrostatic pressure at depth *z*. The ambient hydrostatic pressure can be expressed as $P_\mathrm{z} = P_\mathrm{atm} + \rho gz$. Ebullition can be caused either by a decrease in P_z or by *in situ* production of gases and concomitant increases in partial pressures. The total pressure of the mixture (*P*) can be related to the number of moles of the contributing gases by the ideal gas law equation

$$P\,v = (n_{\mathrm{CH4}} + n_{\mathrm{CO2}} + n_{\mathrm{H2S}} + n_{\mathrm{N2}} + n_{\mathrm{H2O}})RT \tag{4}$$

where v is volume (L), *n* is the number of moles in the gases, R is the universal gas constant (0.082056 L atm $°K^{-1}$ mol^{-1}), and T is temperature (°K).

Ebullition in surface water bodies is usually attributable to CH_4 production in organic-rich sediments (Wetzel 2001). Long-term reductions in diffusive and ebullitive fluxes of CH_4 from the sediments of Onondaga Lake were observed following an abrupt decrease in the flux of organic carbon to the hypolimnion in 1986 (Matthews et al. 2006). Matthews et al. (2006) documented a six-fold decrease in ebullitive flux after 1991. The importance of CH_4 in the formation of bubbles is due in part to its high volatility (low solubility) relative to CO_2, the other gaseous product of methanogenesis. The solubility of selected gases is presented in Table 7 by Henry's Law constants. Although the solubility of N_2 is lower than that of CH_4, relatively high concentrations of N_2 are maintained in surface waters by the higher partial pressure of N_2 in the atmosphere (Table 7). The saturation concentration of N_2 at standard temperature (25°C) and pressure (1 atm) is 13.6 mg N_2/L. The degree of oversaturation necessary for bubble formation increases with depth and hydrostatic pressure. Saturation concentrations of N_2 at 10°C are 35.7 and 53.7 mg N_2/L at depths of 10 and 20 m, respectively. These concentrations correspond roughly to the solubility of N_2 in the surficial sediments of Onondaga Lake.

Table 7. Typical partial pressures of gases in the atmosphere and Henry's Law constants (from Morel and Hering 1993).

Gas	*P* (atm)	log K_H (M atm^{-1})
NH_3	$0.1 - 5 \times 10^{-9}$	+1.76
H_2S	$< 2 \times 10^{-10}$	-0.99
CO_2	3.5×10^{-4}	-1.46
N_2O	3×10^{-7}	-1.59
NO_2	$1 - 5 \times 10^{-9}$	-2.00
NO	$1 - 5 \times 10^{-10}$	-2.72
CH_4	1.7×10^{-6}	-2.89
O_2	0.21	-2.90
N_2	0.78	-3.18

Gas bubbles rising from aquatic sediments are comprised primarily of CH_4 and N_2, with much smaller contributions from CO_2 (Addess and Effler 1996, Chanton et al. 1989, Matthews et al. 2006, Strayer and Tiedje 1978). It is generally believed that N_2 and CO_2 are incorporated into CH_4 gas bubbles by stripping of these gases from the sediment pore water (Chanton et al. 1989). The N_2 content of ebullitive gas from Onondaga Lake increased from 20% in 1989 to 40% in 1999 (Matthews et al. 2006). This pattern is consistent with the reasoning of Chanton et al. (1989), who suggested that N_2 in sediment pore water can be depleted by bubble stripping, resulting in lower N_2 concentrations in gas bubbles at higher rates of ebullition.

The contribution of NO_3^- addition to increased ebullition can be estimated for a worst-case scenario in which all of the added NO_3^- is denitrified to N_2 (i.e., no DNRA) and all of this N_2 exits the hypolimnion as gas bubbles (i.e., no accumulation or vertical transport of dissolved N_2). In this case, the addition of NO_3^- at a rate of 0.95 MT N/day would result in the production of 7.60×10^5 L N_2/day. Expressed on an areal basis, the ebullitive flux due to denitrification of added NO_3^- would be approximately 110 ml/m^2-day. However, in-lake measurements show that ebullition rates did not approach this magnitude during the 14 June to 23 August interval of 2004 when NO_3^- was consumed at a rate of 0.83 MT N/day (Figure 10b). Furthermore, this period of rapid NO_3^- consumption did not correspond to higher rates of ebullitive flux (UFI, unpublished data). This observation is not surprising when the potential contribution of denitrification to hypolimnetic N_2 concentrations is considered. If all of the added NO_3^- was denitrified to N_2 and this N_2 accumulated in the hypolimnion over the 120 day design period, the concentration of N_2 in the hypolimnion would increase by just 2.8 mgN_2/L. Assuming that the hypolimnion has a temperature of 15°C and is saturated with respect to atmospheric N_2 (16.3 mgN_2/L) at the beginning of the design period, the maximum achievable N_2 concentration is $2.8 + 16.3 = 19.1$ mgN_2/L. This concentration is well below the level necessary to produce oversaturation and gas bubbles in the hypolimnion of Onondaga Lake. Although the potential for localized bubble formation in the surficial sediments cannot be discounted, it appears that the proposed addition of NO_3^- is unlikely to result in substantial increases in ebullition or the transport of Hg from the sediments. In fact, reductions in ebullition may be expected in the future as upgrades in nutrient treatment at Metro result in reduced primary production and lower fluxes of labile organic matter to the sediments.

Nitrogen Gas Concentrations – Fish Toxicity Potential

Elevated total dissolved gas concentrations are of concern in aquatic ecosystems because of the potential for dissolved gas supersaturation (DGS) and gas bubble trauma (GBT) in aquatic organisms, particularly fish. Gas bubble trauma occurs when gas becomes supersaturated in the bodily fluids of fish. When the gas is released from the solution, traumatic damage from the bubbles occurs in fish tissues, similar to the condition known as 'the bends' with human SCUBA divers. As with 'the bends' in humans, fish that remain at sufficient depth do not experience gas bubble trauma. Dissolved gas supersaturation can produce a variety of physiological effects that are harmful or fatal to fish and other aquatic organisms (Fidler and Miller 1994). The major signs of GBT, which can cause death or high levels of stress in fish are (Fidler and Miller 1994): (1) bubble formation in the cardiovascular system, causing blockage of blood flow and death; (2) overinflation and possible rupture of the swim bladder, leading to death or problems of overbuoyancy; (3) extracorporeal bubble formation in gill lamella of large fish or in the buccal cavity of small fish, leading to blockage of respiratory water flow and death by asphyxiation; and (4) sub-dermal emphysema on body surfaces, including the lining of the mouth, causing blockage of respiratory water flow and death by asphyxiation.

The US Environmental Protection Agency has published DGS water quality guidelines which recommend a maximum total gas pressure of 110% of local atmospheric pressure (USEPA 1986). This recommendation is because fish can usually tolerate supersaturated water of less than 110% near the surface of the water. At a depth of 1 m, most fish can tolerate a total gas pressure of 120% with tolerance increasing about 10% for each additional meter of depth. For example, fish experiencing supersaturated water of 140%, require at least 3 m of depth to ensure a safe refuge from developing gas bubble trauma. The effects of DGS on fresh water and marine organisms are quite different from those caused by toxic chemicals. For example, water depth plays an important role in protecting fish from the effects of DGS. In addition, many rivers and lakes have naturally occurring levels of DGS that are potentially lethal to fish. However, wild fish appear to have developed strategies for surviving in these environments (Fidler and Miller 1994). The signs of GBT in fish are strongly dependent on the size of the animal.

Dissolved gas supersaturation can result from a wide variety of both man-made and natural causes. Hydroelectric and impoundment dams are known to cause high levels of DGS. Other sources of DGS include warm water discharges from cooling facilities (e.g., nuclear and fossil fuel power generating plants), oxygen production by aquatic plants, solar heating of water bodies, ingestion of air into pumping systems, supplemental oxygen in hatcheries, and air lift re-aeration systems. As a major constituent of the atmosphere and the dominant dissolved gas in most water bodies, N_2 concentrations are an important contributor to DGS. However, we have found no reports of GBT caused by N_2 produced through enhanced denitrification.

The discharge of water through dams has received the greatest attention as a source of DGS (Fidler and Miller 1994). At dam sites, DGS is caused by the entrainment of air in water released over dam sluice ways, through low level ports and radial gates, or through turbine machinery associated with power generation. At the base of dams air is entrained in falling water that plunges to depth in pools. Under elevated hydrostatic pressure, air (in the form of bubbles) is forced into solution at pressures of several atmospheres. Injection air lift systems are often used to increase dissolved oxygen concentrations in lakes (Fast et al. 1975, McQueen and Lean 1983). These systems involve the introduction of air or oxygen into the water column. This often takes place at depths where elevated hydrostatic pressures can quickly force gas, in the form of bubbles, into solution with the potential for producing DGS. The mechanisms that produce DGS in these systems are largely the same as those encountered in dams and water falls.

A number of features of the proposed NO_3^- addition program for Onondaga Lake serve to limit the potential for GBT in fish. For example, the most intense N_2 production will take place in hypolimnetic layers where fish and other aquatic organisms are restricted by anoxic conditions. Furthermore, fish can tolerate a total gas pressure of 210 – 310% at the hydrostatic pressures of 2 to 3 atmospheres present at the 10 – 20 m depths of the hypolimnion. As shown previously (see *Nitrogen Gas Ebullition*) NO_3^- addition could increase hypolimnetic N_2 concentrations by a maximum of about 2.8 mgN_2/L or about 17%. Although hypolimnetic N_2

concentrations may become oversaturated with respect to the atmosphere (e.g., ~117%), DGS would not result because of higher hydrostatic pressures in the hypolimnion.

The rate of vertical mixing between the hypolimnion and epilimnion of Onondaga Lake is generally low during the summer stratification interval (Matthews and Effler 2006), limiting the transport of N_2 to the upper layers that support fish. However, major wind-driven upwelling events have occurred in the lake, which can result in the rapid transport of hypolimnetic waters to the surface (Effler et al. 2004). A fish kill that occurred along the northwest shore in September 2003 was attributed to severe oxygen depletion caused by the upwelling of anoxic hypolimnetic water enriched in the oxygen-demanding reduced species CH_4 and HS^- (Effler et al. 2004). Addition of NO_3^- to the hypolimnion would ameliorate the impact of upwelling events on DO concentrations through abatement of SO_4^{2-} reduction and related decreases in the HS^- pool and its associated DO demand. Upwelling events transport N_2 from the hypolimnion to the upper waters in the same fashion and create the potential for DGS.

On a lake-wide basis the potential for N_2-induced DGS is very limited. This situation can be demonstrated for an extreme scenario in which the epilimnion and hypolimnion are mixed instantaneously. We will assume that the N_2 concentration of the epilimnion is 15 mgN_2/L, which is the saturation concentration at 20 °C. The hypolimnetic N_2 concentration is assumed to be at the highest achievable level of 20 mgN_2/L at 10°C. In the unlikely event that these water masses were mixed instantaneously the resulting concentration for the completely mixed water column would be 16.9 mgN_2/L or 113% saturation. During an upwelling event higher N_2 concentrations might be attained on a more spatially limited basis. Measurements of total dissolved gas (TDG) concentrations would provide the information necessary to evaluate fully the potential for DGS in Onondaga Lake. TDG sensors are widely available and readily added to water quality probe packages that are deployed routinely in the lake. Measurements of TDG should be included as part of a pilot study to evaluate the feasibility of NO_3^- addition to abate MeHg production.

Nitrate - Toxicity Potential

Nitrate is less toxic than the other forms of nitrogen in the aquatic environment, such as nitrite and ammonia. However, at very high concentrations nitrate is toxic to humans and a variety of aquatic organisms. One of the better documented human health effects associated with nitrate is infantile methemoglobinemia. Nitrate toxicity is due primarily to its conversion to nitrite, which oxidizes Fe^{2+} in hemoglobin to Fe^{3+}. This compound (methemoglobin) does not bind oxygen, resulting in reduced oxygen transport from lungs to tissues. The transport of oxygen by the blood is inhibited and suffocation may occur. Most cases of infant methemoglobinemia are associated with exposure to nitrate in drinking water used to prepare infants' formula at NO_3^- levels >20 mgN/L (USEPA 1991). Other health effect claims associated with intake of NO_3^- contaminated groundwater include birth defects, spontaneous abortions, hypertension, thyroid hypertrophy, and certain types of cancer. The U.S. EPA has established a maximum contaminant level (MCL) for NO_3^- in drinking water of 10 mgN/L.

As in humans, the main toxic effect of NO_3^- in aquatic organisms is caused by the conversion of oxygen-carrying pigments to forms that are incapable of carrying oxygen. Nitrate toxicity to aquatic animals increases with increasing NO_3^- concentrations and exposure times and decreases with increasing body size, water salinity, and environmental adaptation (Camargo et al. 2005). During long-term exposures NO_3^- concentrations of 10 mgN/L may adversely affect sensitive freshwater invertebrates, fishes and amphibians (Camargo et al. 2005). Camargo et al. (2005) suggest a maximum NO_3^- level of 2 mgN/L to protect the most sensitive freshwater species. The American Water Works Association (1990) suggested a limit for NO_3^- of 90 mgN/L to protect warm water fish.

The program for NO_3^- addition outlined here is designed to achieve NO_3^- concentrations of > 1 mgN/L in the hypolimnion during the summer months when anoxic conditions prevail. This program is not designed to result in NO_3^- concentrations higher than those that occur presently during spring turnover (2.0 to 2.5 mgN/L; Figure 10b). It is envisioned that NO_3^- will be added to the hypolimnion on an as-needed basis, guided by frequent lake-wide monitoring of NO_3^- concentrations in the lake (see *Monitoring Issues*). In other words, NO_3^- should only be added at the rate at which it is consumed, which limits the potential for NO_3^- accumulation in the hypolimnion. Furthermore, the target area for NO_3^- addition is the anoxic hypolimnion, which does not support aquatic life. In summary, addition of NO_3^- as described here will not result in toxic levels of NO_3^- and does not pose a significant risk to humans or aquatic organisms.

Byproducts of Incomplete Denitrification and DNRA

The byproducts of incomplete denitrification are NO_2^-, N_2O and NO, which result from the incomplete reduction of NO_3^- to N_2. These nitrogen species can also result from the incomplete nitrification of NH_4^+ to NO_3^- (Wetzel 2001). These byproducts are rapidly converted to more stable forms (N_2 or NO_3^-) and are rarely present in high concentrations in natural aquatic ecosystems. However, large accumulations of NO_2^- and N_2O have been observed under anoxic conditions in the hypolimnia of eutrophic lakes (Wetzel 2001). Rates of NO_2^- and N_2O production in these lakes were highest with very low dissolved oxygen concentrations (ca. 0.1 mg/L) and much lower under Fe^{3+} and SO_4^{2-} reducing conditions.

With respect to toxicity potential, NO_2^- is the denitrification byproduct of primary concern. It is well established that NO_2^- is considerably more toxic to fish than is NO_3^- (Russo 1985). The occurrence of high concentrations of NO_2^- is an important water quality concern because this anion is highly toxic to fish, causing hypoxia by the oxidation of hemoglobin to methemoglobin (Rodriquez-Moreno and Tarazona 1994, Russo 1980, Russo et al. 1981). New York State has established water quality standards for NO_2^- of 0.020 and 0.100 mgN/L for salmonid and non-salmonid systems, respectively.

Concentrations of NO_2^- reported for Onondaga Lake over the 1989 – 1998 interval by Gelda et al. (1999) were the highest encountered for lakes in their review of the literature, except for values measured proximate to domestic waste discharges in Hamilton Harbour, Lake Ontario (Barica 1990). Annual NO_2^- maxima ranged from 0.20 to 1.00 mgN/L over this 10 year interval. These conditions represented violations of New York water quality standards (Gelda et al. 1999).

A number of materials have been identified as mitigating against the toxic effects of NO_2^- (Lewis and Morris 1986). The strongest documented interaction is for Cl^- (Lewis and Morris 1986, Russo and Thurston 1977). Onondaga Lake is unusually rich in Cl^- (~400 mg/L), as a result of industrial and natural inputs (Doerr et al. 1994, Effler et al. 1996). An empirical relationship has been developed to adjust NO_2^- toxicity results for the Cl^- mitigation effect (Lewis and Morris 1986). Gelda et al. (1999) applied this relationship for the Cl^- concentration of Onondaga Lake, and found that the documented NO_2^- levels would not be toxic. However, this interpretation should be considered highly uncertain because the relationship was extended in this case beyond the upper bound of Cl^- incorporated in its development (Lewis and Morris 1986). The New York State standard(s) for NO_2^- presently does not consider mitigating effects of water chemistry, including Cl^-.

The status of Onondaga Lake with respect to NO_2^- has improved in recent years, probably largely as a result of more complete nitrification at Metro. Annual NO_2^- maxima are about 0.200 mgN/L and they occur within the anoxic hypolimnion, which indicates that the primary source is incomplete denitrification rather than nitrification (UFI, unpublished data). Concentrations of NO_2^- in the oxic upper waters are consistently below the non-salmonid standard of 0.100 mgN/L and above the salmonid standard of 0.020 mgN/L. Detailed vertical profiles indicate that NO_2^- produced in the hypolimnion does not reach the epilimnion as it is efficiently converted to NO_3^- within the oxic metalimnion. Thus, although nitrate addition may result in higher NO_2^- concentrations in the hypolimnion during summer stratification, NO_2^- concentrations in the upper waters are unlikely to be affected. Detailed monitoring of NO_2^- during a pilot study would provide important information about the magnitude of the NO_2^- increase that might be expected. In the unlikely event that all of the added NO_3^- was converted to NO_2^-, and the NO_2^- remained within the hypolimnion (i.e., no loss via nitrification, denitrification, or transport), a maximum hypolimnetic concentration of 2.84 mg NO_2^--N/L could be achieved.

The oxidation of organic matter results in the stoichiometric production of ammonium, regardless of the redox pathway (Mattson and Likens 1993). The production of ammonium increases when NO_3^- is reduced by DNRA rather than denitrification. Ammonium is of water quality concern because (1) it is the preferred form of N for supporting algae growth (Harris 1986, Wetzel 2001); (2) it can promote oxygen depletion through the nitrification process (Gelda et al. 2000, Hall 1986); and (3) free ammonia is toxic to aquatic life at low concentrations (USEPA 1985, 1998).

Typically used analytical methods determine the concentration of total ammonia ($T\text{-}NH_3$), which is the sum of the ionized (NH_4^+) and unionized (NH_3) forms. The fraction of $T\text{-}NH_3$ that exists as NH_3 (the highly toxic form) increases as pH and temperature increase. However, the toxicity of a certain concentration of NH_3 decreases as pH and temperature increase. These opposing effects have been accommodated in the development of water quality criteria for ammonia (USEPA 1985, 1998). The status of Onondaga Lake with respect to ammonia toxicity has been thoroughly documented (Effler et al. 1990, Matthews et al. 2000). The rate of accumulation of $T\text{-}NH_3$ in the hypolimnion of Onondaga Lake has systematically decreased since 1989 (UFI, unpublished data). Upgraded nitrification treatment at Metro has also contributed to lower $T\text{-}NH_3$ concentrations in the hypolimnion.

Despite the occurrence of high T-NH_3 concentrations, ammonia toxicity is generally not a noteworthy concern in the hypolimnia of lakes because the fraction of T-NH_3 present as NH_3 is low at typical values of pH and temperature. For example, NH_3 accounts for about 0.3% of T-NH_3 under conditions typical of the hypolimnion of Onondaga Lake (pH = 7.2, T = 10°C). The contribution of NH_3 increases to about 5% under typical epilimnetic condition (pH = 8.0, T = 25°C). In addition, ammonia toxicity is not a concern in anoxic hypolimnia as aquatic fauna are unable to inhabit these anaerobic environments. While addition of NO_3^- to the hypolimnion of Onondaga Lake could result in the production of T-NH_3 through DNRA, it is unlikely to be a noteworthy concern with respect to ammonia toxicity.

Hypolimnetic Chemistry, Sedimentation, and Cation Concentrations

Potential for Calcite Formation in Response to Addition of Nitrate Salts

We evaluated the potential for the formation of additional calcite ($CaCO_3$) in response to hypothetical additions of NO_3^- salts to the hypolimnion of Onondaga Lake. Typical late summer concentrations for the hypolimnion (10-19 m) of the lake are shown in Table 8. To conduct this analysis we used the chemical equilibrium model MINEQL+ (Schecher and McAvoy 1998). In the calculations we initially assumed the reference conditions of the hypolimnion of the lake (Table 8) with a temperature of 10°C and ionic strength corrections. For the treatment conditions, we considered the alternative application of Ca^{2+}, Na^+ and K^+ -NO_3^- salts. Assuming a 120 day application period, a hypolimnetic volume of 4.02×10^7 m^3, and that Ca^{2+}, Na^+ and K^+ accumulate in the hypolimnion (i.e., no precipitation reactions) throughout the application period, results in the following increases in concentration: 0.10 mM Ca^{2+}, 0.20 mM Na^+, and 0.19 mM K^+. Nitrate addition as KNO_3 would have an appreciable impact on K^+ concentrations in the lake. Addition of $Ca(NO_3)_2$ or $NaNO_3$ would have negligible impacts on Ca^{2+} or Na^+ concentrations, respectively. We assumed two end-member conditions for each nitrate-salt treatment. The first was that the added salt would remain in the nitrate form. This condition is unrealistic given that the reducing conditions in the hypolimnion of the lake would promote nitrate reduction following the addition of the NO_3^- salt. However it may depict the initial conditions immediately following the application. The second condition was intended to depict the water chemistry response once the added NO_3^- was depleted. Increased denitrification would tend to decrease pH, which could promote dissolution of $CaCO_3$. For this calculation it was assumed that the removal of NO_3^- was replaced by an equivalent quantity of alkalinity. Indeed this end-member calculation would likely be an upper limit for calcite formation as this effect would be offset by decreased sulfate reduction, assuming that denitrification simply replaces sulfate reduction as a decomposition pathway for organic matter.

Table 8. Summary of average ambient hypolimnetic conditions in Onondaga Lake and estimates of added treatments of nitrate salts.

Analyte	Hypolimnion
Ambient conditions	
Temperature	10^{o}C
PCO_2	10.2 atm · 10^{-3}
PH	7.2
TIC	4.4 mM
Ca^{2+}	3.3 mM
Na^+	9.6 mM
K^+	0.11 mM
Treatment Scenarios	
Ca^{2+} added as $Ca(NO_3)_2$	1360 kg/day
Na^+ added as $NaNO_3$	1560 kg/day
K^+ added as KNO_3	2650 kg/day

The results of our analysis with MINEQL+ are summarized in Table 9. Under ambient conditions the hypolimnion of Onondaga Lake has a pH of 7.2 and is slightly oversaturated with respect the solubility of calcium carbonate. The major form of dissolved Ca^{2+} is the aquo complex (i.e., Ca^{2+}). Addition of nitrate salts resulted in little change in hypolimnetic chemistry. pH values changed little. Addition of $Ca(NO_3)_2$ increased the deposition of $CaCO_3$ slightly, largely corresponding to the added Ca^{2+}. Assuming that all of the added Ca^{2+} precipitated as $CaCO_3$, this added deposition (4.07×10^5 kg) would account for approximately 3% of the background flux of $CaCO_3$ delivered to the sediments annually (1.36×10^7 kg, Womble et al. 1996). Addition of $Na(NO_3)$ and $K(NO_3)$ slightly decreased calcite formation due to formation of Na^+ and K^+ aqueous carbonate complexes. However, these effects are minor and likely never would be detected in a field-monitoring program due to the elevated ambient deposition of calcite in the lake. The largest effect was observed associated with the increase in alkalinity following the removal of the added NO_3^- in the hypolimnion. The stimulation of in-lake alkalinity production associated with the addition of NO_3^- resulted in an increase in pH and increased calcite formation. This effect was evident in all three salt treatments (Table 9). Again as the addition of NO_3^- would serve as a substitute for SO_4^{2-} reduction, which also results in in-lake production of alkalinity, it is unlikely that this process would result in significant additional deposition of calcite beyond that which is already occurring in the hypolimnion. The preliminary analysis suggests that NO_3^- addition, in any form, would likely result in minor changes to the calcite deposition patterns of Onondaga Lake.

Table 9. Summary of results from MINEQL+ calculations indicating the pH and partitioning between dissolved and calcite ($CaCO_3$) in the hypolimnion of Onondaga Lake under reference conditions and following the addition of nitrate as a salt in various forms and the complete removal of added nitrate by denitrification (e.g., cation-alkalinity). Shown in parentheses is the percent distribution of calcium.

Analyte/Scenario	pH	dissolved Ca^{2+}	$CaCO_3$
Reference	7.20	3.25 (98.5%)	0.0499 (1.5%)
$Ca(NO_3)_2$	7.19	3.33 (98.3%)	0.0561 (1.7%)
Ca^{2+}-alkalinity	7.24	2.99 (88.1%)	0.405 (11.9%)
$Na(NO_3)$	7.20	3.24 (98.4%)	0.0487 (1.5%)
Na^{+}-alkalinity	7.26	2.90 (87.9%)	0.397 (12.1%)
$K(NO_3)$	7.20	3.24 (98.5%)	0.0488 (1.5%)
K^{+}-alkalinity	7.25	2.91 (88.5%)	0.38 (11.5%)

Vertical Transport

The addition of electron acceptors to the hypolimnion of Onondaga Lake raises concerns related to the potential for increased vertical transport of contaminants (e.g., Hg) from deep layers to the biologically active waters of the epilimnion. In addition, increased vertical transport can transfer heat to the hypolimnion, thereby altering the stratification regime of the lake and causing increases in the metabolic rates of hypolimnetic bacteria. The magnitude of vertical mixing can also affect the fate and transport of electron acceptor additions.

The vertical transport of dissolved constituents between the thermally stratified layers of lakes is regulated by the magnitude of vertical turbulent diffusion (eddy diffusivity) and the concentration gradient. Accumulation and depletion rates can be adjusted for losses and gains due to vertical mixing between the epilimnion and hypolimnion. These adjustments are described here using NO_3^- as an example, though the same methodology can be applied to the other dissolved constituents (Matthews and Effler 2006, Matthews et al. 2006). Fluxes between the hypolimnion and the upper layers (e.g., $NO_3^-{}_{flux}$, mmol m^{-2} d^{-1}) can be estimated for each sampling interval as the product of the vertical heat exchange coefficient (v_t, m d^{-1}) and the concentration difference between the hypolimnion and epilimnion (e.g., $NO_3^-{}_h - NO_3^-{}_e$, mM):

$$NO_{3\ flux}^{-} = v_t \times \left(NO_{3\ e}^{-} - NO_{3\ h}^{-}\right) \tag{5}$$

Values of v_t can be estimated according to (Chapra 1997):

$$v_t = \frac{V_h}{A_t\ t_s} \ln \frac{\overline{T}_e - T_{h,i}}{\overline{T}_e - T_{h,s}} \tag{6}$$

where V_h (m^3) is the volume of the hypolimnion, A_t (m^2) is the area of the upper bound of the hypolimnion, t_s is the calculation interval (days), $\overline{T}_e$ is the average volume-weighted temperature of the epilimnion over the calculation interval, and $T_{h,\ i}$ and $T_{h,\ s}$ are the volume-weighted temperatures of the hypolimnion at the beginning and end of the calculation interval, respectively. These protocols track those adopted by the authors to adjust for vertical mixing inputs of DO to the hypolimnion in AHOD calculations (Matthews and Effler 2006) and vertical mixing losses of CH_4 from the hypolimnion (Matthews et al. 2005).

Matthews et al. (2006) demonstrated that transport of redox constituents by vertical mixing processes was an important determinant of hypolimnetic accumulation/depletion rates in Onondaga Lake, particularly for substances produced or consumed early in the stratification period. In addition, vertical mixing varied substantially from year-to-year. Inputs associated with vertical mixing contributed 21±6 (mean±standard deviation) and 5±4% to the computed rates of hypolimnetic depletion for O_2 and NO_3^-, respectively. Losses due to vertical mixing were estimated to contribute 24±7, 11±6 and 12±6% to the computed rates of hypolimnetic accumulation for DIC, HS^- and CH_4, respectively. The relatively large adjustments for DIC accumulation and O_2 depletion reflect large concentration differences between the epilimnion and hypolimnion and higher values of the vertical heat exchange coefficient (v_t) during May and June, an interval of relatively weak thermal stratification. Likewise, the relatively small input of NO_3^- to the hypolimnion reflects the absence of large concentration gradients between the epilimnion and hypolimnion during this period of weak stratification. Vertical transport is generally small in Onondaga Lake during the peak stratification interval of July to August, as has been observed in other dimictic lakes (Chapra 1997).

The passive addition of NO_3^- salts to the hypolimnion is expected to have minimal impact on the magnitude of vertical mixing (v_t). Furthermore, target concentrations for NO_3^- in the hypolimnion (~ 1 mgN/L) would remain lower than the ambient epilimnetic concentrations, which range from 1.5 to 2.5 mgN/L (Figure 4). The maintenance of lower NO_3^- concentrations in the hypolimnion compared to the epilimnion would promote transport of NO_3^- from shallower to deeper depths. Diffusion from overlying waters would take advantage of this pool of electron acceptors and allow for efficient use of NO_3^- amendments

Downstream Loading

The addition of electron acceptors to Onondaga Lake in any form raises concerns regarding the potential for downstream loading to Seneca River and eventually Lake Ontario. Additions made to the hypolimnion of the lake during summer would largely remain in these stratified layers until fall (see *Vertical Mixing*), when these layers are mixed into the full volume of the lake. Therefore, downstream loading of constituents associated with NO_3^- salt amendments would be largely limited to the time interval around fall turnover, and would reflect concentrations in the upper layers. As demonstrated above the addition of nitrate salts would have a negligible effect on hypolimnetic concentrations of Ca^{2+} and Na^+. Increases in downstream loading of Ca^{2+} and Na^+ would also be insignificant. Addition of KNO_3 could cause as much as a 3-fold increase in hypolimnetic concentrations of K^+ (from 0.11 mM to 0.30 mM), which would likely result in a more noteworthy increase in loading to the Seneca River during the fall. However, K^+ is a largely conservative cation that poses no major known threats to the Onondaga Lake, Seneca River, or Lake Ontario ecosystems.

Downstream loading of amended NO_3^- and the potential byproducts of NO_3^- reduction, primarily N_2, T-NH_3 and NO_2^-, would also be limited to the fall mixing period. Because NO_3^- additions would be made on an “as needed” basis and terminated at fall turnover, there is limited potential for major increases in loading of NO_3^- to the Seneca River. As discussed previously (see *Byproducts of Incomplete Denitrification and DNRA*), NO_3^- addition could cause increases in hypolimnetic concentrations of T-NH_3 and NO_2^-. The pools of T-NH_3 and NO_2^- present in anoxic layers are expected to be reduced substantially via nitrification ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$) as they are mixed with the oxygenated waters of the epilimnion. It is also noteworthy that concentrations of T-NH_3 and NO_2^- in Onondaga Lake have decreased substantially over the last decade (Matthews et al. 2001).

As a means to investigate the potential for increased downstream loading of NO_3^- we will assume that treatment resulted in a fall turnover NO_3^- concentration of 1.5 mgN/L. The NO_3^- concentration was 1.0 mgN/L at fall turnover in 2004. The additional mass of NO_3^- in the lake due to treatment would be approximately 65,500 kg. This is about 15% of the prevailing summertime (June – September) NO_3^- load carried by downstream portions of the Seneca River. Most of the NO_3^- exported from Onondaga Lake following turnover (i.e., after late October) would reach Lake Ontario, because of limited biological uptake associated with low temperatures. As discussed in more detail subsequently (see *Primary Production*), NO_3^- loading is not a concern with respect to primary production in Onondaga Lake, Seneca River, or Lake Ontario.

Trace Contaminants

The candidate NO_3^- salts listed in Table 1 contain trace quantities of soluble and insoluble impurities. Impurity results for a typical analysis of solid form $Ca(NO_3)_2$ are presented in Table 10. The soluble impurities found in the highest concentrations in $Ca(NO_3)_2$ are sodium and sulfate, which are both present in high concentrations in Onondaga Lake. Insoluble impurities are a maximum of 0.1% by weight and consist of calcium phosphate, fluoride, sulfate and silica. In addition, the solid and solution forms of $Ca(NO_3)_2$ contain 1.0% and 0.05% NH_4^+-N, respectively.

Table 10. Soluble and insoluble impurities in solid form $Ca(NO_3)_2$. Information provided by Tully Ag Center, Tully, NY.

Impurities	Percent by Weight
Soluble	
Copper (Cu)	<0.0001
Lead (Pb)	<0.0001
Manganese (Mn)	<0.001
Chloride (Cl)	0.001
Iron (Fe)	0.0015
Magnesium (Mg)	0.002
Aluminum (Al)	<0.005
Potassium (K)	0.005
Sodium (Na)	0.01
Sulfate (SO_4)	<0.02
Insoluble	0.1 (max.)

Primary Production

Background

The magnitude of primary production is generally acknowledged to have three primary drivers with respect to ambient conditions: (1) temperature, (2) light, and (3) availability of critical (e.g., limiting) nutrients (Chapra 1997). Cultural eutrophication is the acceleration of the natural eutrophication process associated with enhanced primary production from anthropogenic inputs of the critical nutrient(s). Onondaga Lake suffers from a number of degraded features of water quality from cultural eutrophication, including: (1) high concentrations of phytoplankton, including nuisance cyanobacteria; (2) low water clarity; (3) rapid loss of DO from the hypolimnion; (4) accumulations of oxygen-demanding reduced by-products of anaerobic decomposition in the hypolimnion; and (5) subsequent depletion of DO lake-wide during fall mixing (Effler et al. 2002). Onondaga County has embarked on a major rehabilitation effort to abate the impacts of its domestic waste inputs to Onondaga Lake. A major goal of this program is the amelioration of the lake's problem of cultural eutrophication through control of the limiting nutrient.

Nitrogen (N) is a critical nutrient for aquatic plants, including the microscopic phytoplankton. Phytoplankton can use either the ammonium ($T\text{-}NH_3$) or NO_3^- forms of N (Harris 1986). Ammonium is the preferred form of N by phytoplankton for energetic reasons, and is generally depleted preferentially before noteworthy uptake of NO_3^- occurs by this community (Wetzel 2001).

Rehabilitation of cultural eutrophication problems focuses on reducing the input, or loading, of the critical, or limiting, nutrient (Cooke et al. 2005). There are two key types of information managers need to consider in such initiatives. First, managers must identify the limiting nutrient (i.e., the nutrient available in the lowest concentrations **relative** to the needs of the phytoplankton to support growth; Hutchinson 1973). Nitrogen is the limiting nutrient in most marine waters, while phosphorus (P) is the limiting nutrient in the vast majority of inland waters (Wetzel 2001). Second, identification of noteworthy sources of the limiting nutrient is necessary. Sources are generally partitioned according to external and internal inputs. The external inputs are usually partitioned according to point and non-point sources. Internal inputs are most often associated with mobilization from hypolimnetic sediments following the development of anoxia in the overlying waters.

Augmentation of the NO_3^- Pool of the Hypolimnion Is Not a Concern for Primary Production in Onondaga Lake

The rehabilitation program for the impacts of domestic waste on Onondaga Lake has adopted an approach that implicitly accepts P, not N, as the target limiting nutrient. This approach manifested in the portion of that program that addresses N. Implementation of the program has sought to convert T-NH_3 to NO_3^- to eliminate toxicity impacts, through nitrification treatment at Metro, rather than substantively reduce the overall loading of N to the lake. This situation is reflected in the fact that denitrification treatment was not considered necessary in the recent renovations of Metro. Moreover, this approach is an intentional strategy, to discourage the development of nuisance N-fixing phytoplankton populations, by maintaining a high N/P ratio in the lake (Effler 1996). Accordingly, the very high NO_3^- levels that are presently maintained in the upper productive layers of the lake have not been identified as a water quality issue. These levels are substantially above those considered limiting to phytoplankton growth (Matthews et al. 2001; e.g., conditions consistent with "nutrient saturation", Bannister 1974). Accordingly, any potential increases in T-NH_3 and NO_3^- in the upper productive layers of the lake from NO_3^- treatment of the hypolimnion would not affect primary production. Some positive feedback on the P limitation strategy (e.g., without regard to NO_3^- level) for the lake has recently been reported at the Eighth Annual Onondaga Lake Scientific Forum (A. Effler, Abstract, 2006). Decreases in primary production from reductions in P inputs were reported, in the presence of very (i.e., saturating) high NO_3^- concentrations.

Finally, the potential increases in the pools of N constituents that serve as nutrients for phytoplankton growth from NO_3^- treatment of the hypolimnion would be minor. The pathway to the overlying epilimnion, where primary production occurs, would be vertical transport by various natural mixing processes, driven by positive vertical concentration gradients (Wodka et al. 1983). This form of transport is strongly limited during the productive summer months by the density gradients associated with the thermal stratification regime. Hypolimnetic accumulations of various constituents that develop during summer do not become incorporated into the overlying productive layers until after the critical summertime interval for primary production (Auer et al. 1993, Effler et al. 2002).

Benthic Community

The biological activity of benthic organisms can disturb the sediments in which they live (bioturbation) and increase the transport of both dissolved and particulate constituents to the water column (Bosworth and Thibodeaux 1990, Schaffner et al. 1997). The effects of bioturbation can include the mixing of sediment layers, alteration of chemical forms of contaminants, bioaccumulation, and transport of contaminants from the sediment to the water column (USEPA 2005). Typical depths of bioturbation activity in freshwater are 0 to 3 cm for oligochaetes and 0 to 15 cm for burrowing insects such as midge and mayfly larvae (USEPA 2005). The presence of macroinvertebrates in sediments may increase, by orders of magnitude, the solute flux across the sediment-water interface due to biologically enhanced advection (Caffrey et al. 1996, Kuwabara et al. 1999). For example, motile ciliates can increase O_2 transport through sediments up to 10 times above molecular diffusion (Glud and Fenchel 1999). Tube-dwelling chironomid larvae have been shown to increase O_2 uptake and denitrification in eutrophic lake sediments (Svensson and Leonardson 1996). Bioturbation is generally the most important mechanism for reworking sediments and releasing contaminants in sediments not subjected to erosion and resuspension (Mohanty et al. 1998). Burrowing organisms may assimilate MeHg directly from underlying anoxic sediments and become vectors of MeHg to benthic predators (Gagnon et al. 1996).

There have been few studies of the role of benthic macrofauna in the processing and transport of Hg in pelagic sediments. Benoit et al. (in press) studied the role of benthic organisms in the production of MeHg in sediments of Boston Harbor. They found that activity of benthic macrofauna deepens the zone of MeHg production and increases the overall sediment pool of MeHg.

Addition of NO_3^- to the hypolimnion will not alter the anoxic condition of the lower waters and sediments during summer stratification, which precludes the existence of benthic invertebrates in the profundal zone of the lake. Therefore, NO_3^- addition would not promote the development of a benthic community and the potential for bioturbation and enhanced transport of materials, including Hg, from pelagic sediments to the water column. Furthermore, maintenance of an anoxic hypolimnion during summer creates distance between fish and other aquatic organisms and the area of intense MeHg production.

Recommendations

The recommendations listed here are activities that would yield technical information pertinent to the conduct of a successful, ecosystem-scale demonstration project on the effects of NO_3^- addition on MeHg production in Onondaga Lake.

Recommendations to further develop the concept of nitrate addition as a remedial approach for the production of MeHg:

1. given the quantities of NO_3^- that may be added to the hypolimnion of Onondaga Lake, and the various potential sink processes for NO_3^- (e.g., canonical denitrification, autotrophic denitrification, DNRA, and anammox), an evaluation of the fate of NO_3^- additions should be conducted.
2. conduct laboratory NO_3^- depletion experiments (i.e., sediment incubations) to quantify sediment NO_3^- demand and the effects of NO_3^- concentration and overlying velocities on this demand. These experiments should also evaluate the relationship between NO_3^- dose and MeHg response.

3. conduct hydrodynamic measurements to assess near-bottom turbulence and velocity, and primary drivers, to quantify conditions that will influence NO_3^- demand. These measurements should be made before and during a potential nitrate demonstration project.
4. continue to investigate alternative approaches to inhibit the activity of SRB (e.g., hypolimnetic oxygenation).
5. use an appropriate mechanistic framework to quantify the combined effects of year-to-year variations in runoff (e.g., dilution of primary NO_3^- input) and meteorological conditions (e.g., timing of stratification and vertical mixing) on features of NO_3^- treatment, including timing, rate, and overall magnitude of NO_3^- addition.
6. quantify the impacts of addition of NO_3^- salts on the stratification and mixing regime of the lake.
7. examine the historic record of availability and cost for $Ca(NO_3)_2$ and other NO_3^- salts.
8. more fully evaluate issues related to safety, handling and storage of NO_3^- salts.
9. use a quantitative hydrodynamic framework to evaluate the efficacy of realistic NO_3^- deployment strategy options (e.g., number of sites, boat tracks).
10. conduct dye studies as necessary to demonstrate success in deploying NO_3^- salt additions to targeted site(s).
11. develop and test an equation of state to effectively predict density based on the specific ionic composition of Onondaga Lake with NO_3^- addition.
12. after selection of a nitrate release strategy (boat-based or shore-based) an engineering design of the system components should be completed, including: mixing tanks, pumps, valves, boats, diffuser, continuous monitoring system, and all associated costs.

Recommendations related to monitoring before and after remediation and assessment of potential treatment effects:

13. analyze the 2006 data set to more fully assess the effect of NO_3^- concentration on the pattern of MeHg release.
14. continue to remain apprised of NO_3^- depletion rates from in-lake monitoring.
15. continue in-lake monitoring to remain apprised of long-term trends, interannual variations, and shifts that would affect NO_3^- dosing. In addition, the 3-D gridding capabilities of the ISUS for NO_3^- and HS^- should be developed and validated, including rapid turnaround of graphical output and interpretations.
16. continue to monitor baseline conditions for constituents associated with potential impacts of NO_3^- addition, including ebullition, total dissolved gas levels, and concentrations of N_2, NO_2^-, and T-NH_3.
17. given the dependence of NO_3^- demand on primary production and sediment diagenesis, it may be prudent to apply quantitative frameworks to project long-term treatment needs.

Conclusions

This report has presented preliminary assessments of the feasibility and potential impacts of controlling MeHg production in the lower waters of Onondaga Lake through the addition of NO_3^-. Scientific justification for the use of NO_3^- to control MeHg production was presented in a review of relevant redox processes and an abbreviated retrospective analysis of redox conditions in Onondaga Lake. Water column results from the summer of 2005 provided preliminary support for the concept of NO_3^- addition to abate sulfate reduction and MeHg production. The historic usage of NO_3^- addition as a management alternative for lakes was reviewed and the feasibility of its use in Onondaga Lake was assessed. In addition, potential impacts of NO_3^- addition on the physical, chemical, and biological status of the lake were preliminarily evaluated.

In-lake observations suggested that noteworthy decreases in MeHg production may be attained by maintenance of adequate NO_3^- concentrations in lower portions of the hypolimnion until fall turnover. Under current conditions, substantial augmentation of the hypolimnetic NO_3^- pool would be required during the July to October interval. Preliminary calculations suggest that NO_3^- addition to the hypolimnion at a rate of approximately 1000 kg NO_3^- -N/day during the July to October interval would be required to maintain NO_3^- concentrations >1 mgN/L at the sediment-water interface and abate the activity of SRB and related MeHg production. However, it is reasonable to expect that the magnitude of NO_3^- amendments would decrease in the future associated with recent reductions in primary production, cleanup of Hg sources to the lake, and burial of Hg in the sediments. Various chemical forms of NO_3^- are suitable for treatment of lake sediments, including calcium nitrate ($Ca(NO_3)_2$), a widely available form of NO_3^- that has been used extensively to treat lake sediments.

Preliminary analyses indicated that NO_3^- addition would not result in noteworthy negative water quality impacts in Onondaga Lake or downstream ecosystems. However, it would be prudent to track the concentrations of nitrite (NO_2^-), total ammonia (T-NH_3), nitrogen gas (N_2), and total dissolved gas (TDG) prior to and during NO_3^- addition. Because a NO_3^- addition program would maintain an anoxic hypolimnion, it is anticipated that exposure of aquatic organisms to Hg contaminated sediments would be limited. This preliminary analysis suggests that hypolimnetic NO_3^- addition holds promise as a method of abating MeHg production in Onondaga Lake with minimal negative environmental effects.

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