INTERPRETIVE REPORT
EVALUATION OF NITRATE ADDITION TO CONTROL METHYLMERCURY PRODUCTION IN ONONDAGA LAKE: 2006 STUDY

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EXECUTIVE SUMMARY

The sediments, water column, and biota of Onondaga Lake are contaminated with mercury (Hg). Metabolic processes, including primary production and decomposition of organic matter, strongly influence the cycling of Hg in the lake. Rehabilitation activities are underway and forthcoming, as described in the Record of Decision, to abate mercury contamination throughout the lake. These activities seek to reduce external loading of mercury to the system and its cycling and bioaccumulation within the lake.

In September and October of 2005 the Upstate Freshwater Institute (UFI) and Syracuse University (SU) made presentations to the regulatory community (including NYSDEC and USEPA) and Honeywell Inc. concerning changes in the oxygen resources and decomposition pathways of the lake. As part of those presentations, a new approach was suggested to potentially abate the accumulation of MeHg in the hypolimnion of the lake. It was proposed that nitrate (NO_3^-) could be added to the hypolimnion of the lake to inhibit sulfate (SO_4^{2-}) reduction and the production of methylmercury (MeHg). A preliminary impact and feasibility analysis for the addition of nitrate to control the production of MeHg in Onondaga Lake has been prepared (UFI and SU 2007a).

The Upstate Freshwater Institute and the Center for Environmental Systems Engineering at Syracuse University conducted a water quality monitoring program on Onondaga Lake during the late March to late November interval of 2006 with the following overarching goals:

- evaluate the role of nitrate in controlling MeHg production in Onondaga Lake;

- document, with sufficient resolution, the interaction between MeHg production and related metabolic and redox processes, with particular emphasis on oxygen and nitrate; and

- evaluate current conditions with respect to methane gas ebullition.

Data collected as part of this monitoring program were presented in the *Data Usability Summary Report, Evaluation of Nitrate Addition to Control Methylmercury Production in Onondaga Lake: 2006 Study* (Exponent 2007). Scientific interpretations of these data are presented here, with particular emphasis on constituents associated with the production of MeHg (i.e., dissolved oxygen, nitrate, sulfide).

The data collected during this study have provided important insights into metabolic processes and Hg cycling in Onondaga Lake. Both dissolved oxygen (DO) and NO_3^- were shown to control the production of MeHg and the associated accumulation in the hypolimnion during the summer stratification interval. Low levels of MeHg (0.1 ng L^{-1}) were observed in the

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hypolimnion during the early portion of the stratification interval when DO was present throughout the water column. Volume-weighted concentrations of MeHg in the hypolimnion were limited to ~1 ng L^{-1} from June 12 to July 17 when NO_3^- concentrations above the sediments were > 0.2 mg N L^{-1}. The surface area of sediment overlain by water with low NO_3^- concentrations (< 0.5 mg N L^{-1}) explained 70% of the weekly variations in hypolimnetic MeHg concentrations. The data indicate that maintenance of higher NO_3^- concentrations (e.g., > 1 mg N L^{-1}) can reasonably be expected to result in yet lower levels of MeHg in the hypolimnion. Markedly higher hypolimnetic MeHg concentrations (volume-weighted average of 3.31 ng L^{-1} and maximum of 5.40 ng L^{-1}) were observed during late summer when both DO and NO_3^- were depleted in the lower layers.

The maximum rates of hypolimnetic NO_3^- depletion observed in 2004 and 2005 were used previously to estimate that a NO_3^- addition rate of 1050 kg N d^{-1} would be necessary to abate SO_4^{2-} reduction and MeHg production. A lower rate of NO_3^- depletion was observed in 2006, resulting in a NO_3^- addition rate (718 kg N d^{-1}) 32% lower than the earlier estimate. Despite the lower estimate for 2006, we recommended that the higher NO_3^- addition rate of 1050 kg N d^{-1} be retained for preliminary design and planning purposes. The average ebullitive flux for the May – October interval of 2006 (73±59 mL m^{-2} d^{-1}, mean±standard deviation) was 3-fold higher than in 2004 (24±20 mL m^{-2} d^{-1}) and 54% lower than observed in 1990 (159±98 mL m^{-2} d^{-1}). A definitive explanation for the increase in ebullition from 2004 to 2006 has not been established.

The 2006 water column data support NO_3^- addition as a promising approach to control the production and accumulation of MeHg in Onondaga Lake. The vertically detailed profiles collected weekly were instructive and allowed for identification and meaningful interpretation of water column signatures. Although control of MeHg production is indicated at NO_3^- concentrations of < 0.5 mg N L^{-1}, a target of 1.0 mg N L^{-1} at the sediment-water interface is recommended for effective treatment, for preliminary purposes. It is anticipated that additional studies will result in further refinement of this target. Incubation experiments, using intact sediment cores, are recommended to better define the dose-response relationships for NO_3^- – MeHg and DO – MeHg.

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INTRODUCTION

The sediments, water column, and biota of Onondaga Lake are contaminated with mercury (Hg). Mercury cycling in the lake is strongly influenced by metabolic activity, including primary production and decomposition processes. Rehabilitation activities are either underway or forthcoming, as described in the Record of Decision, to abate mercury contamination throughout the lake. These activities seek to reduce external loading of mercury to the system and its cycling and bioaccumulation within the lake. Concurrently, another rehabilitation program under the Amended Consent Judgment between Onondaga County and USEPA aimed at abating the impacts of domestic waste discharged to the lake is underway. This initiative has greatly altered lake metabolism by: (1) decreasing the level of gross primary production, and thereby the supply of organic carbon delivered to the lake sediments, and (2) shifting the metabolic pathways by which this organic matter is decomposed. These effects have diminished the role of sulfate (SO_4^{2-}) reduction in decomposition of deposited organic matter. Sulfate reducing bacteria are largely responsible for the methylation of ionic mercury. Monomethylmercury (MeHg) is the form of primary concern because it is a neurotoxin that strongly bioaccumulates in food webs. Recent mercury measurements from the water column of Onondaga Lake suggest that noteworthy changes in the cycling of mercury, and perhaps levels of contamination, may have occurred since the early 1990s (UFI and SU 2007a).

In September and October of 2005 the Upstate Freshwater Institute (UFI) and Syracuse University (SU) made presentations to the regulatory community (including NYSDEC and USEPA) and Honeywell Inc. concerning changes in the oxygen resources and decomposition pathways of the lake. As part of those presentations, a new approach was suggested to potentially abate the accumulation of MeHg in the hypolimnion of the lake. We proposed that nitrate could be added to the hypolimnion of the lake to inhibit SO_4^{2-} reduction and the production of MeHg. A preliminary impact and feasibility analysis for the addition of nitrate to control the production of MeHg in Onondaga Lake was submitted to NYSDEC in December of 2006 (UFI and SU 2007a). Regardless of the means used to control production of MeHg, a comprehensive monitoring program is required to effectively represent spatial and temporal patterns of key substances. Furthermore, such information will need to be available in a timely manner.

The Upstate Freshwater Institute and the Center for Environmental Systems Engineering at Syracuse University conducted a water quality monitoring program on Onondaga Lake during the late March to late November interval of 2006 to address the following overarching goals.

- evaluate the role of nitrate in controlling MeHg production in Onondaga Lake;

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- document, with sufficient resolution, the interaction between MeHg production and related metabolic and redox processes, with particular emphasis on oxygen and nitrate; and

- evaluate current conditions with respect to methane gas ebullition.

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METHODS

A summary of the laboratory analyses conducted is provided in Table 1. Vertically detailed profiles of these parameters were collected on 34 sampling occasions in 2006, including 32 weekly samplings from March 28 to November 1, 2006 and additional samplings on 14 November and 28 November. Sampling for reduced chemical species (H_2S_T, Fe^{2+}, CH_4) focused on anoxic depths. A map showing the sampling location is presented in Figure 1. The rationale for the sampling design is provided in the work plan (UFI and SU 2007b).

Table 1   Target Analyte List, Methods, Method Detection Limits, and Method Reporting Limits

Analyte	Method	Method Detection Limit	Method Reporting Limit
UFI Laboratory			
Chlorophyll a	EPA 445	0.2 µg/L	0.5 µg/L
NO_x	EPA 353.2	5 µgN/L	16 µgN/L
NO_2	EPA 353.2	3 µgN/L	9 µgN/L
T-NH_3	EPA 350.1	12 µgN/L	41 µgN/L
DOC	SM 18-20 5310B	0.2 mgC/L	0.4 mgC/L
TIC	SM 18-20 5310C	0.6 mgC/L	2.0 mgC/L
Chloride	SM18-20 4500 Cl⁻ C	10 mg/L	100 mg/L

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Table 1   Target Analyte List, Methods, Method Detection Limits, and Method Reporting Limits (Continued)

Analyte	Method	Method Detection Limit	Method Reporting Limit
Ferrous Iron	Heaney and Davison 1977	16 µg/L	32 µg/L
Sulfide(1)	SM18 4500 S E	0.5 mg H_2S_T/L	1 mg H_2S_T/L
Sulfide(2)	SM 20 4500 S G	16 µg H_2S_T/L	32 µg H_2S_T/L
Dissolved Methane	Addess, 1990	0.03 mg/L	0.1 mg/L
Dissolved Nitrogen gas	Addess, 1990	0.03 mg/L	0.1 mg/L
Ebullitive N_2	Addess, 1990	0.03 mg/L	0.1 mg/L
Ebullitive CH_4	Addess, 1990	0.03 mg/L	0.1 mg/L
Syracuse University Laboratory			
Total Mercury Water	EPA Method 1631E (U.S. EPA 2002)	0.2 ng/L	0.5 ng/L
Methyl Mercury	EPA Method 1630 (U.S. EPA 2001)	0.02 ng/L	0.05 ng/L

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Figure 1. Bathymetric map of Onondaga Lake.

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RESULTS AND DISCUSSION

Vertical profiles of the data are presented in Appendix A and discussed in this section.

Stratification Regime and Runoff Conditions

The dimictic stratification regime of Onondaga Lake regulates the vertical distributions of important water quality constituents, including electron acceptors (e.g., O_2, NO_3^-), metabolic byproducts (e.g., HS^-, CH_4), and forms of mercury. The water column of the lake was completely mixed in late March and early April of 2006 (Figure 2). The lake began to stratify in mid-April as surface layers warmed faster than deeper layers. The temperature difference between the surface and bottom layers increased in a generally progressive fashion through July and subsequently decreased until the onset of complete fall turnover in late October. Example vertical profiles of temperature are presented in Figure 3, which depict the seasonal pattern of thermal stratification during 2006, including the progressive deepening of the upper mixed layer. Sharp temperature gradients in the metalimnion from June to September severely limited vertical exchange between the hypolimnion and overlying layers as indicated by the low rate of warming at 18 m over this period (Figure 2). Temperature at 18 m warmed less than 1°C over this interval, from 11.0°C on May 30 to 11.9°C on October 2. Temperature is an important determinant of metabolic rates, including rates of carbon catabolism in the hypolimnion and sediments. This effect is often represented as a doubling of metabolic rates for each 10°C increase in temperature (i.e., $Q_{10} = 2$; Chapra 1997).
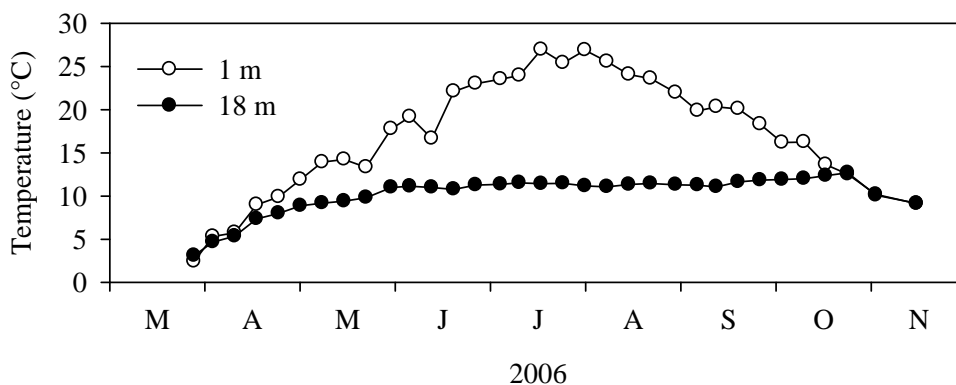

Figure 2. Time series of temperature in the surface and bottom waters of Onondaga Lake for the 2006 study period. These data were collected via a profiling robotic platform located at south deep and operated by UFI.
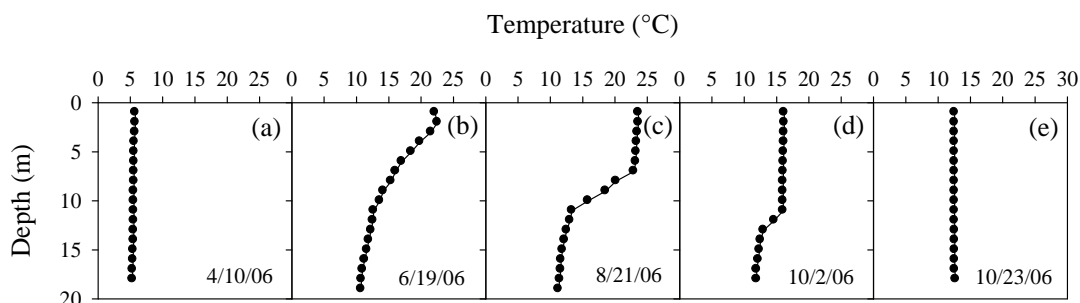
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Temperature (°C)

Figure 3. Selected vertical profiles of temperature collected from the south deep sampling site of Onondaga Lake during 2006: (a) April 10, (b) June 19, (c) August 21, (d) October 2, and (e) October 23. These data were collected via a profiling robotic platform located at south deep and operated by UFI.

Precipitation and associated surface runoff can impact lake ecosystems through the delivery of a variety of dissolved and particulate constituents, including plant nutrients (phosphorus and nitrogen) and suspended solids. In addition, runoff conditions affect water residence times in lakes and rates of water renewal. Onondaga Creek accounts for about 30% of the total annual inflow to Onondaga Lake and is a good indicator of temporal patterns of total lake inflow (Effler 1996). Flows in Onondaga Creek were high relative to historic conditions for most of the 2006 study interval (Figure 4). Following a period of relatively low runoff during April and May, the flow rate in Onondaga Creek from June to November was distinctly elevated compared to median values for the 1971 – 2005 period of record (Figure 4). Major runoff events occurred throughout the early June through early August interval and again during October and November.
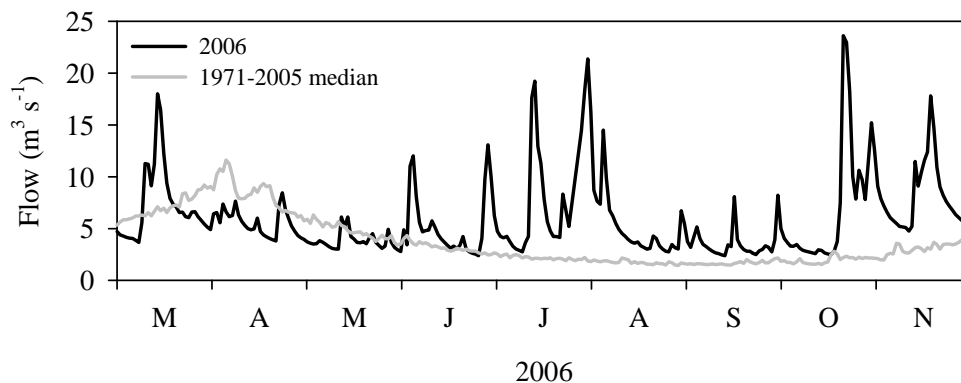
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Figure 4. Time series of daily average flows in Onondaga Creek for the 2006 study period and median values for the 1971 – 2005 interval. Flow data were reported by USGS for the gauge located at Spencer Street.

Temporal and Vertical Distributions of Chlorophyll and Carbon

Chlorophyll **a** (Chl), the principal photosynthetic pigment common to all phytoplankton, is the most widely used surrogate measure of phytoplankton biomass, and is generally considered to be the most direct and reliable measure of trophic state. Primary production in the upper waters and the subsequent deposition of particulate organic carbon to the hypolimnion fuels decomposition processes in the sediments. Concentrations of Chl in the upper waters (average of 0, 2, 4 m values) of Onondaga Lake are presented in Figure 5. The summer average (mid-May to mid-September) Chl concentration in the upper waters was 14.3 μg L^{-1}. This level is distinctly above values commonly used to demarcate the boundary between mesotrophic and eutrophic conditions (e.g., 9 μg L^{-1}, Cooke et al. 2005). Historically, concentrations of Chl in the upper waters of Onondaga Lake were substantially higher (e.g, >30 μg L^{-1}) and indicative of hypereutrophy (Effler et al. 2005). Concentrations of Chl were much lower in the hypolimnion during the June to September interval of 2006, when strong thermal stratification limited mixing of phytoplankton into the deeper layers of the lake.
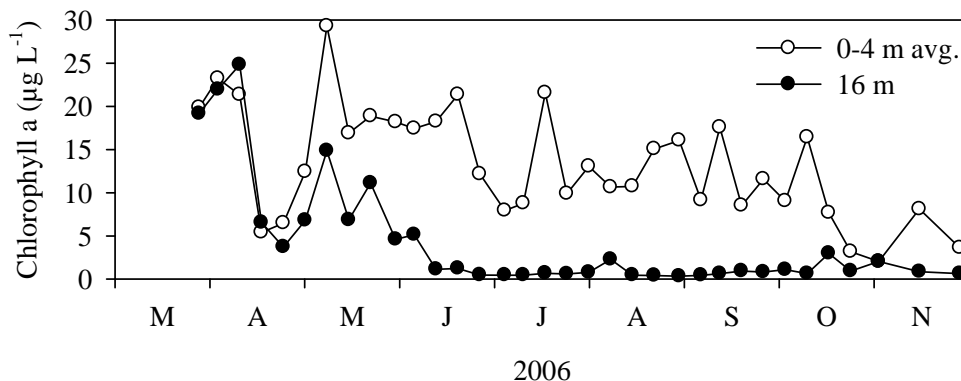
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Figure 5. Time series of chlorophyll **a** concentrations in the upper waters (average of 0, 2, and 4 m measurements) and at 16 m in Onondaga Lake during the 2006 study period.

Inorganic carbon constitutes the major pH buffering system in fresh waters. Chemical reactions and aquatic biota are influenced importantly by pH. Tributary inflows are usually the primary external source of inorganic carbon to lakes. Sinks for inorganic carbon in the epilimnion include photosynthetic uptake of CO_2 and precipitation and deposition of calcite ($CaCO_3$). The respiratory processes of the decomposition of organic matter constitute the principal internal source of inorganic carbon to lakes. Inorganic carbon can accumulate to high concentrations in isolated hypolimnetic layers where respiratory sources of CO_2 greatly exceed loss processes. Concentrations of total inorganic carbon (TIC = $[H_2CO_3]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$) were determined as part of this study. pH measurements can be used to partition TIC into its component species. Bicarbonate (HCO_3^-) is the dominant form at the slightly alkaline pH levels of Onondaga Lake.

TIC concentrations in Onondaga Lake were about 45 mg C L^{-1} and approximately uniform with depth under the nearly isothermal conditions of late March and April of 2006 (Figure 6). Concentrations of TIC in the epilimnion and hypolimnion began to diverge in May as progressive depletion occurred in the upper waters. Depletion of TIC in the upper waters continued through late July, and reached a low value of 31.7 mg C L^{-1} on July 24. Thereafter, concentrations of TIC in the upper waters increased, and by late October concentrations had rebounded to the levels of April. The decrease in TIC observed during the May to late July period is attributable to decalcification as was documented for earlier years (Effler 1996). The subsequent increase in TIC concentrations that began in late July may have been caused by increased tributary loading (Figure 4) and/or decreased primary production as suggested by generally lower Chl concentrations during late summer and fall (Figure 5).

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Concentrations of TIC at 18 m increased in a largely progressive manner from 47 mg C L^{-1} in late June to 61 mg C L^{-1} in mid-September, associated with the decomposition of organic carbon and production of CO_2 (Figure 6). This seasonal pattern of TIC accumulation in the hypolimnion has been recurring and is associated with CO_2 production by both aerobic and anaerobic (denitrification, sulfate reduction, methanogenesis) decomposition pathways (Matthews et al. 2007). The rate of TIC accumulation has been used as a measure of hypolimnetic metabolism for Onondaga Lake (Matthews et al. 2007) and other lakes (e.g., Mattson and Likens 1993). Vertical patterns indicate that the sediments were the dominant source of TIC to the water column (Figure 7).
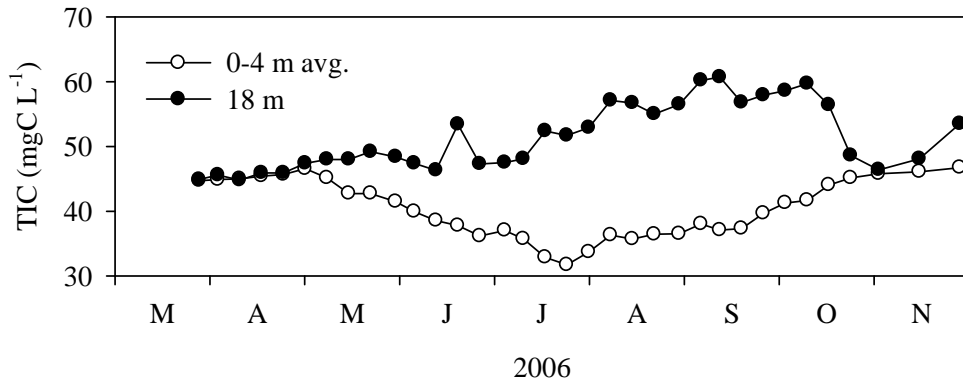

Figure 6. Time series of total inorganic carbon (TIC) concentrations in the upper waters (average of 0, 2, and 4 m measurements) and at 18 m in Onondaga Lake during the 2006 study period.
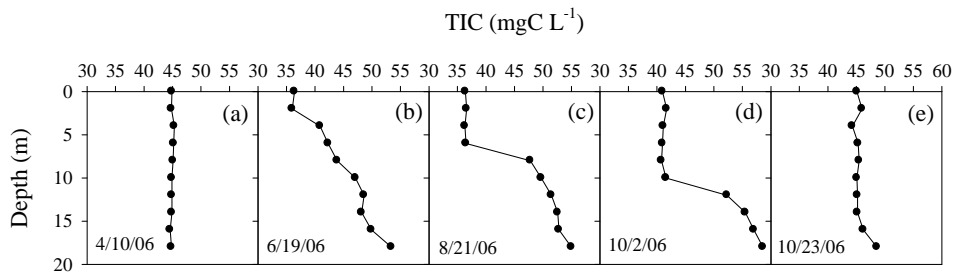

Figure 7. Selected vertical profiles of total inorganic carbon (TIC) collected from the south deep sampling site of Onondaga Lake during 2006: (a) April 10, (b) June 19, (c) August 21, (d) October 2, and (e) October 23.

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The dissolved organic carbon (DOC) pool of lakes consists primarily of carbon compounds, such as humic substances, that are relatively recalcitrant to bacterial decomposition (Wetzel 2001). Cycling of labile organic substrates is often very rapid, and these dynamics would not be resolved at a weekly sampling frequency. The primary allochthonous sources of DOC to lakes are tributary inflows, which generally enter the upper layers of stratified lakes. In-lake sources of DOC include excretion by living organisms, cell breakage (autolysis), and microbial decomposition of dead organisms and detrital material. In many cases inputs of DOC to lakes are approximately balanced by slow rates of microbial degradation. Therefore, spatial and temporal variations in DOC are often observed to be minor (Wetzel 2001). Positive correlations have been documented between DOC concentrations and levels of Hg in fish (Driscoll et al. 2007).

Concentrations of DOC in Onondaga Lake are generally between 3 and 4 mg C L^{-1} (Figure 8), which is substantially lower than the median value reported for eutrophic lakes by Wetzel (2001). The relatively low DOC concentrations in Onondaga Lake may be related to the biogeochemical characteristics of the watershed, including an abundance of inorganic particulates and a relatively small area of contributing wetlands. Clay and $CaCO_3$ particles are known to have a high sorption potential for DOC (Jardine et al. 1989, Otsuki and Wetzel 1973). These particle types are abundant in the Onondaga Lake and its primary tributaries, Onondaga and Ninemile Creeks (Effler 1996).

During the summer months, DOC concentrations were usually highest in the surface and bottom waters with lower values observed in the metalimnion (Figure 9b, c). The peak DOC concentrations of 2006 were observed in the upper waters following a major runoff event in mid-July (Figures 8 and 9b). Sinks for DOC exceeded sources in the upper waters following the mid-July maxima as manifested in progressive decreases in DOC through mid-October (Figure 8). Modest increases in DOC above the sediment-water interface during summer stratification indicate that the sediments were a source of DOC to the water column (Figure 9b and c). This DOC probably originated from the incomplete decomposition of deposited particulate organic matter. Increases in DOC at 18 m suggest that minor accumulations of DOC occurred in the lower layers of the lake during late summer (Figure 8).
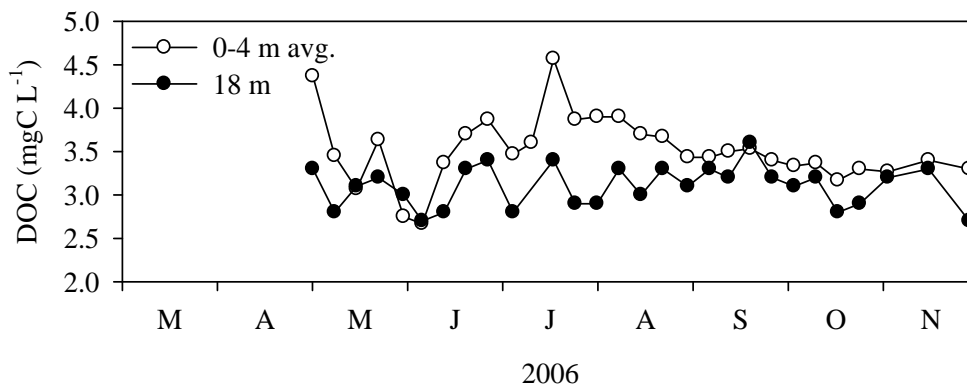
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Figure 8. Time series of dissolved organic carbon (DOC) concentrations in the upper waters (average of 0, 2, and 4 m measurements) and at 18 m in Onondaga Lake during the 2006 study period. A DOC concentration of 1.5 mgC L^{-1} was measured at 18 m on July 10. This data point has been omitted from the time series based on our limnological judgment that it is not valid.
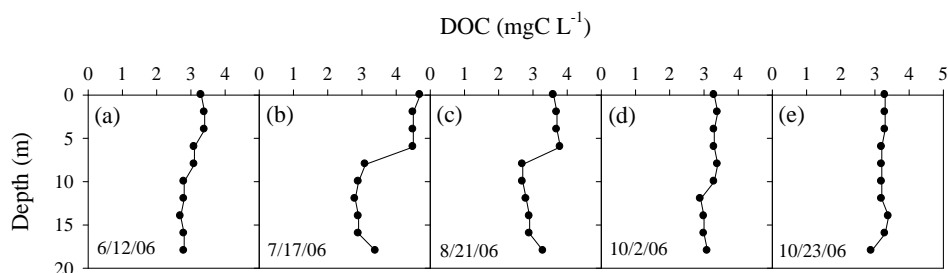

Figure 9. Selected vertical profiles of dissolved organic carbon (DOC) collected from the south deep sampling site of Onondaga Lake during 2006: (a) June 12, (b) July 17, (c) August 21, (d) October 2, and (e) October 23

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Vertical and Temporal Patterns of Dissolved Oxygen

Dissolved oxygen (DO) is an important resource of lakes and a fundamental indicator of ecosystem health and metabolism (Wetzel 2001). It regulates lake chemistry through oxidation and reduction processes, and is intimately associated with various biological processes that occur in lakes, from its origin as a byproduct of photosynthesis to its utilization in the mineralization of organic matter. Increased oxygen depletion, particularly in hypolimnia, is often a symptom of cultural eutrophication, associated with excessive nutrient loading, enhanced primary production, and the subsequent deposition and decomposition of organic matter. Severe oxygen depletion results in anoxic conditions in hypolimnia, which in turn promotes nutrient release from the sediments (Mortimer 1941, 1942; Nürnberg 1984) and the accumulation of oxygen-demanding reduced species (Mortimer 1941, 1942, 1971; Gelda et al. 1995). Adequate DO levels are necessary for most forms of aquatic life. Establishment of anoxic or hypoxic conditions in a hypolimnion excludes a major volume of the lake and its sediments to habitation by many aquatic organisms (Wetzel 2001).

Concentrations of DO in Onondaga Lake were essentially uniform with depth during April 2006 when the water column was nearly isothermal (Figures 10 and 11a). DO concentrations at 18 m decreased progressively during May as thermal stratification caused the lower waters to be isolated from sources of DO (Figure 10). By mid-June the 18 and 19 m layers were essentially anoxic (Figures 10 and 11b). The entire hypolimnion was anoxic by late June, and by mid-August anoxic conditions were present at depths below 7 m and included metalimnetic layers (Figure 11c). As the upper mixed layer deepened during late summer and fall, previously depleted layers were replenished with DO (Figure 10d). With the onset of complete fall turnover in late October, DO was present throughout the water column at concentrations greater than 5 mg L^{-1} (Figure 11e). Appreciable depletion of DO did not occur in the upper waters during fall turnover (Figures 10 and 11e). Severe depletion of DO (< 4 mg L^{-1}) in the upper waters during fall turnover, associated with the oxidation of reduced chemical species (e.g., HS^-, CH_4), was a common occurrence through the mid-1990s (Matthews and Effler 2006b). This feature of water quality has improved markedly over the last decade associated with decreases in hypolimnetic accumulations of HS^-, CH_4, and ammonia (Effler and Matthews 2007). Historically, lake wide hypoxia in fall caused fishes to leave the lake and seek refuge in the Seneca River (Tango and Ringler 1996). It is likely that improved DO conditions during fall turnover have made this migration unnecessary. Increased residence time in the lake may result in increased exposure of fishes to Hg.
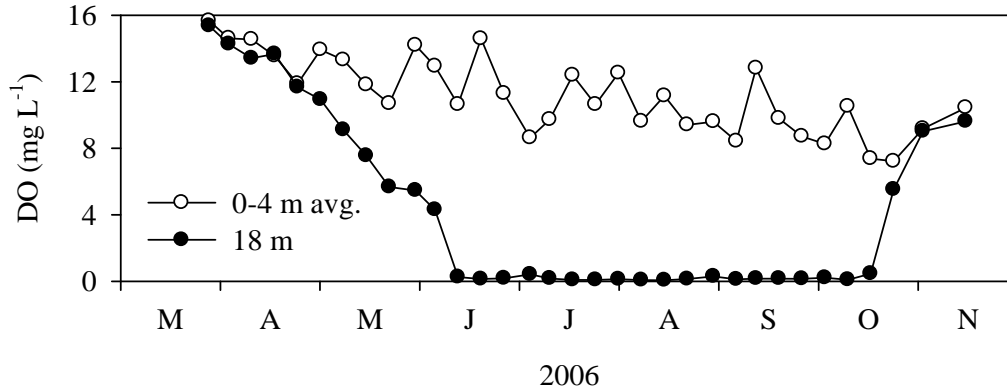
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Figure 10. Time series of dissolved oxygen (DO) concentrations in the upper waters (average of 0 to 4 m measurements) and at 18 m in Onondaga Lake during the 2006 study period.
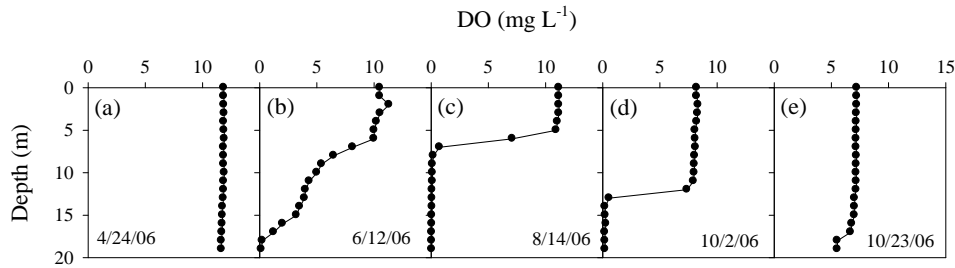

Figure 11. Selected vertical profiles of dissolved oxygen (DO) collected from the south deep sampling site of Onondaga Lake during 2006: (a) April 24, (b) June 12, (c) August 14, (d) October 2, and (e) October 23.

Oxygen consumption in hypolimnia and sediments reflects decomposition of settling and deposited particulate organic matter that is formed mostly through primary production in the overlying trophogenic zone (Hutchinson 1938, 1957). The rate of hypolimnetic oxygen depletion has long been recognized as an integrator of lake metabolism. The rate of loss of the mass of DO, normalized for the surface area of the hypolimnion, described as the areal hypolimnetic oxygen deficit (AHOD; $g\ m^{-2}\ d^{-1}$), is recognized as a quantitative representation of this oxygen depletion (Wetzel and Likens 2000). AHOD has been found to be correlated with primary production and its surrogates, total phosphorus concentration (TP) (Rast and Lee 1978; Chapra and Canale 1991), chlorophyll *a* concentration (Chl *a*) (Vollenweider and Janus 1981)

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and Secchi disc transparency (SD) (Lasenby 1975). AHOD values for Onondaga Lake decreased 49%, from an average of 2.12 g m^{-2} d^{-1} for the 1978 – 1986 interval, to an average of 1.08 g m^{-2} d^{-1} for the 1997 – 2002 interval (Matthews and Effler 2006a). This decrease was driven by an abrupt decrease in the deposition of particulate organic carbon into the hypolimnion starting in 1987.

AHOD was calculated for 2006 using the protocols of Matthews and Effler (2006a). The upper bound of the hypolimnion was set at 10.5 m and adjustments were made for vertical mixing inputs of DO to the hypolimnion. The mass of DO in the hypolimnion decreased linearly during the late April to late June period except for a notable aberration in late May (Figure 12). The increase in DO mass in late May was accompanied by a temperature decrease in the upper waters (Figure 2) and was probably caused by high winds that enhanced vertical mixing between the epilimnion and hypolimnion. A similar mixing event was documented for 1998 (Matthews and Effler 2006a). The AHOD value calculated for 2006 was 1.22 g m^{-2} d^{-1}, which is somewhat higher than the average value for the 1997 – 2002 interval (1.08 g m^{-2} d^{-1}; Matthews and Effler 2006a) and slightly less than the average for the 2003 – 2005 interval (1.34 g m^{-2} d^{-1}; unpublished data). The higher rates of DO depletion observed in recent years may be attributable to the absence of *Daphnia* in the lake since 2003 or higher phosphorus loading rates (Matthews et al. 2007). Either mechanism could cause an increase in the downward flux of particulate organic carbon to the hypolimnion and an increase in DO consumption. The rate of loss of DO has important implications for the relative contributions of decomposition pathways in the hypolimnion (Matthews et al. 2007). Of particular importance here is the duration and rate of sulfate reduction and the associated production of MeHg (Benoit et al. 2003).
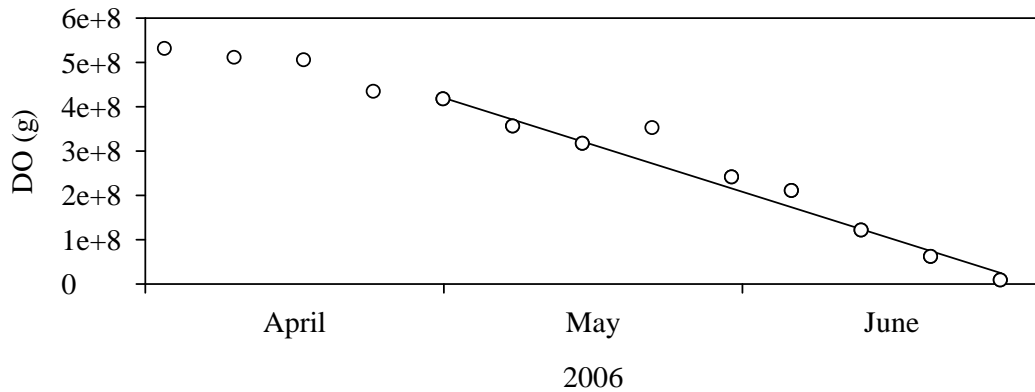

Figure 12. Time series of the mass of dissolved oxygen (DO) in the hypolimnion (depths below 10.5 m) in Onondaga Lake during the April to June interval of 2006.

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Dissolved Inorganic Nitrogen Species and Depletion of Hypolimnetic Nitrate

The dissolved inorganic nitrogen pool of lakes is generally dominated by nitrogen gas (N_2), nitrate (NO_3^-), and ammonia (T-NH_3 = [NH_4^+] + [NH_3]). Nitrite (NO_2) is an intermediary of two microbially-mediated nitrogen transformations that are important in lakes, nitrification (T-$NH_3 \rightarrow NO_2^- \rightarrow NO_3^-$) and denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2$). Because of its reactive nature, NO_2^- is present in very low concentrations in lakes under natural conditions. Forms of nitrogen are involved in a variety of important processes in lakes. Ammonia is a product of the decomposition of organic matter and the preferred form of nitrogen to support phytoplankton growth. Nitrate can also be used to meet the nitrogen requirements of phytoplankton, and serves as an electron acceptor for the decomposition of organic matter in anoxic environments. Unionized ammonia (NH_3) and NO_2^- are toxic to aquatic biota at low concentrations. At very high concentrations NO_3^- can also have toxic effects on freshwater organisms.

During April 2006 NO_3^- concentrations were nearly uniform with depth and ranged from 1.9 to 2.3 mg N L^{-1} (Figures 13 and 14a). Noteworthy variations in NO_3^- concentrations in the upper waters included a distinct peak on May 8, a sudden decrease between July 10 and 17, and a more gradual decrease in October with the approach to fall turnover (Figure 13). The abrupt increase on May 8 was probably caused by the entry of the NO_3^- enriched Metro effluent into the upper layers of the lake. This phenomenon was documented more completely by Prestigiacomo et al. (2007) using rapid profiling measurements of NO_3^-. The major decrease in NO_3^- that occurred in mid-July was associated with a major runoff event that began on July 12 (Figure 4). Apparently, the relatively low NO_3^- tributary inflows served to dilute the NO_3^- enriched waters of the lake. The gradual decrease in NO_3^- concentrations in the upper waters during October reflect entrainment of the NO_3^- depleted waters of the hypolimnion into the upper mixed layer (Figure 13).

The concentration of NO_3^- at 18 m decreased at a nearly constant rate from May through early July, before decreasing precipitously between July 10 and July 17 (Figure 13). Following a brief period of replenishment in late July that was presumably caused by wind-induced mixing, NO_3^- concentrations in the near-bottom waters decreased again in early August and remained below 0.05 mg N L^{-1} through mid-October (Figure 13). NO_3^- concentrations increased progressively during October with the approach to complete fall turnover. By late November the concentration of NO_3^- at 18 m increased to 1.7 mg N L^{-1}, which approached the level observed during spring turnover. Selected vertical profiles from June 12, August 14, and October 2 depict the seasonal progression of NO_3^- depletion in the hypolimnion (Figure 14b, c, d).
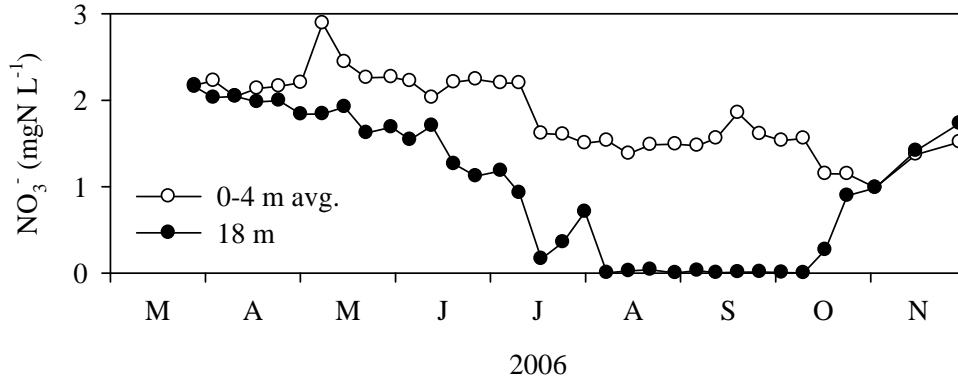
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Figure 13. Time series of nitrate (NO_3^-) concentrations in the upper waters (average of 0, 2, and 4 m measurements) and at 18 m in Onondaga Lake during the 2006 study period.
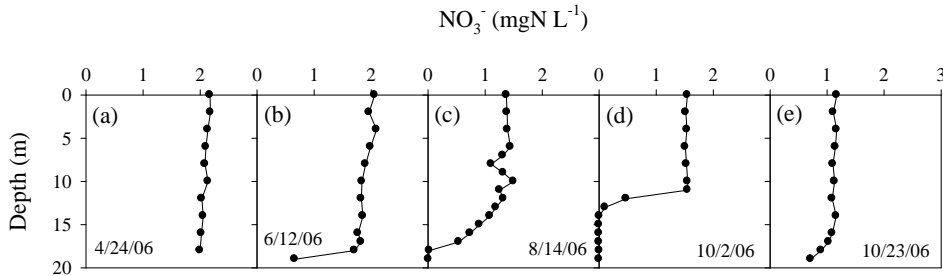

Figure 14. Selected vertical profiles of nitrate (NO_3^-) collected from the south deep sampling site of Onondaga Lake during 2006: (a) April 24, (b) June 12, (c) August 14, (d) October 2, and (e) October 23.

Further insights into patterns of NO_3^- depletion in the hypolimnion are available through inspection of the time series of volume-weighted concentrations (Figure 15). The high variability observed at 18 m during July decreased substantially in the volume-weighted representation. This observation highlights the presence of strong vertical gradients within the hypolimnion (Figure 14b-d) and the need for vertically detailed measurements to identify these structures and support reasonably accurate estimates of NO_3^- depletion rates in the hypolimnion. In addition, the volume-weighted representation (Figure 15) demonstrates that NO_3^- remained present in the upper layers of the hypolimnion throughout the summer stratification interval despite near total depletion in the lower layers (e.g., Figure 14d).

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The volume-weighted concentration of NO_3^- in the hypolimnion decreased in a highly linear (r^2=0.95) fashion following the depletion of oxygen from the hypolimnion in early July (Figure 15). The observed rate of hypolimnetic NO_3^- depletion during the July 4 to September 25 interval was 98 mg N m^{-2} d^{-1} or 103 mg N m^{-2} d^{-1} when vertical mixing inputs from upper layers are included. This is lower than the maximum NO_3^- consumption rates observed in 2004 (119 mg N m^{-2} d^{-1} from June 14 to August 23) and 2005 (140 mg N m^{-2} d^{-1} from July 5 to September 6) (UFI and SU 2007a). The 2004 and 2005 depletion rates were used to estimate that a NO_3^- addition rate of 1050 kg N d^{-1} would be necessary to abate SO_4^{2-} reduction and MeHg production (UFI and SU 2007a). Based on the 2006 data, the required rate of NO_3^- addition (718 kg N d^{-1}) would be 32% lower than the earlier estimate. In light of the inherent uncertainty of these estimates, the wide year-to-year variations observed, and the desire for a margin of safety it is recommended that the higher NO_3^- addition rate of 1050 kg N d^{-1} be retained for preliminary design and planning purposes. This estimate does not address the possibility of increased demand under a NO_3^- addition program associated with increased concentration gradients at the sediment-water interface. This issue will be addressed explicitly through the conduct of incubation experiments using intact sediment cores. This estimate of the rate of NO_3^- addition may be adjusted in the future to reflect new information, including the results of sediment incubation experiments.

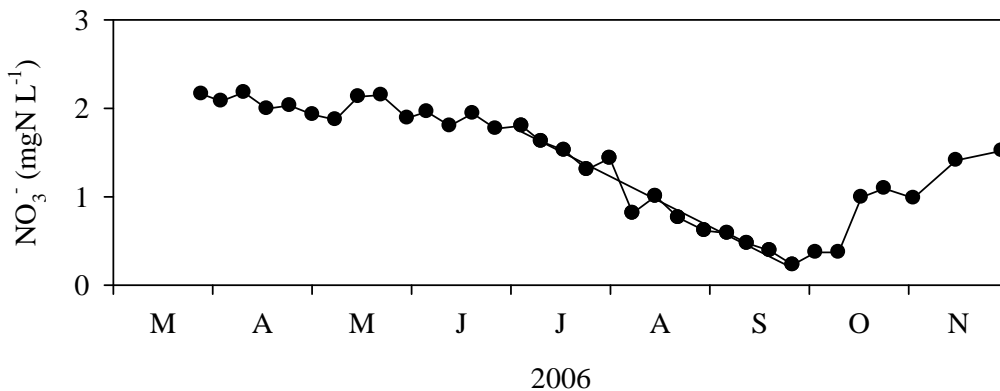**Figure 15.** Time series of volume-weighted nitrate (NO_3^-) concentrations in the hypolimnion (depths below 10 m) of Onondaga Lake during the 2006 study period. Linear regression used to calculate NO_3^- consumption for the July 4 to September 25 interval is shown for reference.

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Under the nearly isothermal conditions of late April and late October concentrations of NO_2^- were largely uniform throughout the water column at about 0.05 mg N L^{-1} (Figure 16a, e). During the summer stratification interval NO_2^- concentrations varied substantially with depth (Figure 16b, c, d). Particularly sharp gradients were observed in the hypolimnion, presumably as a result of the vertical distributions of the important source and sink processes for this constituent. Aerobic conditions are expected to promote the nitrification of $T-NH_3$ to NO_3^- while denitrification is expected to reduce NO_3^- to N_2 under anaerobic conditions. As NO_2^- is an intermediary in both nitrification and denitrification, both processes can serve as sources or sinks for NO_2^-. The available evidence does not support a definitive source for the observed peaks of NO_2^- (Figure 16b, c, d). The NO_2^- peak observed between 10 and 15 m on August 7 is within anoxic depths and appears to be a product of incomplete denitrification (Figure 16c). The peaks on June 19 and October 2 (Figure 16b, d) were likely caused by incomplete denitrification, but incomplete nitrification cannot be ruled out. New York State has established water quality standards for NO_2^- of 0.020 and 0.100 mg N L^{-1} for salmonid and non-salmonid systems, respectively. The salmonid standard was exceeded frequently in 2006, while the non-salmonid standard was exceeded only in hypolimnetic NO_2^- peaks (e.g., Figure 16c, d). The significance of these exceedances is limited by the low DO concentrations that accompany NO_2^- peaks and preclude habitation of these depths by aerobic organisms. 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.
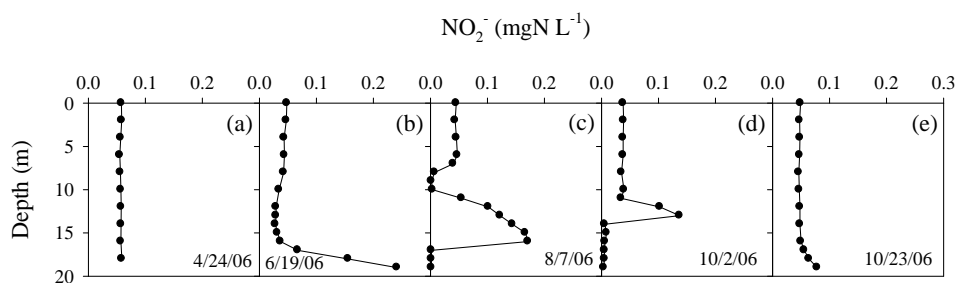

Figure 16. Selected vertical profiles of nitrite (NO_2^-) collected from the south deep sampling site of Onondaga Lake during 2006: (a) April 24, (b) June 19, (c) August 7, (d) October 2, and (e) October 23.

Concentrations of nitrogen gas (N_2) were tracked in this study because N_2 is the principal nitrogenous byproduct of denitrification. Concentrations of N_2 in surface waters are high relative to other forms of nitrogen because of the high partial pressure of N_2 in the atmosphere (0.78 atm). The saturation concentration of N_2 at standard temperature (25°C) and pressure (1 atm) is 13.6 mg N_2 L^{-1}. 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

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L^{-1} 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.

During summer stratification concentrations of N_2 are expected to increase in the hypolimnion as a result of denitrification in profundal sediments. In the upper waters N_2 is expected to be in approximate equilibrium with atmospheric concentrations (e.g., 15 mg N_2 L^{-1} at 20°C). The analytical results for this study are for the sum of N_2 and O_2. Results reported here have been adjusted for O_2 concentrations measured by calibrated probes deployed from the in-lake robotic monitoring platform.   Due to the highly variable nature of the results, N_2 concentrations are reported here in a simplified format in order to depict the central features observed during the 2006 study (Figure 17).   Generally progressive increases in N_2 concentrations were observed during summer stratification (Figure 17). The rate of increase was faster in the hypolimnion, consistent with the occurrence of N_2 production (i.e, denitrification of NO_3^-) in anoxic sediments.
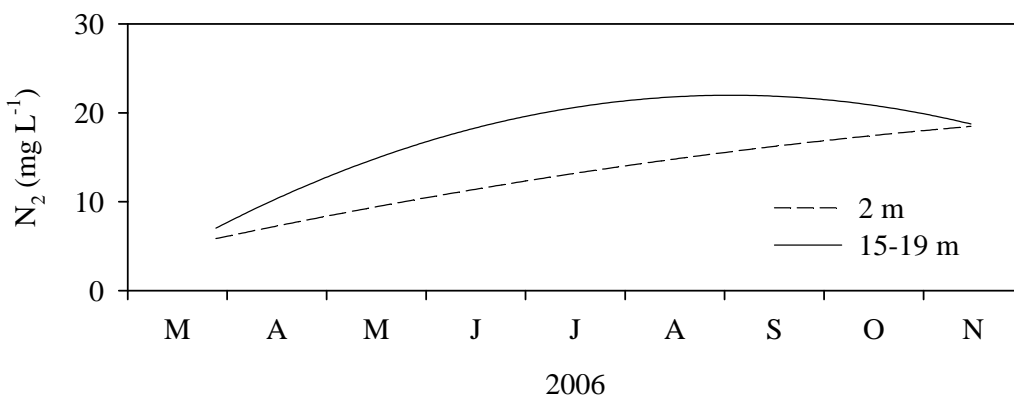

Figure 17.   Polynomial fits to the time series of dinitrogen gas (N_2) concentrations in the upper waters (2 m measurements) and lower waters (15-19 m average) of Onondaga Lake during the 2006 study period.

During spring turnover of 2006 concentrations of T-NH_3 in the water column of Onondaga Lake were vertically uniform at approximately 0.25 mg N L^{-1} (Figures 18 and 19a). With the onset of thermal stratification in May, concentrations of T-NH_3 decreased in the upper waters and increased in the lower waters. During the June to August interval T-NH_3 concentrations in the upper waters were relatively low (< 0.08 mg N L^{-1}) due to uptake by phytoplankton. Concentrations in the upper waters increased in September with the approach to fall turnover and attained a maximum of 0.50 mg N L^{-1} in early November (Figure 18). The concentration of T-NH_3 at 18 m increased during the summer stratification interval and peaked at 2.4 mg N L^{-1} in mid-September (Figure 18). Higher rates of T-NH_3 accumulation were observed over the 1988 –

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1990 interval (Effler 1996) and in 2002 (Figure 18), prior to the establishment of year-round nitrification at Metro and the occurrence of higher in-lake NO_3^- concentrations. This observation suggests a decrease in the overall rate of organic matter decomposition since 2002, as $T-NH_3$ is a product of all terminal decomposition pathways (e.g., aerobic respiration, denitrification, sulfate reduction, methanogenesis). This pattern also suggests that increased NO_3^- reduction has not resulted in major increases in hypolimnetic $T-NH_3$. Detailed vertical profiles clearly indicate release of $T-NH_3$ from the sediments and diffusion into the hypolimnion (Figure 19). Bottom water concentrations decreased precipitously during October as the enriched hypolimnion was entrained into the relatively dilute upper mixed layer. Loss processes for this entrained $T-NH_3$ include phytoplankton uptake and potentially nitrification in the water column.

Onondaga Lake has a long history of exceedances of New York State standards for ammonia toxicity (Brooks and Effler 1990, Matthews et al. 2000). Improved nitrification treatment at Metro has dramatically improved the status of the lake with respect to ammonia toxicity. Contemporary concentrations of $T-NH_3$ in the upper waters are below levels established to protect aquatic organisms from toxic effects. Although $T-NH_3$ concentrations in the hypolimnion are high during summer stratification, levels of NH_3, the toxic form, remain below toxic thresholds because of relatively low pH in the lower layers.
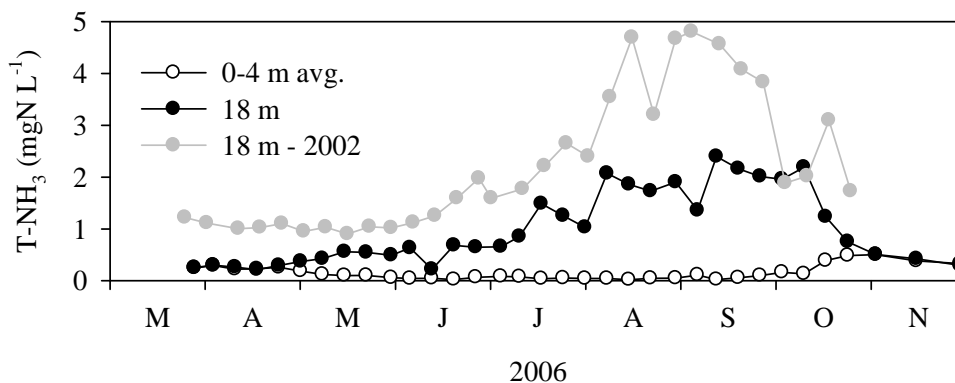
Figure 18. Time series of ammonia ($T-NH_3$) concentrations in the upper waters (average of 0, 2, and 4 m measurements) and at 18 m in Onondaga Lake during the 2006 study period. Concentrations of $T-NH_3$ at 18 m are presented in gray for 2002 to depict conditions prior to year-round nitrification at Metro.
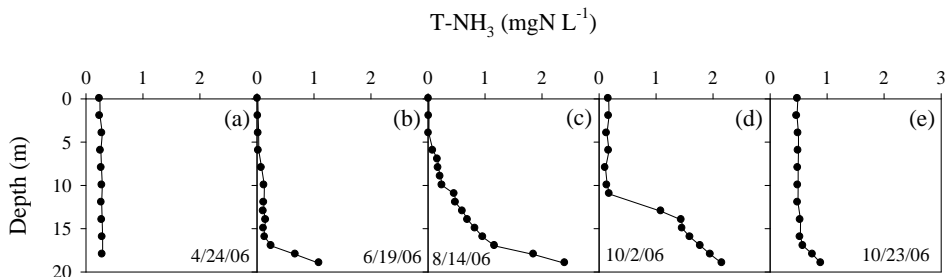
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Figure 19. Selected vertical profiles of total ammonia (T-NH$_3$) collected from the south deep sampling site of Onondaga Lake during 2006: (a) April 24, (b) June 19, (c) August 14, (d) October 2, and (e) October 23.

Ebullition and Composition of Ebullitive Gas

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 suggested 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). 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.

Measured values of ebullitive flux exhibited wide temporal and spatial variations during the 2006 study interval (Figure 20). Average values of ebullitive flux from the sediments for the 2006 study interval were 66.5 mL m^{-2} d^{-1} at south deep and 40.1 mL m^{-2} d^{-1} at north deep (Figure 20a). Somewhat lower average values (57.4 mL m^{-2} d^{-1} at south deep and 30.8 ml m^{-2} d^{-1} at north deep) are obtained when the 7 August to 9 August measurements are omitted as outliers due to the unusually high flux measurements and shorter deployment intervals. Small-scale spatial variability in ebullition, as determined by triplicate gas cone deployments at south deep, was small relative to temporal variations and differences between south deep and north deep (Figure 20). The average coefficient of variation for triplicate measurements at south deep was 0.27 (Figure 20b).

Ebullitive flux at south deep was generally 1.5 to 2-fold higher than at north deep. Ebullition rates at north deep would be expected to be slightly higher than at south deep based upon the shallower depth and lower hydrostatic pressures. Addess (1990) also reported higher ebullitive flux at south deep compared to north deep, and suggested that a higher organic content

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in south deep sediments could cause this pattern. Despite systematic differences in the magnitude of ebullition, temporal variations at south deep and north deep were highly correlated ($r = 0.88$, $p < 0.01$). Large short-term variations in rates of ebullition, similar to those observed for Onondaga Lake (Figure 20a), are commonly observed in productive lake systems (Strayer and Tiedje 1978, Casper et al. 2000). These variations are thought to be driven by physical disturbances and changes in barometric and hydrostatic pressures (Chanton et al. 1989, Mattson and Likens 1990, Takita and Sakamoto 1993). Addess and Effler (1996) reported a weak relationship between ebullitive flux and hydrostatic pressure for Onondaga Lake during the May to September interval of 1989, although events of greatest ebullitive flux occurred over periods of decreasing or low hydrostatic pressure.

A seasonal pattern in the rate of ebullitive flux is suggested by the weekly time series for 2006 (Figure 20a). Ebullition rates were very low (often zero) in early spring and late fall, when the lake was isothermal and DO was present in high concentrations at the sediment-water interface. Rates of ebullitive flux were generally higher during the summer stratification interval. This seasonal pattern was not observed in 1989 (Addess and Effler 1996), 1990 or 2004 (Matthews et al. 2005). Higher rates of ebullition during the summer months might be explained by increased production of CH_4 and/or N_2, or by decreased loss rates of dissolved CH_4 and/or N_2. Either mechanism could cause dissolved gas concentrations in the sediments to exceed saturation, resulting in the formation of gas bubbles. The summer stratification interval is clearly a period of active NO_3^- depletion (Figure 15), N_2 production (Figure 17), and CH_4 production (Figure 25e).

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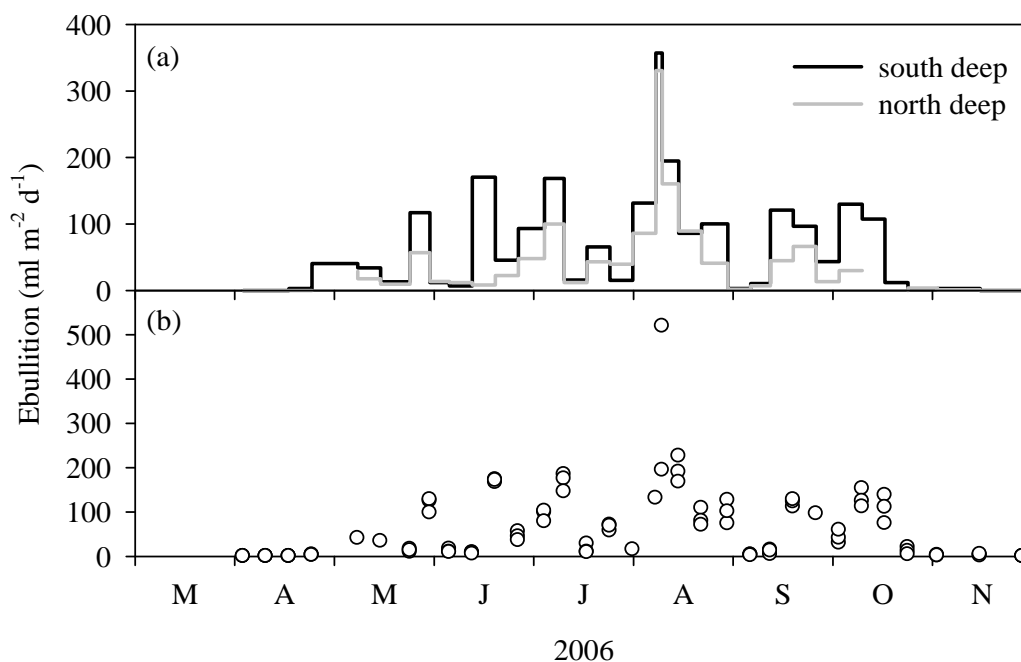
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Figure 20.   Ebullitive flux measurements from collections made approximately weekly from the south deep and north deep sampling sites of Onondaga Lake during 2006: (a) time series for south deep (black line) and north deep (gray line), and (b) triplicate measurements made from three gas cones located proximate to the south deep sampling site.

The average ebullitive flux at south deep for the May – October interval was calculated as 73 ± 59 mL m^{-2} d^{-1} (mean±standard deviation), omitting the high value in early August, in order to facilitate comparisons with earlier studies. This value is 3-fold higher than the May – October average for 2004 (24 ± 20 mL m^{-2} d^{-1}; Matthews et al. 2005) and 54% lower than observed in 1990 (159 ± 98 mL m^{-2} d^{-1}; Matthews et al. 2005). The major decrease in ebullition from 1990 to 2004 was attributed to a decrease in organic carbon deposition to the sediments and lower rates of methanogenesis (Matthews et al. 2005). A cause for the significant (Welch t-test, $p < 0.01$) increase in ebullition from 2004 to 2006 has not been established. Increases in either denitrification or methanogenesis might explain such an increase, but similar rates of hypolimnetic NO_3^- depletion (see page 21) and CH_4 accumulation (UFI unpubl.) were observed in 2004 and 2006. Continuation of ebullition measurements will help determine the permanence of the observed increase in ebullitive flux.

During the interval when gas cones were deployed in anoxic waters (mid-June to early October) the ebullitive gas was comprised of 54% N_2, 46% CH_4, and trace amounts of CO_2

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(average of 14 collections). This represents a potentially noteworthy, albeit statistically insignificant ($\alpha = 0.05$), shift in the composition of ebullitive gases since 1999 when these measurements were last made. In 1999, the average composition of ebullitive gases was 59% CH_4 and 41% N_2 (Matthews et al. 2005). The increased contribution of N_2 may be related to increased availability of NO_3^- in the hypolimnion to support denitrification and the production of N_2. A larger shift in the composition of ebullitive gas was documented from 1989 to 1999 (Matthews et al. 2005). The statistically significant (Welch t-test, $p < 0.01$) decrease in CH_4 content from 1989 (80±9%) to 1999 (59±10%) was consistent with the observed decrease in ebullition. Dissolved nitrogen in sediment pore water can be depleted by methane bubble stripping, resulting in lower N_2 concentrations in gas bubbles at higher rates of ebullition (Chanton et al. 1989). These results support the arguments of Chanton et al. (1989), who suggested that bubble nitrogen content may be a sensitive indicator of CH_4 ebullition rates.

Reduced Byproducts of Anaerobic Metabolism: Fe^{2+}, H_2S_T, and CH_4

In the absence of DO and NO_3^- the decomposition of organic matter proceeds through alternate microbially-mediated pathways, including iron reduction, sulfate reduction, and methanogenesis. Chemically reduced byproducts of these oxidation reactions (Fe^{2+}, H_2S_T, CH_4) accumulate in the anoxic hypolimnion of Onondaga Lake during the summer stratification interval and are oxidized during fall turnover. The spatial and temporal patterns of these reduced byproducts in the water column can provide insights into the occurrence, rates, and locations of these alternate decomposition pathways. Here we present selected vertical profiles of Fe^{2+} (Figure 21), H_2S_T (Figure 22), and CH_4 (Figure 23) from the 2006 study to depict features that bear importantly on metabolism in the hypolimnion and sediments.
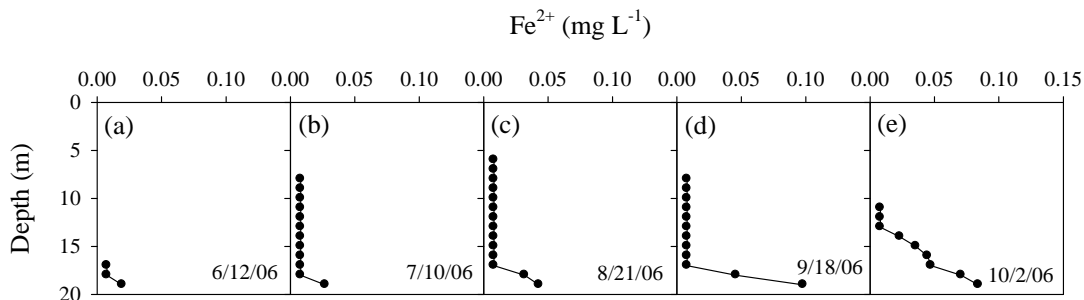

Figure 21. Selected vertical profiles of ferrous iron (Fe^{2+}) collected from the south deep sampling site of Onondaga Lake during 2006: (a) June 12, (b) July 10, (c) August 21, (d) September 18, and (e) October 2.

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H_2S_T (mg L^{-1}), NO$_3^-$ (mg L^{-1})

Figure 22. Selected vertical profiles of total sulfide (H_2S_T) and nitrate (NO_3^-) collected from the south deep sampling site of Onondaga Lake during 2006: (a) June 12, (b) July 10, (c) August 21, (d) September 18, and (e) October 2.

CH_4 (mg L^{-1})

DO (mg L^{-1})

Figure 23. Selected vertical profiles of dissolved methane (CH_4) and dissolved oxygen (DO) collected from the south deep sampling site of Onondaga Lake during 2006: (a) June 12, (b) July 10, (c) August 21, (d) September 18, and (e) October 2.
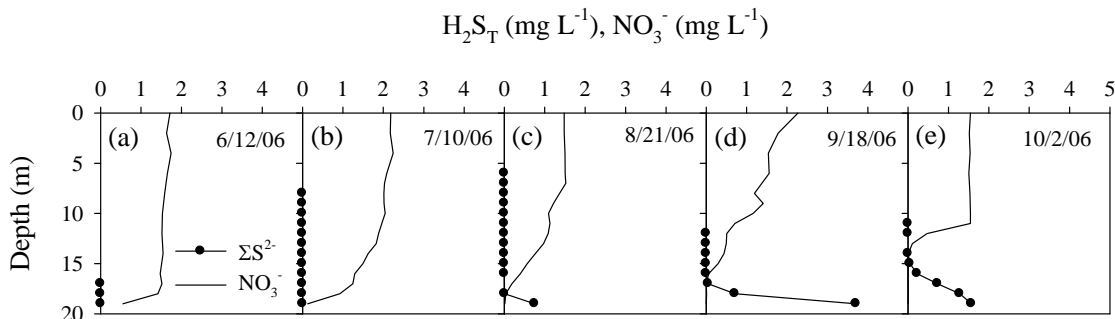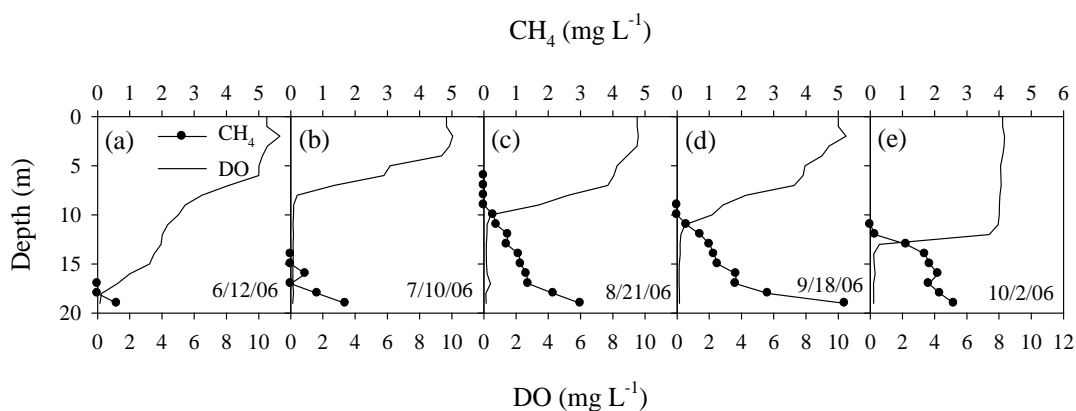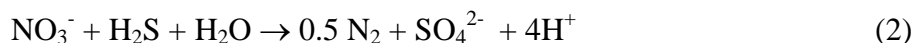
Vertical profiles of the reduced byproducts Fe^{2+} (Figure 21), H_2S_T (Figure 22), and CH_4 (Figure 23) displayed a pattern of progressively increasing concentrations with the approach to the sediment-water interface. These vertical structures are indicative of a sedimentary source and diffusion into the incompletely mixed hypolimnion. Generally progressive increases in Fe^{2+}, H_2S_T, and CH_4 concentrations occurred during summer stratification, and these reduced substances were not detected in oxic portions of the water column. Iron reduction was a minor decomposition pathway as indicated by the relatively low concentrations of Fe^{2+} in the hypolimnion (Figure 21). The iron reduction pathway has accounted for less than 1% of the total

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organic carbon decomposition in the hypolimnion of Onondaga Lake (Effler 1996, Matthews et al. 2007). Precipitation of FeS minerals represents a major sink for Fe^{2+}, but likely had little effect on H_2S_T concentrations (Driscoll et al. 1993). Fe^{2+} and CH_4 began accumulating in the lower layers of the hypolimnion immediately after depletion of DO in mid-June (Figure 21a and 23a).

Substantial accumulations of H_2S_T were not observed until late August, after depletion of NO_3^- in the lower layers of the hypolimnion (Figure 22c). In addition, H_2S_T was not present in layers that contained measurable concentrations of NO_3^- (Figure 22). These observations suggest that NO_3^- was being used as an electron acceptor in the oxidation of H_2S_T. At least two alternate reactions, with different nitrogenous byproducts, have been proposed for the oxidation of H_2S_T with NO_3^-. Simplified representations of these reactions are presented here (Eq. 1 and 2).

$$NO_3^- + H_2S + H_2O \rightarrow NH_4^+ + SO_4^{2-} \qquad\qquad (1)$$

$$NO_3^- + H_2S + H_2O \rightarrow 0.5\ N_2 + SO_4^{2-} + 4H^+ \qquad\qquad (2)$$
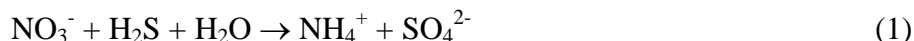
Dissimilatory nitrate reduction to ammonia (DNRA; Eq. 1), in which NH_4^+ replaces N_2 as the nitrogenous product of NO_3^- reduction, has recently been identified as an important sink for NO_3^- in organic-rich marine and freshwater sediments (Brunet and Garcia-Gil 1996, Bonin et al. 1998, An and Gardner 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 H_2S_T concentrations, NO_3^- is reduced mostly via denitrification whereas at higher H_2S_T concentrations there is a shift to DNRA and incomplete denitrification (Brunet and Garcia-Gil 1996, Senga et al. 2006). *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). This reaction produces N_2 as shown in Eq. 2. 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.

The relative importance of alternate NO_3^- reduction reactions has implications for a NO_3^- addition approach to reduce MeHg production in Onondaga Lake. This approach is predicated on the promotion of denitrification and abatement of SO_4^{2-} reduction/MeHg production through increased availability of NO_3^-. The quantity of NO_3^- consumed via H_2S_T oxidation could influence the efficiency of this approach and the rate of NO_3^- addition required to abate SO_4^{2-} reduction. In addition, these reactions are important as they determine the fate of added NO_3^- (e.g., N_2, NH_4^+).

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Sequence of Decomposition Pathways in the Hypolimnion and Sediments

A sequence of organic carbon 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). 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 24), 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 systems (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 24) where they are utilized in the oxidation of recently deposited organic matter. Methanogenesis predominates in the deeper sediments beyond the diffusive limits of external electron acceptors (Matthews et al. 2005).

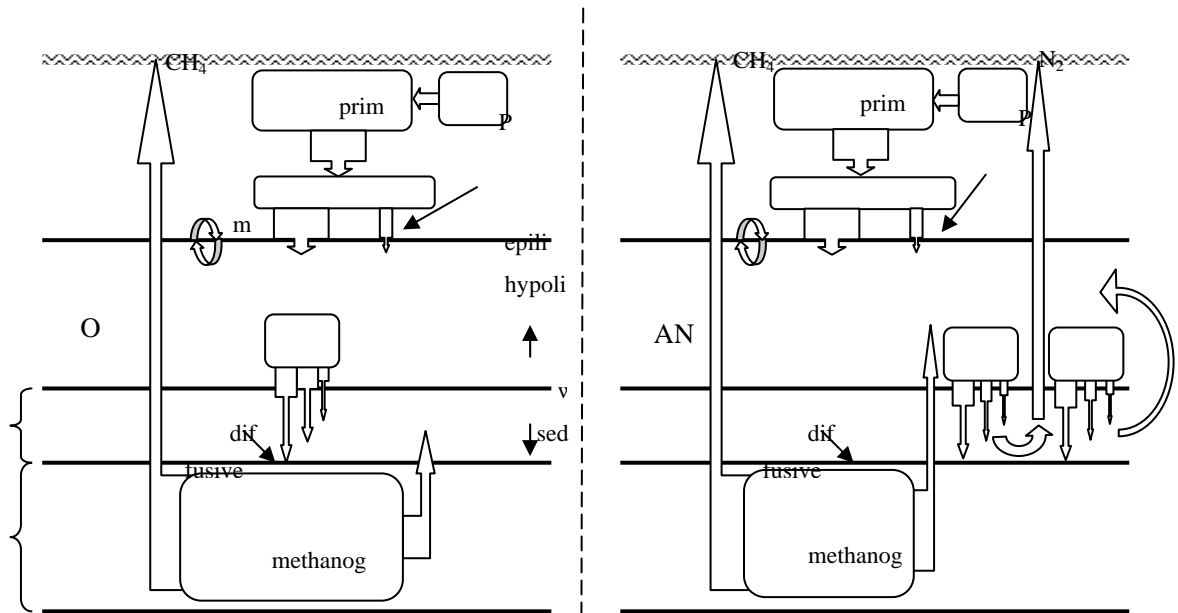**Figure 24.** Conceptual models of processes of decomposition in oxic and anoxic hypolimnion and sediments, with epilimnetic drivers, metabolic pathways and byproducts identified. Sediment oxygen demand is partitioned into surficial (SOD_s) and deep (SOD_d) components.

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The sequence of electron acceptors consumed in the hypolimnion of Onondaga Lake was somewhat different than expected from thermodynamic considerations, as depicted here with volume-weighted concentrations for the hypolimnion (Figure 25). Consumption of O_2 and NO_3^- occurred first, as expected. The rate of hypolimnetic NO_3^- depletion increased following depletion of DO. Accumulation of Fe^{2+} began in June, after DO was depleted from the lower layers. Ebullition of CH_4 was observed in late April, and accumulation of dissolved CH_4 began immediately following the onset of anoxia in the hypolimnion. However, appreciable accumulations of H_2S_T were observed well after increases in dissolved CH_4. Significant increases of H_2S_T began approximately 2 months after the commencement of CH_4 accumulation (Figure 25d, e). This delay is interesting because methanogenesis and SO_4^{2-} reduction are expected to occur at about the same redox potential (Stumm and Morgan 1996). This apparent thermodynamic anomaly is an artifact of the spatial separation of these processes within the sediments (Figure 24). Methanogenesis occurs continuously in the subsurface sediments, resulting in a continuous flux of dissolved CH_4 toward the sediment-water interface (Matthews et al. 2005). Accordingly, CH_4 began to accumulate in the hypolimnion immediately after depletion of O_2 and before the redox potential corresponding to methanogenesis was attained in the overlying water. Sulfide was not observed in the water column until NO_3^- was depleted and presumably the appropriate redox potential for SO_4^{2-} reduction was achieved in the upper sediments.

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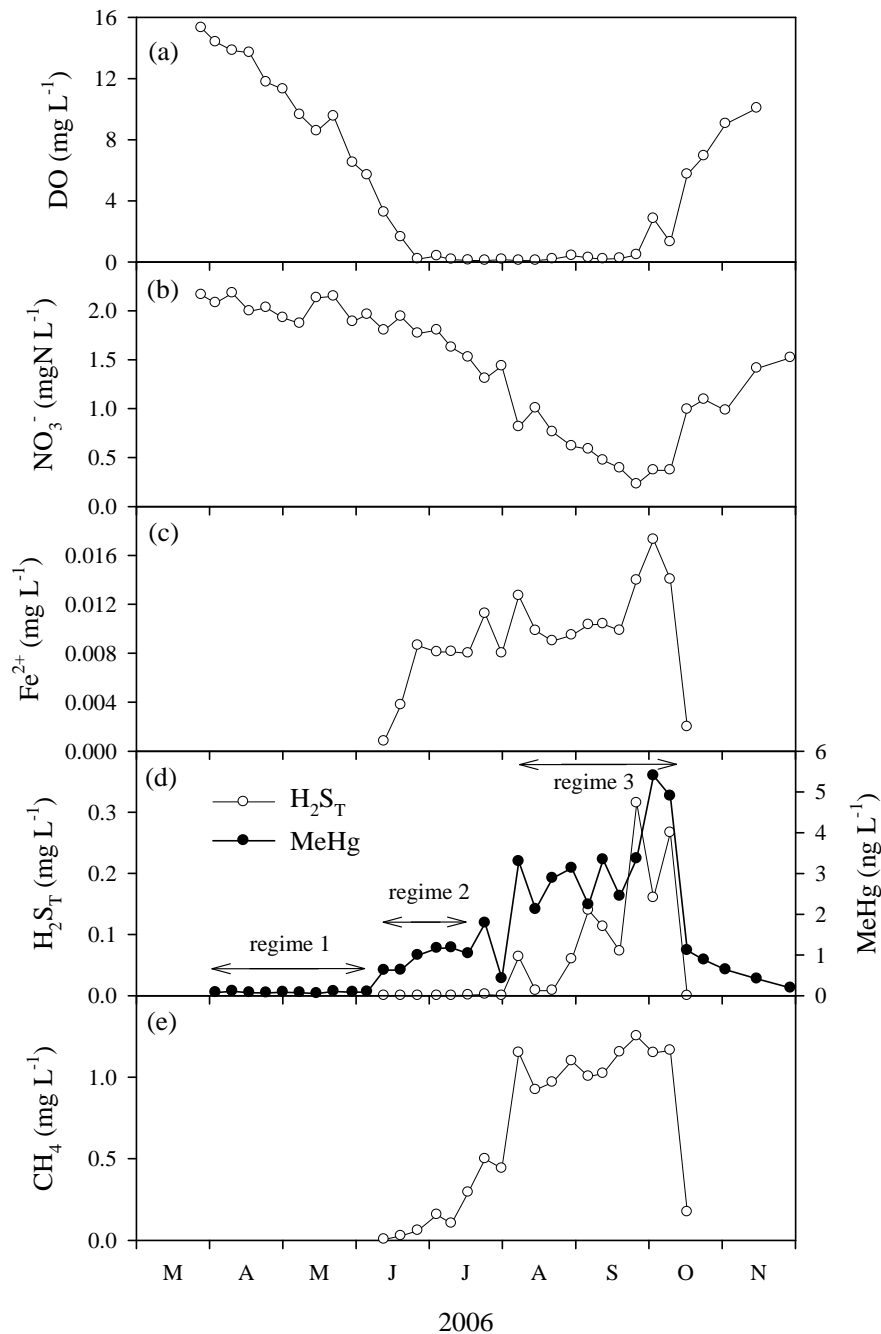
Figure 25. Time series of hypolimnetic (11-19 m) volume-weighted concentrations of redox constituents in Onondaga Lake during the March to November interval of 2006: (a) dissolved oxygen (DO); (b) nitrate (NO_3^-); (c) ferrous iron (Fe^{2+}); (d) total sulfide (H_2S_T) and monomethylmercury (MeHg), with three hypolimnetic regimes identified; and (e) dissolved methane (CH_4).

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Vertical and Temporal Patterns of Total and Methyl Mercury

The major Hg species of concern in Onondaga Lake is monomethylmercury (MeHg). Monomethyl Hg bioaccumulates at the base of the aquatic food chain, resulting in elevated concentrations in biota. Exposure to humans and wildlife is through consumption of MeHg in fish (Clarkson 1990, 1998). The production of MeHg is a biotic process largely mediated by sulfate-reducing bacteria (Benoit et al. 2003). Factors controlling Hg methylation include the availability of labile organic carbon to drive anaerobic conditions and support bacterial function, sulfide concentrations, and availability of ionic Hg. 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). Monomethyl Hg removal occurs via the process of demethylation. Mainly biologically mediated, demethylation can occur either by a reductive or oxidative pathway that results in the production of ionic or elemental Hg. Demethylation is a critical process as it can influence the fate of Hg in the ecosystem.

Total Hg (THg) concentrations represent total reducible Hg in both ionic and organic forms. Thus, THg concentrations include MeHg concentrations, although the portion of THg occurring as MeHg varies in the water column depending on redox conditions. While MeHg is generally internally produced, the source of ionic Hg to the lake can be either allochthonous or autochthonous (Benoit et al. 2003). Accumulation of MeHg is a net result of production and loss in the ecosystem. In this respect, we can determine only net rates of production of MeHg and determine the predominant source of the observed concentration patterns (e.g., the sediments or water column).

Vertical and Temporal Patterns of MeHg

Monomethyl Hg concentrations remained uniformly low in the water column during the oxic period, with an average of 0.01 ± 0.03 ng L^{-1} (Figure 26a). As oxygen was depleted from the bottom of the lake, MeHg concentrations increased starting above the sediment-water interface (Figure 26b). MeHg concentrations in the hypolimnion generally increased during summer stratification (Figure 26c,d, 27). Fall turnover marked the end of the period of substantial net MeHg production, and uniform MeHg concentrations were re-established throughout the water column in late October (Figure 26e, Figure 27).
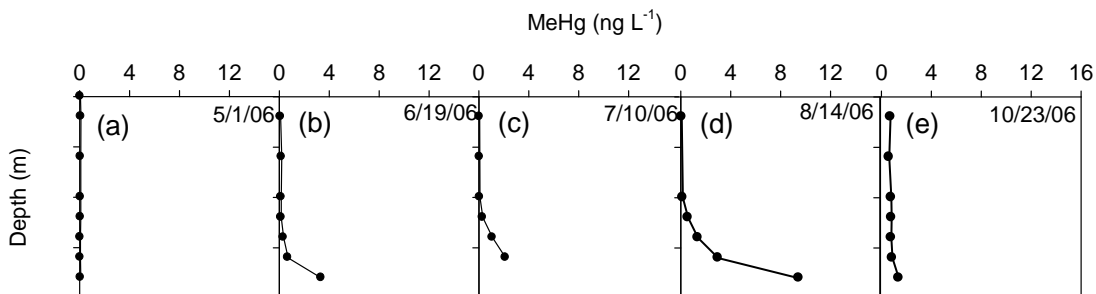
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Figure 26. Selected vertical profiles of monomethyl Hg (MeHg) collected from the south deep sampling site of Onondaga Lake during 2006: (a) May 1, (b) June 19, (c) July 10, (d) August 14, and (e) October 23.

Temporal variations in MeHg were mainly evident in the hypolimnion. Depletion of DO and NO_3^- in the hypolimnion promoted sulfate reduction that, in turn, resulted in substantially elevated concentrations of MeHg during August and September (Figure 27). After turnover, hypolimnetic MeHg concentrations decreased substantially but remained on the order of 4-5 times higher than the observed concentrations at the beginning of the season, with an average of 0.53 ± 0.18 ng L^{-1}. Epilimnetic MeHg concentrations were persistently low until fall turnover, with an average of 0.12 ± 0.04 ng L^{-1}. The post turnover period was characterized with elevated average epilimnetic MeHg concentrations ranging between 0.34 ng L^{-1} and 0.69 ng L^{-1}, with the highest value detected immediately after turnover and concentrations decreased gradually for the following month.
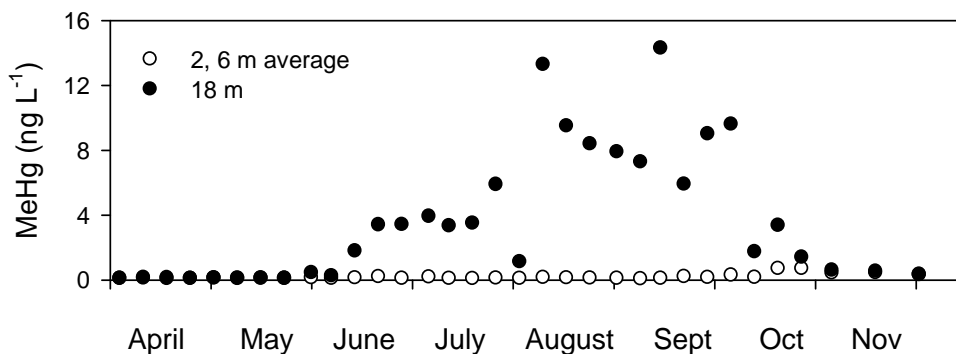

Figure 27. Time series of monomethyl Hg (MeHg) concentrations in the upper waters (average of 2 and 6 m measurements) and at 18 m in Onondaga Lake during the 2006 study period.

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Vertical and Temporal Patterns of THg

Total Hg concentrations in Onondaga Lake generally followed the pattern of MeHg. During the oxic period, low THg concentrations were established throughout the water column with an average of 1.99 ± 0.83 ng L^{-1} (Figure 28a). This condition was maintained until mid-June, when depletion of oxygen started in the bottom layers. Immediately following the initiation of DO depletion, an increase in concentrations of THg was observed at the 18 m depth (Figure 28b), while epilimnetic concentrations remained nearly constant. As the season progressed, and NO_3^- was depleted from the lower layers, concentrations of THg increased in the hypolimnion (Figure 29). The maximum values for the season occurred during September, when THg concentrations were well above 10 ng L^{-1} in the bottom 2 meters of the water column. Temporal variation in hypolimnetic THg concentrations was pronounced in the bottom layers, driven mainly by the progression of the redox phases and net production of MeHg (Figure 29). With the exception of the month of July, when runoff and high wind event contributed to elevated epilimnetic THg concentrations (Figure 4, also see subsequent discussion on the influence of external sources), concentrations of THg in the epilimnion remained relatively stable over the study period and averaged 2.73 ± 1.11 ng L^{-1}.

THg (ng·L^{-1})
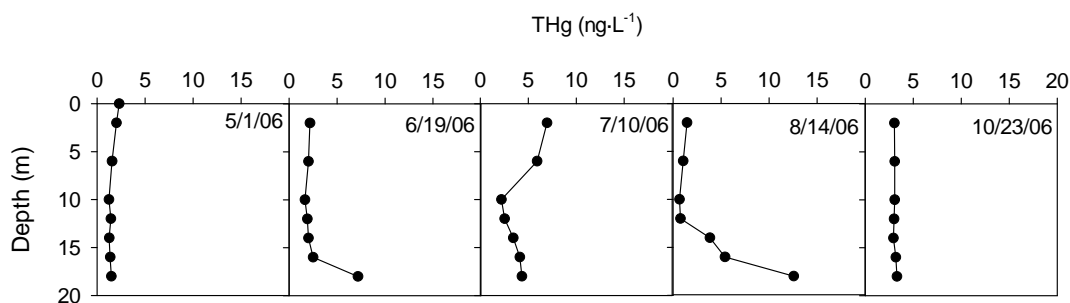
Figure 28. Selected vertical profiles of total Hg (THg) collected from the south deep sampling site of Onondaga Lake during 2006: (a) May 1, (b) June 19, (c) July 10, (d) August 14, and (e) October 23.

With the approach of turnover, THg concentrations decreased in the hypolimnion until uniform conditions were reached at the end of October (Figure 29). Note that epilimnetic THg concentrations increased between mid-October and mid-November, when the average THg concentration at the 2 m depth was 3.66 ± 0.70 ng L^{-1}. This increase in THg in the upper waters was the result of entrainment of the Hg-enriched hypolimnetic waters with the approach to fall turnover. The portion of THg that is not MeHg, is predominantly inorganic Hg (InHg). Concentrations of InHg were similar in the upper and lower waters, with InHg volume-weighted

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average concentrations of 2.41 ng L^{-1} and 2.34 ng L^{-1} for the epilimnion and hypolimnion, respectively (Figure 30).
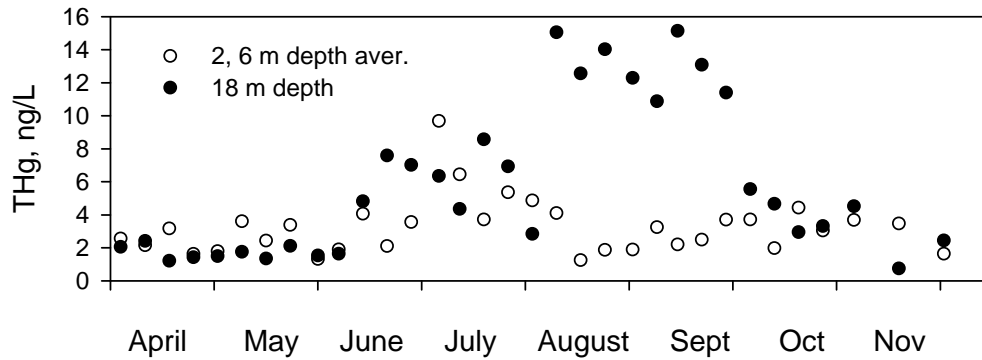
Figure 29. Time series of total Hg (THg) concentrations in the upper waters (average of 2 and 6 m measurements) and at 18 m in Onondaga Lake during the 2006 study period.
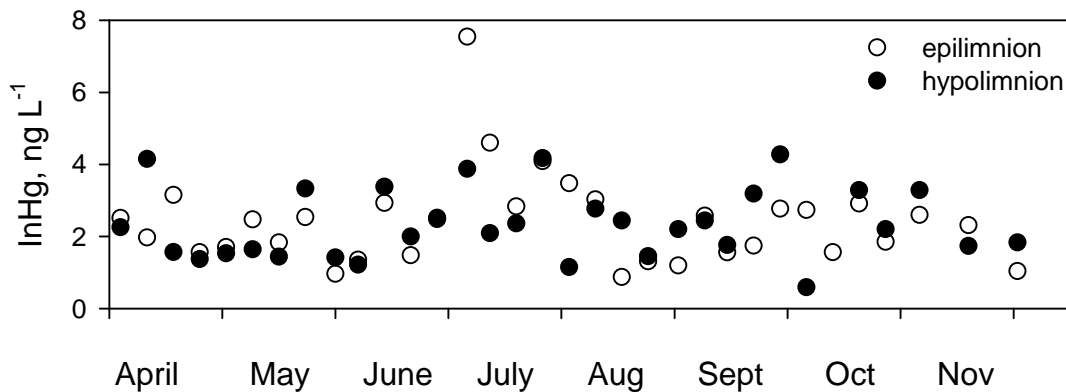
Figure 30. Time series of volume-weighted inorganic Hg (InHg) concentrations in the epilimnion and hypolimnion of Onondaga Lake during the 2006 study period.

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Vertical and Temporal Patterns in the Percent of THg Occurring as MeHg

The percent of THg occurring as MeHg is usually about 10% in lake waters (Morel el al. 1998). The contribution of MeHg to THg was on average $5\pm4\%$ in Onondaga Lake in spring when the water column was completely oxygenated (Figure 31a). With the onset of anoxic conditions in the bottom layers of the lake, the proportion of THg occurring as MeHg increased in the hypolimnion and was on average $26\pm23\%$, while epilimnetic values remained low ($3\pm2\%$; Figure 31b). As summer stratification progressed and NO_3^- was depleted from the lower layers of the hypolimnion, vertical profiles of % MeHg exhibited distinct patterns, with increases in the lower 6 meters to values ranging between 25-95% (e.g., Figure 31c, d). The vertical pattern of % MeHg is consistent with increases in MeHg concentrations in the hypolimnion during anaerobic conditions in the lake, suggesting that the increase of THg during this period is mainly driven by internal production of MeHg. Uniform % MeHg values were established again after fall turnover, but at higher levels than observed during spring (Figure 31e).
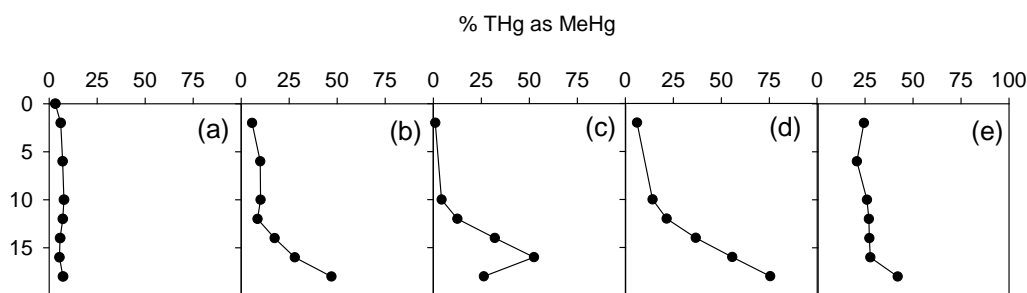

Figure 31. Selected vertical profiles of percent total Hg (THg) occurring as monomethyl Hg (MeHg) for the south deep sampling site of Onondaga Lake during 2006: (a) May 1, (b) June 19, (c) July 10, (d) August 14, and (e) October 23.

Temporal variability in the percent of THg occurring as MeHg was observed both in the epilimnion and hypolimnion waters. Overall, the % MeHg in the epilimnion of Onondaga Lake ranged between 1% and 23% (Figure 32). Epilimnetic % MeHg remained relatively stable and low between spring and fall turnover ($< 9\%$). During post turnover period, the % THg as MeHg increased, reaching a maximum epilimnetic value of 23%. The observed increase was probably due to mixing of MeHg enriched hypolimnetic waters during the fall turnover. In contrast, the % MeHg as THg at 18m depth exhibited high variability during the stratification period. Values were generally low (on average $9\pm8\%$), and comparable to epilimnetic values, while oxygen was present in the hypolimnion; once oxygen was depleted from the 18m depth (but NO_3^- still present), the percent of THg occurring as MeHg increased reaching $44\pm24\%$. Note that two weeks before oxygen was depleted from the bottom of the lake, an increase in the % MeHg was

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observed. This increase was likely a result of MeHg production in the sediments with a subsequent release to the water column. Large increases in % MeHg at the bottom of the lake occurred during August and September, reaching the highest values for the season (Figure 32). The average percent of THg as MeHg over this period was 68±19%. On July 31 a marked decrease was observed in the % of THg occurring as MeHg. This decrease in % MeHg to 4%, a value comparable to the epilimnetic levels, coincided with the reintroduction NO_3^- at the 18 m depth. This result is also consistent with observations in Florida Everglades (Gilmour et al., 1998) where % MeHg decreased at sites with higher NO_3^- concentrations.
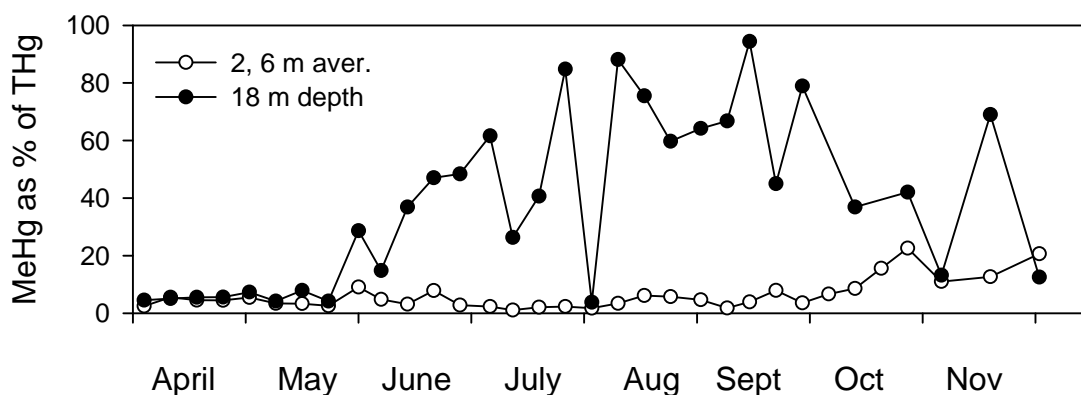
Figure 32. Time series of percent total Hg (THg) occurring as monomethyl Hg (MeHg) in the upper waters (average of 2 and 6 m measurements) and at 18 m in Onondaga Lake during the 2006 study period.

Comparison with Past MeHg Patterns in Onondaga Lake

Volume-weighted monthly MeHg concentrations in the hypolimnion were compared with results from past studies (Figure 33). Note that such a comparison is somewhat problematic as the sampling frequency and extent has varied greatly from study to study. Therefore, any comparison should be viewed as tentative. It appears that since 1992, MeHg concentrations in the hypolimnion have decreased for the months of summer stratification. Probably most noteworthy is the large decreases in hypolimnetic MeHg in July in recent years (2005, 2006) compared to values observed for 1992 and 2000. This pattern coincides with the large increases in NO_3^- from Metro and the persistence of NO_3^- in the water column longer during stratification, thereby inhibiting Hg methylation. Major water quality improvements have occurred in Onondaga Lake between 1992 and 2006, including decreases in primary production, improved water clarity, water column oxygen sustained for longer periods, and Metro upgrade resulting in higher NO_3^- concentrations at spring turnover. While in 1992 a major increase in MeHg concentrations started in June, in 2006 this increase was shifted later in the year to August. Post

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turnover MeHg concentrations have decreased markedly in recent years, but remain higher than the spring values. The mean MeHg concentration for May of 1992-2000 was 0.52 ng L^{-1}, while in 2006 the concentration was 0.09 ng L^{-1}. The mean MeHg concentration for November was 1.62 ng L^{-1} and 0.55 ng L^{-1} for 1992-2000 and 2005-2006 periods, respectively.

Note: 1992 and 1999 data was collected monthly; 2000 data was collected twice a month; 2005 and 2006 data was collected weekly

Figure 33. Monthly historical hypolimnetic volume-weighted monomethyl Hg (MeHg) concentrations in Onondaga Lake during the 1992, 1999, 2000, 2005, and 2006.

The pattern of volume-weighted epilimnetic concentrations of MeHg during 1992-2006 was less distinctive that hypolimnetic patterns (Figure 34). Methyl Hg concentrations during fall 2006 were on the order of 3 to 6 times lower than the concentrations observed in 1992 and 1999, respectively. However, the volume-weighted epilimnetic MeHg values were substantially higher in 1999 compared to 1992, while the opposite pattern was evident for the hypolimnetic MeHg concentrations. The values of annual volume-weighted concentrations for 1999 and 1992 were calculated on the basis of one sampling event per month and this coarse sampling interval may contribute to the inconsistency in annual concentrations.

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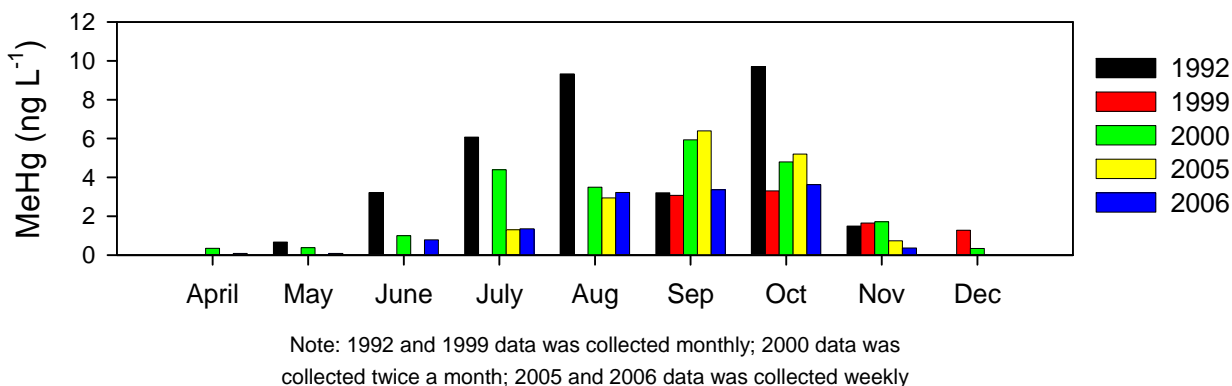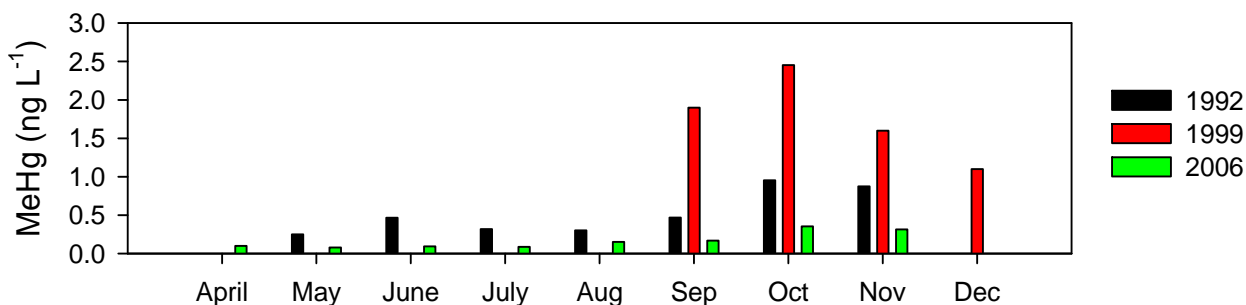**CONTROL METHYLMERCURY PRODUCTION**
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Figure 34. Monthly historical epilimnetic volume-weighted monomethyl Hg (MeHg) concentrations in Onondaga Lake during the 1992-2006.

The influence of external sources on THg and MeHg concentrations

Sources of Hg to the lake can be either allochthonous or autochthonous. External sources are expected to have more marked effects on THg concentrations, due to the fact that THg can be strongly impacted by external sources while MeHg is mainly influenced by internal production. Interesting variations in THg concentrations were noticed and two events were closely examined. On July 4 a peak THg concentration was observed at 6 m depth (Figure 29), without a corresponding peak in MeHg concentration (Figure 27). This increase in THg concentration may reflect tributary inflows of THg associated with interflow from a summer storm event (Figure 4) or could be a result of a wind-driven resuspension of the ILWD as a consequence of high wind event occurred on July 2. On October 9, a decrease of THg concentrations at the 18m depth was observed (Figure 29). The decrease in THg coincided with a decrease in MeHg concentration at that depth (Figure 27). At the beginning of October, Onondaga Lake was still stratified and the bottom layers were anoxic, with substantial concentrations of MeHg. An external, oxygenated source likely decreased the concentrations of Hg species. The dilution likely reflects a plunging inflow. Inflows to the lake have the potential to increase or decrease concentrations of Hg species depending where in the water column they enter, which is a function the density of the inflow relative to the lake. The effects of external sources are site-specific and cannot be extrapolated to the whole lake. These variations in water column Hg concentrations, however, suggest the need for measurements of tributary and resuspension inputs of Hg to the lake to better interpret anomalous patterns in Hg profiles.

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Partitioning dissolved and particulate THg and MeHg

Water samples from two depths, 2 m and 16 m, representing conditions in the epilimnion and hypolimnion, were collected during the sampling period and analyzed as filtered and non-filtered. Non-filtered samples consistently had higher concentrations for both THg and MeHg than filtered samples (Figure 35), representing a statistically significant difference (Table 2). The contribution of suspended particulate matter (SPM) in non-filtered samples was greater for THg than for MeHg. On average, SPM accounted for 79% and 74% of THg concentrations at 2m and 16m depths, respectively (Table 2). Suspended particulate matter made a smaller contribution to MeHg concentrations, accounting for 53% and 46% at 2 m and 16 m depths, respectively (Table 2). The origin of SPM was not examined as part of this study.

Non-filtered THg values at 2 m depth demonstrated considerably variability that was not evident in the filtered sub-samples (Figure 36). Concentrations fluctuated around a mean value of 3.04 ng L^{-1} (Table 2). Phytoplankton populations occupy the upper waters (trophogenic zone) of the lakes. A simple linear regression between THg and chlorophyll a for the 2 m depth did not reveal any significant relationship. Non-filtered THg samples from the 16m depth increased slightly at the start of anoxia, which occurred at the end of July-beginning of August. Overall, the mean value of 4.29 ng L^{-1} did not differ significantly from the average epilimnetic THg concentration of 3.04 ng L^{-1} (Table 2).

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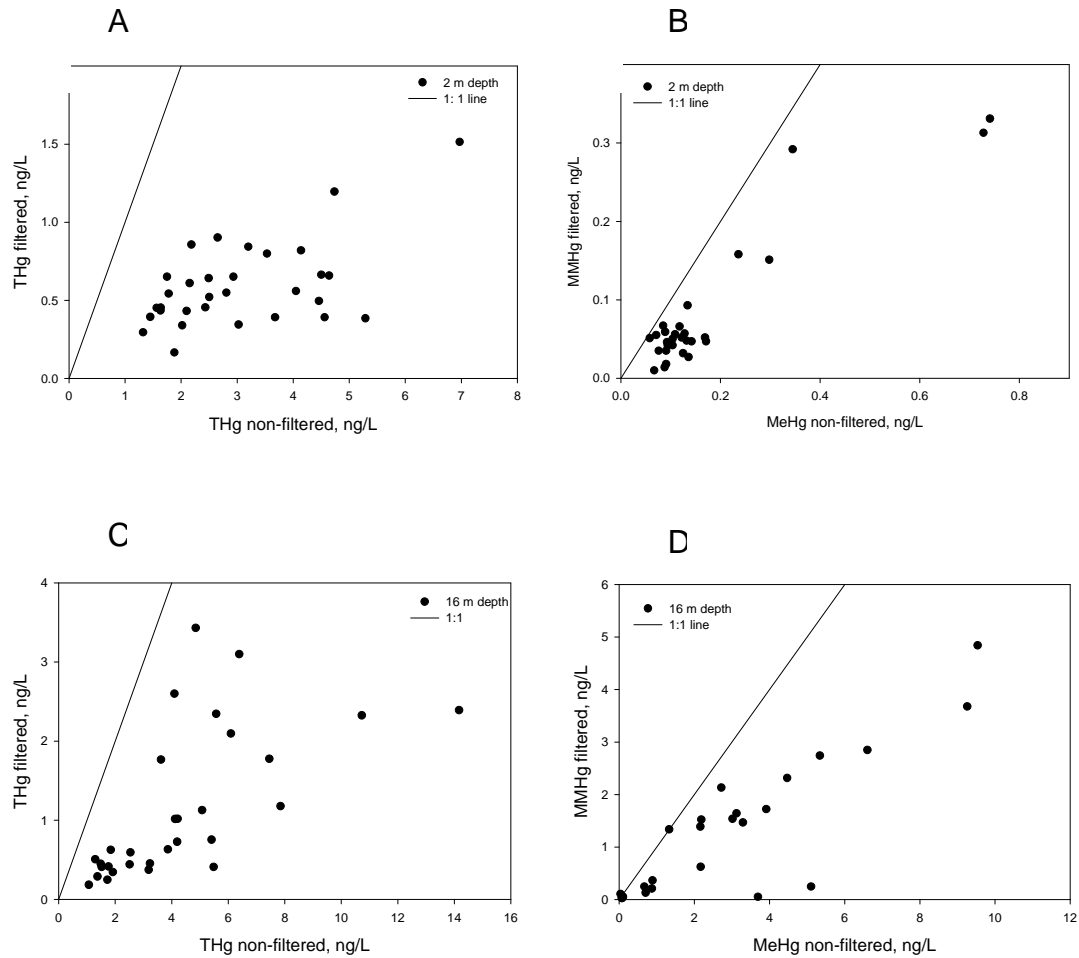
Figure 35. Evaluations of the relationships between filtered and non-filtered samples collected in Onondaga Lake during 2006: (a) THg filtered vs. THg non-filtered, 2 m samples, (b) MeHg filtered vs. MeHg non-filtered, 2 m samples, (c) THg filtered vs. THg non-filtered, 16 m samples, and (d) MeHg filtered vs. MeHg non-filtered, 16 m samples.

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Table 2.   Selected Statistical Analysis for Filtered and Non-Filtered Samples, Collected at 2 m and 16 m Depths.

Parameter	Total Hg		Methyl Hg	
	2 m	16 m	2 m	16 m
SPM[1] contribution	79%	74%	53%	46%
Coefficient of determination F vs. NF	0.31	0.41	0.86	0.78
Pearson correlation coeff. F vs. NF	0.55	0.64	0.93	0.89
Mean and standard deviaton, ng L^{-1} – NF[2]	3.04±1.33	4.29±2.96	0.17±0.17	2.47±2.62
Mean and standard deviation, ng L^{-1} – F[3]	0.59±0.27	1.33±0.93	0.08±0.07	1.09±1.27
T-test between F and NF	t =11.38 p« 0.0001	t =7.05 p«0.0001	t =5.08 p=0.00001	t =4.50 p=0.00011

Note: [1]SPM = suspended particulate matter [2]NF = non-filtered samples, [3]F = filtered samples

An interesting pattern was observed in MeHg concentrations at the 2m depth. Through mid-September, filtered and non-filtered concentrations remained below 0.07 ng L^{-1} and 0.17 ng L^{-1}, respectively (Figure 36b). Between the end of September and middle of November, MeHg increased on average three times for both filtered and non-filtered samples at the 2 m depth. This marked increase in MeHg is likely due to the supply of MeHg from the hypolimnion associated with mixing during fall turnover. Epilimnetic MeHg concentrations for filtered and non-filtered samples followed a similar pattern, indicating that both dissolved and particulate MeHg are driven by a similar mechanism. Hypolimnetic MeHg concentrations increased conspicuously from the beginning of August, reflecting the establishment of NO_3^- depleted conditions at the bottom of the lake.

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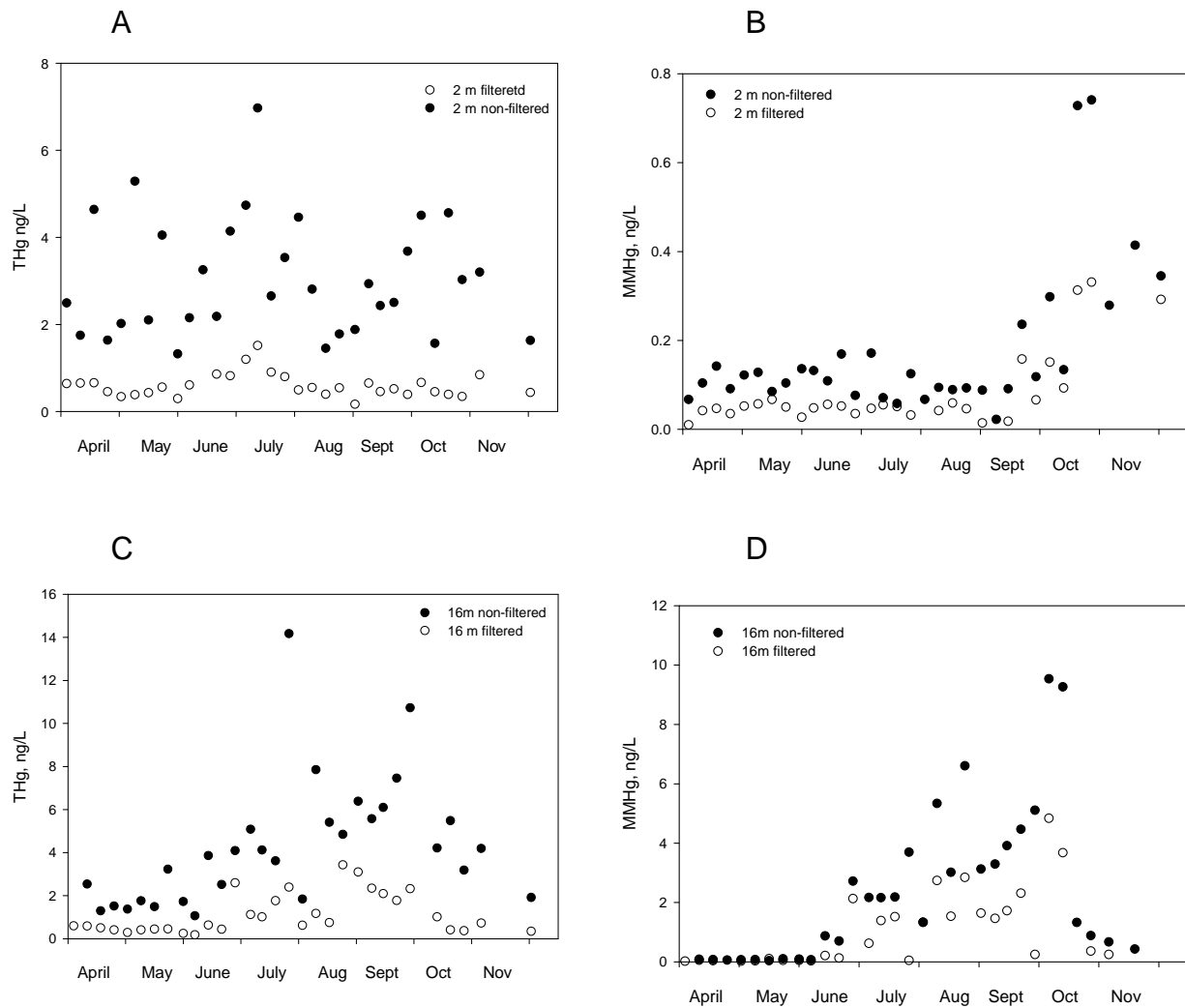
Figure 36. Time series of weekly observations of filtered and non-filtered forms of Hg for Onondaga Lake in 2006: (a) THg filtered and THg non-filtered, 2 m samples, (b) MeHg filtered and MeHg non-filtered, 2 m samples, (c) THg filtered and THg non-filtered, 16 m samples, and (d) MeHg filtered and MeHg non-filtered, 16 m samples.

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Control of MeHg Production by O_2 and NO_3^-

One of the major goals of this study was to document, with sufficient resolution, the interaction between MeHg production and related metabolic and redox processes, with particular emphasis on DO and NO_3^-. A more specific objective of this section is to identify threshold concentrations of DO and NO_3^- that correspond to observed levels of MeHg in the hypolimnion. These goals are addressed here through detailed analyses of water column measurements of DO, NO_3^-, H_2S_T, and MeHg made during the 2006 study. Three regimes are identified according to the availability of electron acceptors in the hypolimnion: (1) stratified conditions with DO present at the sediment-water interface; (2) anoxic conditions with NO_3^- present at the sediment-water interface; and (3) anoxic conditions without NO_3^- at sediment-water interface. The levels of MeHg observed in the hypolimnion during the three electron acceptor regimes provide preliminary insights into the performance of electron acceptor additions to abate MeHg production. However, interpretations and extrapolations of these monitoring results should be conducted with caution. Monitoring results are representative of ambient conditions, and are not a substitute for controlled laboratory experiments and large-scale demonstration projects.

From May 8 to June 5 the water column was stratified (Figure 2) and DO concentrations at 18 m exceeded 4 mg L^{-1} (Figure 10). This interval is identified as regime 1 (Figure 25d). Volume-weighted concentrations of MeHg in the hypolimnion were generally less than 0.1 ng L^{-1} prior to the onset of anoxia in lower layers of the hypolimnion in mid-June (Figure 25d). Very modest increases in MeHg were observed above the sediment-water interface prior to the onset of anoxia (Figure 29). On June 12 depths below 18 m were anoxic (Figure 11b), and the volume-weighted hypolimnetic MeHg concentration increased from 0.10 ng L^{-1} on June 5 to 0.63 ng L^{-1} on June 12 (Figure 25d). The DO concentration at 19 m on June 5 was 3.3 mg L^{-1}, which suggests that consistently low levels of MeHg (~0.1 ng L^{-1}) might be achieved through maintenance of DO concentrations ≥ 3 mg L^{-1}.

During the June 12 to July 17 interval of 2006 anoxic conditions existed in the hypolimnion (Figure 10) and NO_3^- concentrations above the sediment-water interface remained > 0.2 mg N L^{-1} (e.g., Figure 14b). This 5-week period is identified as regime 2 (Figure 25d). The volume-weighted concentration of MeHg in the hypolimnion increased over this interval to a maximum of 1.18 ng L^{-1} on July 10 (Figure 25d). On July 24, the NO_3^- concentration at 19 m was measured as 0.005 mg N L^{-1} (below the limit of detection) and the volume-weighted concentration of MeHg in the hypolimnion increased abruptly to 1.78 ng L^{-1}. These patterns suggest that volume-weighted concentrations of MeHg may be limited to ~1 ng L^{-1} by maintenance of > 0.2 mg N L^{-1} NO_3^- throughout the hypolimnion. Maintenance of higher NO_3^- concentrations (e.g., > 1 mg N L^{-1}) can reasonably be expected to result in yet lower levels of MeHg in the hypolimnion.

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The third regime, defined by anoxic conditions without NO_3^- at the sediment-water interface, spanned the two-month interval of August 7 to October 9 (Figure 25d). Volume-weighted concentrations of MeHg were markedly higher during regime 3, averaging 3.31 ng L^{-1} with a maximum concentration of 5.40 ng L^{-1} on October 2 (Figure 25d). Concomitant increases in H_2S_T during regime 3 indicate the occurrence of SO_4^{2-} reduction with associated production of MeHg (Figure 25d). The highest rates of accumulation of MeHg and H_2S_T were observed during late September (Figure 25d) when the pool of NO_3^- in the hypolimnion was nearly depleted (Figure 25b).

The mechanism for control of MeHg production by NO_3^- is presumed to be inhibition of SO_4^{2-} reduction through increased availability of an energetically favorable electron acceptor. It is expected that NO_3^- diffuses into the upper sediments and displaces SO_4^{2-} reduction as the dominant pathway for the decomposition of organic matter (Figure 24). Thus, sediments with little or no NO_3^- in the overlying waters are expected to be an important site for SO_4^{2-} reduction and associated MeHg production. Volume-weighted concentrations of MeHg in the hypolimnion were tracked closely by the sediment area below water with low (< 0.5 mg N L^{-1}) NO_3^- concentrations (Figure 37). In fact, the area of sediment overlain by water with low NO_3^- concentrations explained 70% of the weekly variations in hypolimnetic MeHg concentrations (Figure 38). This observation supports the positions that the sediments are an important site for MeHg production and that maintenance of adequate NO_3^- concentrations at the sediment-water interface can significantly abate both SO_4^{2-} reduction and associated production of MeHg. In addition, this analysis suggests that NO_3^- concentrations on the order of 0.5 mg N L^{-1} can substantially impact the accumulation of MeHg in the hypolimnion. This analysis assumes that hypolimnetic concentrations of MeHg and NO_3^- as measured at the south deep site are representative of lake wide conditions.

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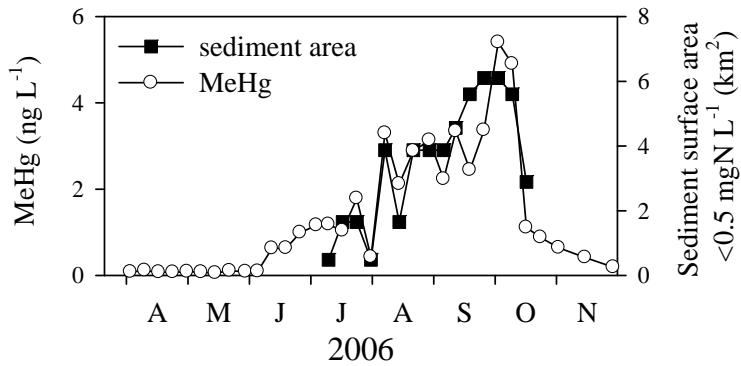
Figure 37. Time-series of volume-weighted MeHg concentrations in the hypolimnion of Onondaga Lake and the sediment surface area overlain by water depleted in NO_3^-. Note the similarity in the progression between these two measurements.

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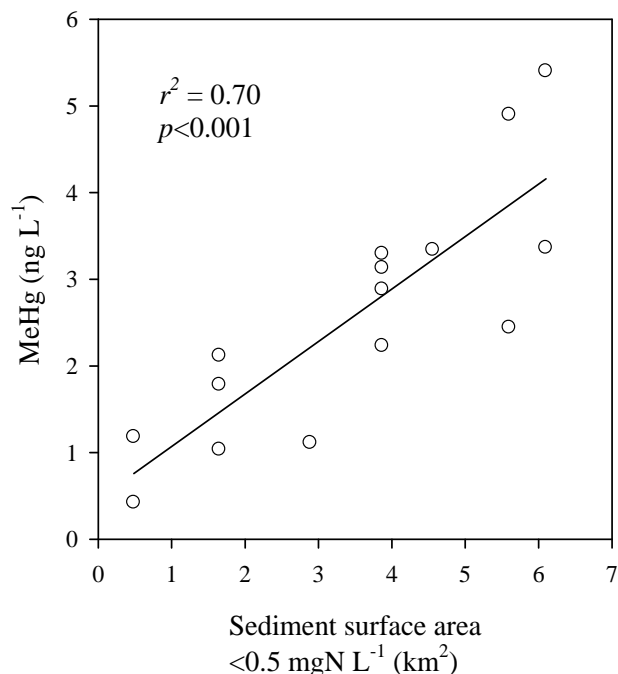
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Figure 38. Evaluation of the relationship between volume-weighted MeHg concentrations in the hypolimnion of Onondaga Lake and the sediment surface area underlain by water depleted in NO_3^- (< 0.5 mg N L^{-1}).

The influence of NO_3^- on MeHg is exemplified by patterns observed in detailed vertical profiles collected on July 24, July 31, and August 7 (Figure 39). Concentrations of DO in the hypolimnion were uniformly low (< 0.2 mg L^{-1}) on these sampling dates and consistent with anoxia within the limitations of the measurements. At the low concentrations measured on these sampling dates it is assumed that DO had little or no impact on hypolimnetic MeHg concentrations. In contrast to the invariant pattern observed for DO, concentrations of NO_3^- varied widely over the three sampling dates. On July 24 NO_3^- was undetectable at 19 m and the vertical pattern of MeHg indicated release from the sediments (Figure 39a). The lower layers were replenished with NO_3^- on July 31, presumably as a result of turbulent mixing (Figure 39b). Concentrations of MeHg decreased markedly in the July 31 profile, and sediment release was not observed (Figure 39b). One week later, on August 7, NO_3^- was not detected below 16 m and substantial release of MeHg from the sediments was observed (Figure 39c). The patterns revealed over this short interval suggest that NO_3^- can, in the absence of DO, regulate the accumulation of MeHg in the hypolimnion.
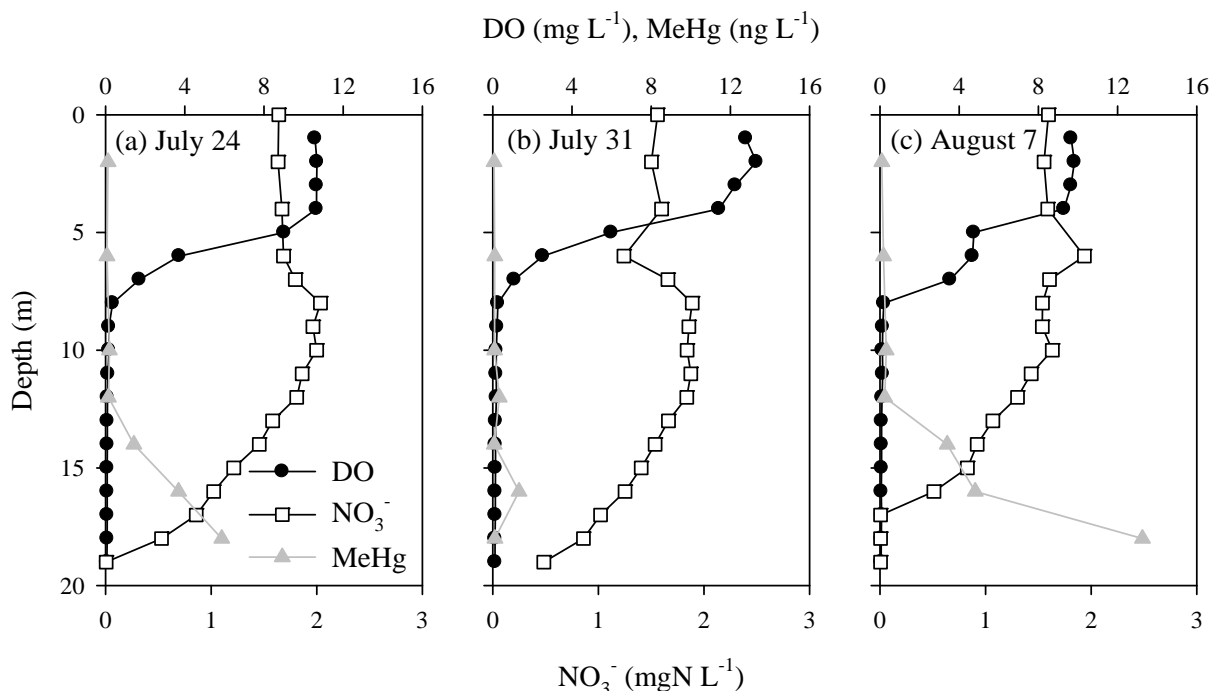
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Figure 39. Vertical profiles of dissolved oxygen (DO), nitrate (NO$_3^-$), and monomethylmercury (MeHg) collected from the south deep sampling site of Onondaga Lake during 2006: (a) July 24, (b) July 31, and (c) August 7.

CONCLUSIONS

The data collected during this study have provided important insights into metabolic processes and Hg cycling in Onondaga Lake. Both DO and NO$_3^-$ were shown to control the production of MeHg and the associated accumulation in the hypolimnion during the summer stratification interval. Low levels of MeHg (0.1 ng L^{-1}) were observed in the hypolimnion during the early portion of the stratification interval when DO was present throughout the water column. Volume-weighted concentrations of MeHg in the hypolimnion were limited to ~1 ng L^{-1} from June 12 to July 17 when NO$_3^-$ concentrations above the sediments were > 0.2 mg N L^{-1}. The surface area of sediment overlain by water with low NO$_3^-$ concentrations (< 0.5 mg N L^{-1}) explained 70% of the weekly variations in hypolimnetic MeHg concentrations. The data indicate that maintenance of higher NO$_3^-$ concentrations (e.g., > 1 mg N L^{-1}) can reasonably be expected to result in yet lower levels of MeHg in the hypolimnion. Markedly higher hypolimnetic MeHg

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concentrations (volume-weighted average of 3.31 ng L^{-1} and maximum of 5.40 ng L^{-1}) were observed during late summer when NO_3^- was depleted in the lower layers.

The maximum rates of hypolimnetic NO_3^- depletion observed in 2004 and 2005 were used to estimate that a NO_3^- addition rate of 1050 kg N d^{-1} would be necessary to abate SO_4^{2-} reduction and MeHg production (UFI and SU 2007a). A lower rate of NO_3^- depletion was observed in 2006, resulting in a NO_3^- addition rate (718 kg N d^{-1}) 32% lower than the earlier estimate. Despite the lower estimate for 2006, we recommended that the higher NO_3^- addition rate of 1050 kg N d^{-1} be retained for preliminary design and planning purposes.

The 2006 water column data support NO_3^- addition as a promising approach to control the production and accumulation of MeHg in Onondaga Lake. The vertically detailed profiles collected weekly were instructive and allowed for identification and meaningful interpretation of water column signatures. However, it is important to recognize that the processes that govern these water column patterns occur in the sediments. Sediment pore water information would contribute to a more comprehensive understanding of the mechanisms that regulate MeHg production. Although control of MeHg production is indicated at NO_3^- concentrations of approximately 0.5 mg N L^{-1}, a target of 1.0 mg N L^{-1} may achieve lower levels of MeHg in the hypolimnion. This concentration was used previously to assess the feasibility and impact of a NO_3^- addition approach to control MeHg production in Onondaga Lake (UFI and SU 2007a). The conduct of incubation experiments, using intact sediment cores, is recommended to better define the dose-response relationships for NO_3^- – MeHg and DO – MeHg.

Important factors, beyond those discussed here, must be considered in deliberations over alternate methods to control the accumulation of MeHg in the hypolimnion of Onondaga Lake. For example, the rates and pathways of Hg demethylation may differ under various DO – NO_3^- regimes. In addition, Hg levels in biota may not respond proportionally to decreases in the hypolimnetic concentrations of MeHg. Habitation of Hg-contaminated sediments by benthic macrofauna could confound the relationship between MeHg in the water column and Hg levels in biota (UFI and SU 2007a). A NO_3^- addition approach 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.

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REFERENCES

Adams D. D., N. J. Fendinger and D. E. Glotfelty. 1997. "Biogenic gas production and mobilization of in-place sediment contaminants by gas ebullition" in Sediments: Chemistry and Toxicity of In-Place Pollutants, R. Baudo, J. Geisy and H. Muntau (Editors), Lewis Publishers, Boca Raton, FL, 215 –236

Addess, J. M. 1990. Methane cycling in Onondaga Lake, New York. M.S. thesis, College of Environmental Science and Forestry, State University of New York, Syracuse, NY.

Addess, J. M. and S. W. Effler. 1996. Summer methane fluxes and fall oxygen resources of Onondaga Lake, New York. Lake and Reserv. Manage. 12:91-101.

An, S. and W. S. Gardner. 2002. Dissimilatory nitrate reduction to ammonia (DNRA) as a nitrogen sink, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). Mar. Ecol. Prog. Ser. 237:41-50.

Beller, H. R., P. G. Chain, T. E. Letain, A. Chakicherla, F. W. Larimer, P. M. Richardson, M. A. Coleman, A. P. Wood and D. P. Kelly. 2006. The genome sequence of the obligately chemolithoautotrophic, facultatively anaerobic bacterium *Thiobacillus denitrificans*. J. Bacteriology 188:1473-1488.

Benoit, J. M., C. C. Gilmour, A. Heyes, R. P. Mason and C. L. Miller. 2003. Geochemical and biological controls over methylmercury production and degradation in aquatic ecosystems. P. 262-297. *In:* Y. Cai and O. C. Brouds (eds). Biogeochemistry of environmentally important trace elements, ACS Symposium Series 835. American Chemical Society, Washington, D.C.

Bisogni, J. J. and C. T. Driscoll. 1977. Denitrification using thiosulfate and sulfide. J. Environ. Engin. Div. (ASCE) 103:593-604.

Bonin, P., P. Omnes and A. Chalamet. 1998. Simultaneous occurrence of denitrification and nitrate ammonification in sediments of the French Mediterranean Coast. Hydrobiologia 389:169-182.

Brooks, C. M. and S. W. Effler. 1990. The distribution of nitrogen species in polluted Onondaga Lake, NY, USA. Water Air Soil Pollut. 52:247-262.

P:\Honeywell -SYR\444151 - 2008 SMU 8\09 Reports and Work Plans\Nitrate Interpretive Report (2006 study)\2006 Interp Rpt 040908.doc

April 23, 2008

48

Brunet, R. V. and L. J. Garcia-Gil. 1996. Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments. FEMS Microbiol. Ecol. 21:131-138.

Capone D.G. and Kiene R.P. 1988. Comparison of microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon catabolism. Limnol. Oceanogr. 33: 725-749.

Casper, P., Maberly, S. C., Hall, G. H. & Finlay, B. J. (2000): Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere. – Biogeochemistry 49: 1-19.

Chanton, J. P., Martens, C. S. & Kelly, C. A. (1989): Gas transport from methane-saturated, tidal freshwater and wetland sediments. – Limnol. Oceanogr. 34: 807-819.

Chapra, S. C. 1997. Surface water-quality modeling. McGraw-Hill, New York. 844 p.

Chapra, S. C., and R. P. Canale. 1991. Long-term phenomenological model of phosphorus and oxygen for stratified lakes. Wat. Res. 25: 707-715.

Clarkson T. W. 1990. Mercury—An element of mystery. N Engl J Med 323:1137-1139.

Clarkson, T. W. 1998. Human toxicology of mercury. J. Trace Ele. Exp. Med. 11: 303-317.

Cooke, G. D., E. B. Welch, S. A. Peterson and S. A. Nichols. 2005. Restoration and management of lakes and reservoirs, 3rd ed. CRC Press, Boca Raton, FL. 591 p.

Dannenberg, S., M. Kroder, W. Dilling and H. Cypionka. 1992. Oxidation of H_2, organic compounds and inorganic sulfur compounds coupled to reduction of O_2 or nitrate by sulfate-reducing bacteria. Archiv. Microbiol. 158:93-99.

DiToro, D. M. 2001. Sediment flux modeling. John Wiley and Sons, Inc., New York, NY. 624 p.

Driscoll, C. T., S. W. Effler, M. T. Auer, S. M. Doerr, and. M. R. Penn. 1993. Supply of phosphorus to the water column of a productive hardwater lake: Controlling mechanisms and management considerations. Hydrobiologia 253: 61-72.

Driscoll, C.T., Y-J. Han, C.Y. Chen, D.C. Evers, K.F. Lambert, T.M. Holsen, N.C. Kamman, and R.K. Munson. 2007. Mercury contamination in forest and freshwater ecosystems in the Northeastern United States. BioScience 57:17-28.

P:\Honeywell -SYR\444151 - 2008 SMU 8\09 Reports and Work Plans\Nitrate Interpretive Report (2006 study)\2006 Interp Rpt 040908.doc

April 23, 2008

49

Effler, S. W. 1996. Limnological and engineering analysis of a polluted urban lake. Prelude to environmental management of Onondaga Lake, New York. Springer-Verlag, New York, NY. 832 p.

Effler, S. W., R. K. Gelda, S. E. Field, A. J. P. Effler, E. B. Wallenberg and D. A. Matthews. 2007. Implications of redox processes for the rehabilitation of an urban lake, Onondaga Lake, NY. Lake and Reserv.Manage. (in review).

Effler, S. W. and D. A. Matthews. 2007. Changes in primary production in Onondaga Lake, NY: Magnitude, metrics, and drivers. Lake and Reserv.Manage. 21:49-60.

Exponent. 2007. Data usability summary report, evaluation of nitrate addition to control methylmercury production in Onondaga Lake: 2006 study.

Fendinger, N. J., D. D. Adams and D. E. Glotfelty. 1992. The role of gas ebullition in the transport of organic contaminants from sediments. Sci. Total Environ. 112: 189– 201.

Gelda, R. K., M. T. Auer and S. W. Effler. 1995. Determination of sediment oxygen demand by direct measurements and by inference from reduced species accumulation. Mar. Freshwat. Res. 46:81-88.

Gilmour C.C., Riedel G.S., Ederington M.C., Bell J.T., Benoit J.M., Gill G.A. and M.C. Stordal. 1998. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry 40: 327-345.

Heaney, S.I., and W. Davison. 1977. The determination of ferrous iron in natural waters with 2,2′-bipyridyl. Limnol. Oceanogr. 22(4):753–759.

Henry, E. A., L. J. Dodge-Murphy, G. N. Bigham and S. M. Klein. 1995. Modeling the transport and fate of mercury in an urban lake (Onondaga Lake, NY). Water Air Soil Pollut. 80:489-498.

Hutchinson, G. E. 1938. On the relation between oxygen deficit and the productivity and typology of lakes. Int. Revue ges. Hydrobiol. Hydrogr. 36: 336-355.

Hutchinson, G. E. 1957. A treatise on limnology V. 1. Geography, physics and chemistry. Wiley.

P:\Honeywell -SYR\444151 - 2008 SMU 8\09 Reports and Work Plans\Nitrate Interpretive Report (2006 study)\2006 Interp Rpt 040908.doc

April 23, 2008

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Honeywell

Jardine, P.M., N.L. Weber, and J.F. McCarthy. 1989. Mechanisms of dissolved organic carbon adsorption on soil. Soil Sci. Soc. Am. J. 53:1378–1385.

Lasenby, D. C. 1975. Development of oxygen deficits in 14 southern Ontario lakes. Limnol. Oceanogr. 20:993-999.

Lovley, D. R. and M. J. Klug. 1986. Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments. Geochim. Cosmochim. Acta 50:11-18.

Matthews, D. A., and S. W. Effler. 2006a. Long-term changes in the areal hypolimnetic oxygen deficit (AHOD) of Onondaga Lake: Evidence of sediment feedback. Limnol. Oceanogr. 51: 702-714.

Matthews, D. A. and S. W. Effler. 2006b. Assessment of long-term trends in the oxygen resources of a recovering urban lake, Onondaga Lake, NY. Lake and Reserv.Manage. 22:19-32.

Matthews, D. A., S. W. Effler and C. M. Matthews (Brooks). 2000. Ammonia and toxicity criteria in polluted Onondaga Lake, New York. Wat. Environ. Res. 72:731-741.

Matthews, D. A., S. W Effler, and C. M. Matthews. 2005. Long-term trends in methane flux from the sediments of Onondaga Lake, NY: Sediment diagenesis and impacts on dissolved oxygen resources. Arch. Hydrobiol. 163: 435-462.

Matthews, D. A., S. W. Effler, S. M. O'Donnell, C. T. Driscoll and C. M. Matthews. 2008. Electron budgets for the hypolimnion of a recovering urban lake, 1989-2004: Responses to changes in organic carbon deposition and availability of electron acceptors. Limnol. Oceanogr. 53: 743-759.

Mattson, M. D. & Likens, G. E. (1990): Air pressure and methane fluxes. – Nature 347: 718-719.

Mattson, M. D. and G. E. Likens. 1993. Redox reactions of organic matter decomposition in a soft water lake. Biogeochemistry 19:149-172.

Morel F.M.M., Kraepiel A.M.L. and M. Amyot. 1998. The chemical cycle and bioaccumulation of mercury. Annual Review of Ecology and Systematics, 29: 543-566.

P:\Honeywell -SYR\444151 - 2008 SMU 8\09 Reports and Work Plans\Nitrate Interpretive Report (2006 study)\2006 Interp Rpt 040908.doc

April 23, 2008

51

Mortimer, C. H. 1941. The exchange of dissolved substances between mud and water in lakes: I and II. J. Ecol. 29: 280-329.

Mortimer, C. H. 1942. The exchange of dissolved substances between mud and water in lakes: III and IV. J. Ecol. 30: 147-201.

Mortimer, C. H. 1971. Chemical exchanges between the sediments and water in the Great Lakes - speculations on probable regulatory mechanisms. Limnol. Oceanogr. 16:387-404.

Nürnberg, G. K. 1984. The prediction of internal phosphorus load in lakes with anoxic hypolimnia. Limnol. Oceanogr. 29:111-124.

Ohle, W. 1958. The dynamics of lake metabolisms in relation to the gas ebullition of muds. Vom Wasser 25:127-149.

Otsuki, A. and R. G. Wetzel. 1973. Interaction of yellow organic acids with calcium carbonate in freshwater. Limnol. Oceanogr. 18:490-493.

Pak, K. -R. and R. Bartha. 1998. Mercury methylation and demethylation in anoxic lake sediments by strictly anaerobic bacteria. Appl. Environ. Micrbiol. 64:1013-1017.

Prestigiacomo, A. R., S. W. Effler, D. A. Matthews and L. J. Coletti. 2007. Nitrate and bisulfide patterns in Onondaga Lake, New York, following implementation of nitrification treatment. Wat. Environ. Res. (in preparation).

Rast, W., and G. F. Lee. 1978. Summary analysis of the North American project (US portion) OECD eutrophication project: Nutrient loading-lake response relationships and trophic state indices. EPA-600/3-78-008. USEPA Corvallis Environmental Research Laboratory.

Regnell, O., G. Ewald and E. Lord. 1997. Factors controlling temporal variation in methyl mercury levels in sediment and water in a seasonally stratified lake. Limnol. Oceanogr. 42:1784-1795.

Senga, Y., K. Mochida, R. Fukumori, N. Okamoto and Y. Seike. 2006. N_2O accumulation in estuarine and coastal sediments: The influence of H_2S on dissimilatory nitrate reduction. Estuarine, Coastal and Shelf Science 67:231-238.

P:\Honeywell -SYR\444151 - 2008 SMU 8\09 Reports and Work Plans\Nitrate Interpretive Report (2006 study)\2006 Interp Rpt 040908.doc

April 23, 2008

52

Strayer, R. F. and J. M. Tiedje. 1978. In situ methane production in a small, hypereutrophic, hard water lake: Loss of methane from sediments by vertical diffusion and ebullition. Limnol. Oceanogr. 23:1201-1206.

Stumm, W. and J. J. Morgan. 1996. Aquatic Chemistry, 3rd ed. John Wiley & Sons, New York, NY. 1022 p.

Takita, M. & Sakamoto, M. (1993): Methane flux in a shallow eutrophic lake. – Verh. Internat. Verein. Limnol. 25: 822-826.

TAMS. 2002. Onondaga Lake remedial investigation report. Prepared with YEC, Inc for NYSDEC, Division of Environmental Remediation, Albany, New York. TAMS, New York, New York.

Tango, P. J. and N. H. Ringler. 1996. The role of pollution and external refugia in structuring the Onondaga Lake fish community. Lake and Reserv.Manage. 12:81-90.

UFI and SU. 2007a. Preliminary feasibility analysis for control of methylmercury production in the lower waters of Onondaga Lake through nitrate addition. A report prepared for Honeywell by Upstate Freshwater Institute, Syracuse, NY and Syracuse University, Center for Environmental Systems Engineering, Syracuse, NY.

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

Urban N.R., Dinkel C. and Wehrli B. 1997. Solute transfer across the sediment surface of a eutrophic lake: I. Porewater profiles from dialysis samplers. Aquat. Sci. 59: 1-25.

Van Den Berg G. A., Loch, J. P. G., Van Der Heijdt, L. M. and Zwolsman, J. J. G. 2000. Redox processes in recent sediments of the river Meuse, The Netherlands. Biogeochemistry 48: 217-235.

Vollenweider, R. A., and L. L. Janus. 1981. The OECD cooperative program on eutrophication: summary report-Canadian contribution. Inland Waters Directorate Scientific Series No. 131, Environment Canada.

P:\Honeywell -SYR\444151 - 2008 SMU 8\09 Reports and Work Plans\Nitrate Interpretive Report (2006 study)\2006 Interp Rpt 040908.doc

April 23, 2008

53

Watras, C. J., N. S. Bloom, S. A. Claas, K. A. Morrison, C, C. Gilmour and S. R. Craig. 1995. Methylmercury production in the anoxic hypolimnion of a dimictic seepage lake. Water Air Soil Pollut. 80:735-745.

Wetzel, R. G. 2001. Limnology: lake and reservoir ecosystems. Academic Press, New York.

Wetzel, R. G. and G. E. Likens. 2000. Limnological Analysis. 3rd edition. Springer-Verlag, New York. 429 p.

P:\Honeywell -SYR\444151 - 2008 SMU 8\09 Reports and Work Plans\Nitrate Interpretive Report (2006 study)\2006 Interp Rpt 040908.doc

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APPENDIX A

VERTICAL PROFILES

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THg, ng/L

Depth (m)

MeHg, ng/L

A-7

Cl⁻ (mg·L⁻¹)

A-12

S²⁻ titration (mgS²⁻·L⁻¹)

S²⁻ titration (mgS²⁻·L⁻¹)

S²⁻ titration(mgS²⁻·L⁻¹)

S²⁻ titration (mgS²⁻·L⁻¹)

S²⁻ titration (mgS²⁻·L⁻¹)

S²⁻ titration(mgS²⁻·L⁻¹)

A-13

CH$_4$(mg·L^{-1})

CH$_4$ (mg·L^{-1})

CH$_4$ (mg·L^{-1})

CH$_4$ (mg·L^{-1})

CH$_4$ (mg·L^{-1})

CH$_4$ (mg·L^{-1})

N₂ (mg·L⁻¹)

A-15