Honeywell

WORK PLAN FOR ONONDAGA LAKE SMU 8 SEDIMENT INCUBATIONS AND SUPPORTING STUDIES
Syracuse, New York

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1.0 INTRODUCTION

As described in the Record of Decision for the Onondaga Lake Bottom Subsite (NYSDEC and USEPA, 2005), the selected remedy for Onondaga Lake includes performance of a pilot study to evaluate the potential effectiveness of oxygenation at reducing the formation of methylmercury in the water column, while preserving the normal cycle of stratification within the lake. In addition, the Statement of Work appended to the Consent Decree requires Honeywell to conduct a study to determine if nitrate addition would effectively reduce methylmercury formation in the water column while preserving the normal cycle of stratification. This study of nitrate addition may later include performance of a nitrification pilot study (or demonstration) as determined by NYSDEC. Both oxygen and nitrate are electron acceptors potentially capable of blocking the biogeochemical pathway leading to methylmercury production. A decision to implement oxygenation and/or nitrate addition will be informed by the outcome of these studies.

This work plan describes a series of laboratory measurements, supported by field monitoring and mathematical modeling activities, to provide the information required to design pilot demonstrations for oxygenation and nitrate addition and to enable a comparison of the relative advantages of both of these electron-acceptors, establishing:

- Efficacy of oxygen and nitrate augmentation in blocking methylmercury production;
- Quantities of nitrate and oxygen required to meet the sediment demand; and
- Interplay between conditions in the water column and sediment dynamics.

The final report on this work will document the results of the sediment incubation tests and associated mathematical redox modeling.

Sample locations, data-gathering methods, and details of the analyses and testing to be performed are described in this document. Core samples will be collected in accordance with applicable procedures outlined in the Onondaga Lake Phase I Pre-Design Investigation (PDI) Work Plan (Parsons, 2005), the Quality Assurance Project Plan (QAPP) for Onondaga Lake 2007 nitrate evaluation studies (Upstate Freshwater Institute, 2007), the Project Safety Plan (PSP) for Onondaga Lake 2007 nitrate evaluation studies (Syracuse University and Upstate Freshwater Institute, 2007), and project-specific Standard Operating Procedures presented in Appendix A. Mathematical redox modeling to be conducted as part of this sediment incubation work is summarized in Appendix B.

2.0 PROJECT OBJECTIVES

The Record of Decision calls for pilot testing of an oxygenation system to assess the potential for reducing methylmercury production in the hypolimnion and the Statement of Work appended to the Consent Decree requires an assessment of nitrate as an alternate electron-acceptor to accomplish the same objective.

An assessment of oxygenation and nitrate addition needs to include laboratory-scale tests of the merits of each of the two electron-acceptors to provide additional basis for proceeding with a pilot demonstration. Towards this end, extensive water column sampling was conducted in SMU 8 during 2006 and 2007 to assess oxygen and nitrate uptake, as well as methylmercury production. While this information was encouraging and provided significant insights into the factors controlling methylmercury production, the very nature of water column samples warrants caution in drawing firm conclusions, because Onondaga Lake is a dynamic lake stratified each year from May through most of October with concentrations of the electron-acceptors above the sediment-water interface constantly changing during stratification. The goal of an engineered electron-acceptor addition system would be to maintain steady target concentrations above the sediments. That scenario can be simulated in a laboratory setting by means of sediment incubations.

The laboratory-scale tests proposed in this work plan are designed to answer questions critical to determining the merits and design for a pilot demonstration and comparing a full range of effects of systems employing a selected electron-acceptor. Such questions include:

1. What extent of mercury methylation reduction or elimination is achievable?
2. What would electron-acceptor demand be under anticipated full-scale conditions?
3. What are reasonable expectations for future electron acceptor demand and system requirements to block methylmercury formation?
4. What effect would such systems have on the release of other compounds (such as phosphorus and ammonia) within the hypolimnion, and other interactions in the water column?
5. What is the relative effect of freshly-deposited organic material on sediment oxygen and nitrate demand compared to effects of previously deposited organic material (called legacy deposits)?

The work described herein is intended to provide the information needed to compare effects of oxygenation and nitrate addition, to design pilot demonstrations, and to enable a comparison of the two electron acceptors in terms of the issues captured in the questions cited above.

3.0 MOBILIZATION AND LOGISTICS

This section covers the mobilization and logistics to support the field tasks outlined in this addendum. Field work will be conducted by Upstate Freshwater Institute and by Cornell

University. Laboratory work will be conducted by Michigan Technological University, Upstate Freshwater Institute, and Syracuse University.

3.1 HEALTH AND SAFETY

Parsons ranks health and safety as the highest priority. A copy of the PSP is presented in Appendix C of the Phase I PDI (Parsons, 2005) and will be strictly followed by personnel. Copies of the plan will be maintained at the support zone and on each vessel.

3.2 SITE FACILITIES

Support zone and site facilities were established during the Onondaga Lake Phase I PDI near existing permanent structures at the west end of Wastebed B. These facilities are still in use and will be utilized to support the field activities presented in this work plan.

3.3 DECONTAMINATION AND WASTE HANDLING

Decontamination will be conducted at the decontamination area established during Phase I and on the UFI boat. Decontamination and waste disposal procedures will be conducted in accordance with the Phase I PDI Sampling and Analysis Plan (Parsons, 2005).

4.0 FIELD WORK

Two elements of field work are necessary for this project: emplacement and operation of hydrodynamic sensors by Cornell University, and sediment sample collection by Upstate Freshwater Institute.

4.1 INSTALLATION OF HYDRODYNAMIC SENSORS

The purpose of installing hydrodynamic sensors in deep, stratified waters of SMU 8 is to quantify mixing and boundary layer conditions at the sediment-water interface. Sediment incubation chambers will be designed to match these levels of turbulence and mixing conditions.

Three Nortek Vector Acoustic Doppler Velocimeters (ADVs) or equivalent were deployed at one location within the South Basin and within the Saddle (Figure 1) at three different vertical elevations approximately 4, 12, and 28 inches (10, 30 and 70 centimeters) above the top of sediment or mudline. The mean profile of turbulence levels varies with the logarithm of depth so these elevations were chosen to be approximately logarithmically separated. The selected elevations are representative of typical turbulent boundary layer regions of lakes of the size of Onondaga. Two points could be used to estimate the structure of the turbulence boundary layer, but three are preferable. There is no risk of bed irregularities affecting acoustic Doppler current profiler (ADCP) deployment given the size of the lake and the narrow track of a survey.

Given the South Basin and the North Basin have similar morphology and similar geographic alignments (Figure 1), measurements in the South Basin are assumed to be representative of conditions in both basins. The primary source of current and turbulence at the sediment-water interface in the profundal areas of Onondaga Lake is wind-driven movement of water (i.e., seiche events; Effler et al. 2004). Seiche events occur primarily along the long axis of the lake and are expected to affect the north and south basins similarly. Additional site work in the future, such as dye testing, could be conducted to confirm this assumption. A specification sheet for the Nortek Vector velocimeter has been submitted to the New York State Department of Environmental Conservation (NYSDEC) (Parsons, 2007). The Nortek device was selected due to its proven compatibility with an oxygen sensor, compatibility with other equipment to be used, price and proven technical support.

Deployment utilizes a rigid aluminum or steel frame, typically a tripod or A-Frame. Extra weight is to be added at the bottom of each leg, and in soft bottom environments flat "feet" are used to distribute the load on the bed. In general a ground line is run from the frame to a separate bottom weight, which then runs to a surface marker buoy. The frame is deployed in a rotation such that the probe head is not in the wake of the mean currents interacting with the frame. If the frame does interact with the mean current it will leave a signature that is recognizable in the ADV record - the Strouhal shedding frequencies of the Karman vortex street - and this phenomenon can be identified. Similarly, if the ADV measurement volume becomes buried below the sediment surface this, too, is discernable from the ADV record itself. For the type of deployments envisioned, it is not critical that the ADV be located closer than 10 centimeters to the bottom so it is not anticipated there will be any problem with measurement volume burial. No fouling of the instrument heads should occur over a short deployment and, in general, the ADV record would show signs of deteriorating signal-to-noise ration should this be a problem. Alignment will be such that there is no interference from instrument frame or mooring obstructions. The ADV deployment frame was sited so that the frame supports were located in the cross-flow direction relative to the principal axis (and seiche-driven flow direction) of Onondaga Lake. This minimized any interference of the frame wake with the measurement volume. Should flow direction occasionally lead to wakes in the measurement volume, these are easily identified by their characteristic Karman Vortex Street, which is readily apparent in temporal frequency spectra and can be removed.

Two deployments of the velocity meters were completed from late September 2007 through most of October 2007 while the lake was stratified. From September 27 to October 13 the velocity meters were deployed at the Saddle, a relatively shallow area that divides the north and south basins of the lake. On October 13, the velocity meters were moved to a deep location in the south basin, where they remained until late October. Data collected by the ADVs will be inspected for quality prior to subsequent deployments. The battery is capable of powering all three ADVs for longer than 14 days. Attempts will be made to measure a broad range of wind forcing effects on the bottom boundary layer turbulence levels. Coincident measurements of wind velocity and direction will be made at a meteorological station operated in the lake's south basin by the Upstate Freshwater Institute. The measured turbulence levels will be used to guide a series of turbulence simulations for the sediment incubation laboratory tests.

To assess bottom water velocity measurements from one South Basin location with respect to overall lake dynamics, two thermistor chains were deployed; one was deployed in the South Basin and one was deployed on the saddle between the North Basin and the South Basin (Figure 1). The thermistor chains included temperature loggers at 1 to 2 meter vertical intervals as needed to sufficiently identify temperature gradients. In addition, water temperature measurements collected every day from a second South Basin location will be assessed. The ADVs and the thermistor chains will be deployed with the assistance of the Upstate Freshwater Institute.

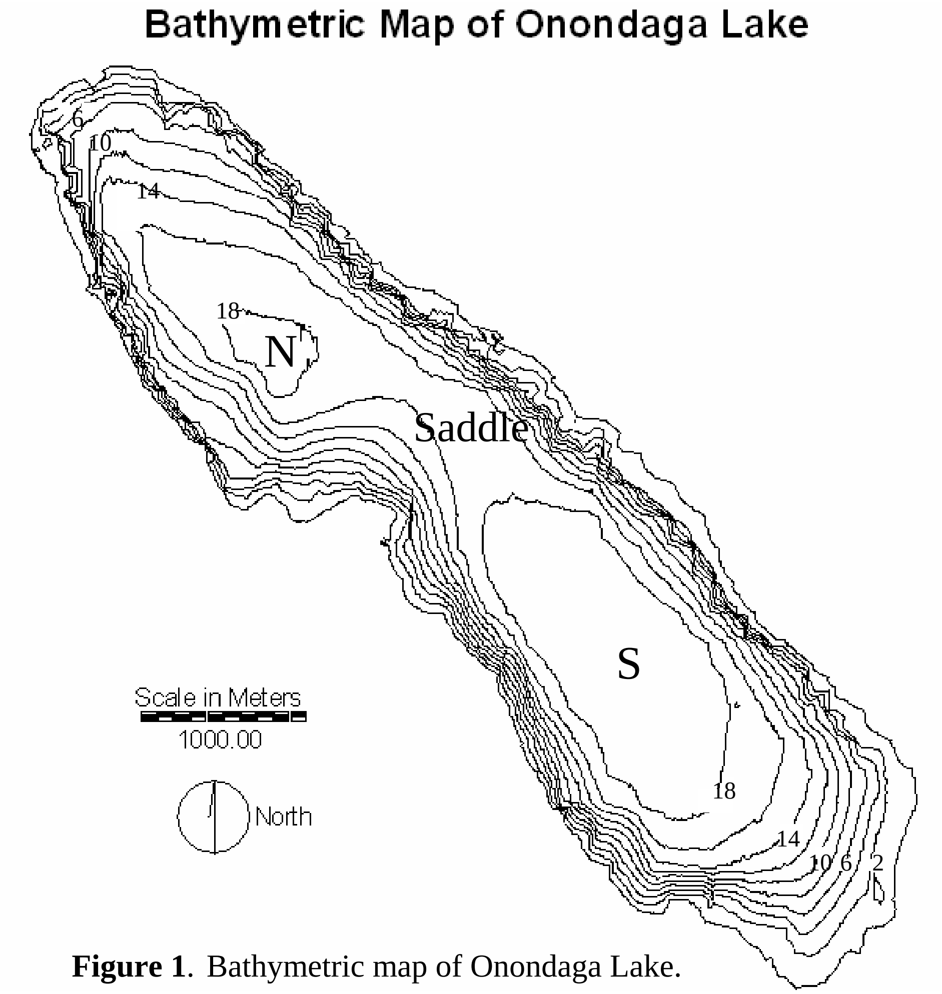


Figure 1. Bathymetric map of Onondaga Lake.

N – North Deep Basin Station

S – South Deep Basin Station

4.2 SAMPLING LOGISTICS

Sediment for use in flux measurements will be collected at Onondaga Lake's South Deep station (depth ~19 m) using an Ocean Instruments GM-2525-II GOMEX box corer (Figure 2). Made of stainless steel, the coring device is approximately 22 cm by 22 cm by 44 cm high and weighs ~75 pounds without sediment. Box corers are routinely used to collect large sediment samples with a minimum of disturbance. The penetration depth of the corer is regulated by the drop distance and the amount of additional weight added to the device. In Onondaga Lake, a drop distance of 1 m (with no additional weight) results in a collection chamber that contains approximately one-third water and two-thirds sediment. The sediment-water interface was retained while using the box corer.

The box corer will be sub-sampled by inserting core liners of various sizes to obtain sediment: short cores (for porewater profiles), long cores (for stratigraphy) and sediment incubation chambers (for flux measurements). Field notes and photographs will be used to document core collection. Sediment samples will be maintained in the dark at the ambient sediment-water interface temperatures and redox (oxic/anoxic) conditions until the measurements are initiated.

FIGURE 2. BOX CORER

5.0 TASK DESCRIPTIONS

5.1 HYDRODYNAMIC STUDY

Sediment uptake of available electron-acceptors in the water column is significantly affected by the hydrodynamic turbulence regime directly over the sediment-water interface. Such turbulence can be caused naturally by wind events, or mechanically by the action of oxygenation devices such as a Speece Cones (which discharge oxygen-rich water over the sediments) or line diffusers (which release bubbles in to the hypolimnion and generate weak bottom currents). The anticipated modes of nitrate delivery are not expected to generate significant currents or bottom turbulence. A proper assessment of wind-generated and device-generated turbulence regimes is necessary to the design of the incubation runs so that this important process affecting electron acceptor uptake is taken into account.

The hydrodynamic study will be led by Dr. Edwin (Todd) Cowen of the DeFrees Hydraulics Laboratory at Cornell University. It will involve a preliminary quantitative characterization of the bottom boundary layer turbulence in Onondaga Lake and will use highly accurate quantitative imaging methods to guide the team's selection, quantitative characterization, and operation of a laboratory method for generating controlled turbulence in laboratory sediment incubation experiments. Using quantitative imaging techniques for turbulence (velocity/ momentum) and for oxygen concentration (mass), the study will determine the effect of turbulence level on the electron acceptor concentration boundary layer in the laboratory.

The hydrodynamic study has five specific objectives:

1. Quantitatively characterize the bottom boundary layer turbulence in the profundal zone of Onondaga Lake.
2. Quantitatively characterize turbulence generated in laboratory sediment incubation chambers.
3. Recommend a specific method for the generation of turbulence using in a laboratory incubation chamber using the chamber’s jets.
4. Deliver a calibration chart for implementation of the agreed-upon method for the generation of turbulence in a laboratory incubation chamber (jet settings vs. target turbulence).
5. Make measurements of the oxygen concentration boundary layer in the presence of sediment as a function of turbulence level using the agreed-upon method of turbulence generation.

Field hydrodynamic measurements

Onondaga Lake is known to have significant internal wave motion (e.g., Effler et al. 2004). These wave motions, in general the response to wind, lead to current of the order of tens of centimeters per second along the bed. Frictional effects at the bed lead to a momentum boundary layer which is the region near the bed where the current velocity goes from its typical "free stream" value away from the bed (as forced by the internal waves), to essentially zero at the bed. This shear generates turbulence near the bed which enhances the vertical mixing and hence potentially enhances the vertical fluxes to or from the bed. This shear can also lead to sediment resuspension if it is sufficiently strong and/or the sediments are of sufficiently small particle size.

Given the future considerations of delivering either oxygen by Speece Cones or line diffusers (bubbling), or injecting a nitrate rich solution near the mudline, it is important to understand baseline turbulence conditions in order to predict and ultimately measure and compare the effects on the turbulence levels of these processes.

The approach is to directly measure the mean currents and turbulence levels using Acoustic Doppler velocimeters (ADVs) as the principal measurement device. ADVs measure all three components of velocity at a point with high accuracy (typically one millimeter per second plus or minus 0.5 percent of the measured value) in a small measurement volume (approximately one cubic centimeter) at high temporal resolution (to 64 cycles per second). They incorporate a compact measurement head that allows them to be deployed close to the lake bottom and they do not suffer any blanking region near the bed.

The principal ADV deployment frame will include three ADVs each at different vertical elevations (for example, 4, 12, and 28 inches above the mudline). The stack of three ADVs will be used to resolve the momentum boundary layers and boundary layer generated turbulence at the bed. There will be a quantitative characterization of these turbulence levels to support design and the conduct of the sediment incubation chamber measurements.

To place the turbulence and boundary shear measurements in the larger picture of the overall lake dynamics two thermistor chains will be deployed, one in the southern profundal zone and one on the saddle, in addition to using the thermal structure measurements of the Onondaga Lake "South Deep" monitoring station which resolves the lake's vertical temperature structure every 6 hours at one meter increments. The thermistor chains will include temperature loggers at one to two meter increments as needed. The combination of the temporally resolved vertical structure at three locations in Onondaga Lake in conjunction with the meteorological data from the "South Deep" monitoring station will reveal the state of the internal wave climate in Onondaga Lake allowing an interpretation of the basin-scale lake conditions that lead to significant turbulence and vertical momentum fluxes at the water sediment interface.

As indicated in Section 4.1 of this work plan, the goal is to make two to three 10 to 14 day deployments in Onondaga Lake during the late summer to early fall interval of 2007. Optimum conditions would include a weather window where strong winds are predicted during the measurement period, to capture a broad range of wind forcing effects on the bottom boundary layer turbulence levels. The measured turbulence levels will be used to guide a series of laboratory measurements.

Laboratory hydrodynamic measurements

The fundamental hydrodynamic measurement tools in the laboratory are quantitative imaging (QI) techniques (e.g., Sveen & Cowen, 2004). For the purposes of this project there are two fundamental techniques of interest; particle image velocimetry (PIV) and laser induced fluorescence (LIF). The former involves the tracking of small clouds of particles illuminated by a laser light sheet as the particles move through a fluid flow. The latter involves detecting the intensity of fluorescence of an oxygen-sensitive fluorescent dye, in the case at hand, as it has its fluorescence quenched by the amount of oxygen locally dissolved in the water. PIV, as developed by Cowen and Monismith (1997), will be used to measure the turbulence characteristics near the bed in sediment incubation chambers. PIV will allow very high-resolution (to better than one millimeter) instantaneous measurements of the velocity over a two-dimensional region of approximately 30 X 30 independent measurements. These instantaneous measurements are easily averaged into the mean and turbulent velocity profiles from which quantities such as the bed stress can be directly calculated.

PIV will be used to survey the various methods that have been implemented by researchers (e.g., Beutel et al., 2007) to quantify the turbulence levels generated as well as understand the characteristics of the turbulence and the mean flow.

After evaluating the various methods that have been successfully employed to generate turbulence within an incubation chamber the scientific team will select the optimal method. One option is to utilize the random synthetic jet approach developed by Dr. Cowen's group (Variano, Bodenschatz and Cowen, 2004; Variano and Cowen, 2007; Variano, 2007). This technique randomly turns on and off individual jets in an array of synthetic jets that have their intake and excurrent co-located along a boundary so as to leave no net momentum added to the flow. With an agreed upon turbulence generation technique selected, a specific configuration of the selected technique will be characterized and a calibration provided (e.g., turbulence level as a function of operating parameters) to the team that will support all the incubation experiments.

Finally, using oxygen sensitive LIF we will investigate the effects of various levels of turbulence on the oxygen boundary layer characteristics. All of the above laboratory measurements will be guided by the field measurements of turbulence levels in Onondaga Lake.

5.2 SEDIMENT INCUBATIONS

Professor Martin T. Auer of Michigan Technological University will lead this effort.

5.2.1 Methodology

The flux of oxygen and nitrate from the water to the sediment and the flux of ammonia, methylmercury and phosphorus from the sediment to the water will be measured in the laboratory using custom-designed sediment incubation chambers. These microcosm devices (Figure 3) will be 30 cm tall and 10 cm in diameter and outfitted with an inlet port for introduction of electron acceptors, an outlet port for sample collection and ports accepting jets for adjustment of turbulence levels.

The sediment incubation chambers will be constructed with a friction-fit detachable base, allowing the introduction of sediment by sub-sampling box core collections (Section 4.2). After sub-sampling, the devices will contain ~12.5 cm of water, representing the lake's hypolimnion and ~12.5 cm of sediment. A basis for partitioning of water and sediment volumes required to support the measurement will be provided at a later date. Preliminary modeling analyses show that 12.5 cm of sediment depth is more than sufficient sediment to encompass the vertical zone of mercury methylation. Note that the sediment incubation chambers are not designed to simulate stratification because significant stratification is not anticipated at a length scale of centimeters. The water overlying the sediment in the chamber may be viewed as either a completely-mixed water column (i.e., during periods of circulation) or the hypolimnion of a stratified system.

Turbulence levels will be maintained by a system of jets placed in the top of the chamber. The jets will be driven by three peristaltic pumps operating in parallel and reversing direction of flow to the jets in a random fashion. Pump settings (e.g. $mL \cdot min^{-1}$) will regulate the magnitude of the turbulence and randomization of the reversal times will insure random net transport and thus a homogenous boundary layer. Three turbulence levels will be considered: (1) those matching ambient conditions at the sediment-water interface, (2) those associated with nitrate addition and (3) those associated with oxygen addition. The magnitude of turbulence associated with each of these conditions, and thus the pump settings during operation, will be established as part of the Hydrodynamics Study (Section 5.1). NYSDEC will be notified when the three levels of turbulence are determined.

Sediment incubation chambers will be maintained at ambient hypolimnetic temperatures in controlled environment chambers at the Upstate Freshwater Institute. The microcosms will be operated in a flow-through mode, i.e. a feed stock of artificial or natural lake water (Appendix C) will deliver the electron acceptor to the chamber and the resulting outflow will provide sample for chemical analysis. Water samples will be collected at a time frequency dictated by the particular analyte in question (e.g. hours for oxygen and nitrate and days for mercury, phosphorus, and ammonia). Guidance for the timing of sample collection will be provided by modeling analysis (Appendix B).

Chemical analysis of water samples collected during sediment incubations will be performed by Michigan Tech University (oxygen and nitrate using microsensors), Syracuse University (filtered total mercury and methylmercury) and Upstate Freshwater Institute (ammonia and phosphorus).

5.2.2 Screening Measurements

Inspection of field data from Onondaga Lake suggests that the initiation of methylmercury flux from the sediments is coincident with elimination of oxygen and nitrate from the hypolimnion. The range of oxygen levels, appropriate for the purpose of mediating methylmercury flux is reasonably well defined by the biogeochemistry of the target chemical species and the logistics of the oxygenation technology. Little guidance is available from this or other sites as to the nitrate level that should be targeted in seeking to reduce or eliminate methylmercury flux. For this reason, a screening round of measurements will be conducted in the Fall of 2007 to establish the effective range of nitrate addition. Here, nitrate will be added via a de-oxygenated artificial lake water feed stock until a steady state nitrate concentration is maintained in the water compartment. Mercury flux will then be measured and the nitrate feed reduced, seeking a second steady state. The mercury flux will be measured once again. This will continue, over a nitrate range of 10, 4, 2, 1 and zero mg N·per liter in sequence, until the breakpoint for initiation of methylmercury flux is identified (Figure 4). This breakpoint will be used to establish the range of nitrate concentrations for subsequent testing. NYSDEC will be notified when the breakpoint nitrate concentration is determined.

There will be 15 samples collected for the screening assessment (based on five conditions and three samples per condition). All of the samples from the screening assessment will be analyzed for methylmercury**.**

5.2.3 Electron Acceptor Matrix Measurements

Next, a series of measurements will be made over a matrix of electron acceptor concentrations (Table 1) to establish target concentrations for oxygen and nitrate that provide the best logistic benefit (e.g., economics, ecological impact) and process efficacy (i.e., reduction or elimination of methylmercury flux). Positions on the matrix will reflect the:

- Natural condition for denitrification (0/0; absence of nitrate and oxygen);
- Range of oxygen levels described above (nitrate at ambient, 2 mg $N \cdot L^{-1}$); and
- Range of nitrate levels described above (absence of oxygen).

In these measurements, the feed stock will be artificial lake water (Appendix C), amended with electron acceptor. Artificial lake water is the appropriate candidate for feed stock in this series of measurements as it offers the greatest degree of control and chemical integrity. Turbulence levels in matrix measurements will correspond to the appropriate electron acceptor scenario, e.g. ambient turbulence for the 0/0 case and that associated with nitrate and oxygen addition for the corresponding matrix positions (Table 1). Experiments will be repeated such that triplicate determinations are available at target concentrations, supporting estimates of uncertainty in projections of the impact of electron acceptor addition.

A total of 54 samples will be collected as part of the matrix assessment (based on six conditions, three replicates, and three samples per replicate). The variability of the replicate analyses will be assessed in conjunction with NYSDEC to determine the extent to which the number of replicate analyses can be reduced. Thus, it may not be necessary to analyze all of the matrix assessment samples and all of the seasonal assessment samples**.**

5.2.4 Seasonal Measurements

Having established target electron acceptor levels, a series of seasonal measurements will be made to quantify variability in electron acceptor demand and efficacy in flux mediation as rates of sediment deposition (organic carbon and mercury) and electron acceptor availability (oxygen and nitrate) change. Filtered natural lake water (hypolimnion) will serve as the base component of the feed stock, appropriately reflecting ambient levels of organic carbon and other components of the chemical matrix that might influence environmental mercury dynamics. Oxygen and nitrate will be maintained at their target levels and turbulence will match that associated with the particular electron acceptor addition during these measurements. Fluxes of filtered total mercury, filtered methylmercury, ammonia, and phosphorus from the sediment will be measured at target nitrate and oxygen levels to evaluate the effect of electron acceptor addition on the release of these chemicals to the water column.

Three rounds of seasonal measurements are planned, corresponding to the expected change in water chemistry of the hypolimnion. A fourth (contingency) round will be held in reserve to respond to unexpected changes in conditions. Nominal dates for the three rounds and the reasoning behind their selection are provided in Table 2.

Like the matrix assessment, there will also be 54 samples collected as part of the seasonal assessment (based on three dates, two conditions for each date, three replicates, and three samples per replicate). As discussed in Section 5.2.3 for the matrix measurements, an assessment will be made of the variability of replicate analyses from the seasonal measurements. That assessment will be reviewed with NYSDEC to identify the extent to which the number of replicate analyses can be reduced.

5.2.5 Anticipated Results

The sediment incubation measurements will establish target concentrations of nitrate and oxygen for the in-lake demonstration program planned subsequently. These results will also quantify the electron acceptor demand, seasonal variability, and the impact of chemical amendment on ammonia and nitrate flux. Extension of these results to estimate levels of oxygen, nitrate, sulfide and methylmercury in the hypolimnion will be accommodated by applying measured fluxes to a coupled, sediment-water column model (Appendix B). The present work plan does not treat the lake's epilimnion, either experimentally or through modeling analysis.

TABLE 1. EXPERIMENTAL DESIGN FOR MATRIX MEASUREMENTS.

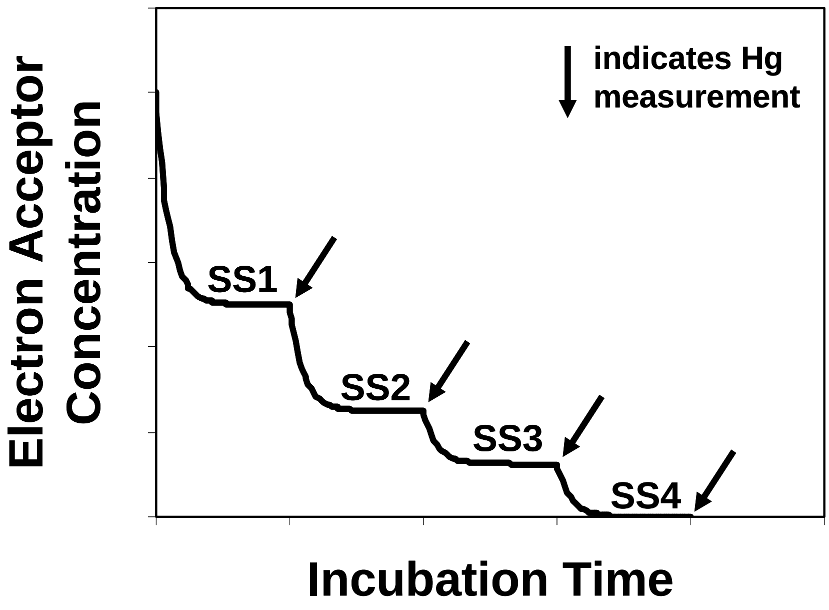
Oxygen/Nitrate	0 mg N·L^{-1}	Breakpoint	2 mg N·L^{-1}
0 mg O_2 L^{-1}	*ambient*	*nitrate addition*	*nitrate addition*
1 mg O_2 L^{-1}			*oxygen addition*
2 mg O_2 L^{-1}			*oxygen addition*
4 mg O_2 L^{-1}			*oxygen addition*

TABLE 2. TIMELINE FOR SEASONAL MEASUREMENTS

Round	Timing	Rationale
1	April 2008	prior to the onset of thermal stratification; freshly-deposited labile organic carbon at its annual minimum; porewater levels of electron acceptors at their annual maximum.
2	July 2008	immediately following the exhaustion of hypolimnetic oxygen reserves; freshly-deposited labile organic carbon increasing; porewater oxygen depleted, nitrogen remains at maximum levels.
3	August 2008	prior to the exhaustion of hypolimnetic nitrate reserves; freshly-deposited labile organic carbon nearing the annual maximum; porewater nitrogen approaching depletion.

FIGURE 3. SEDIMENT INCUBATION CHAMBER.

FIGURE 4. SCREENING MEASUREMENTS – ANTICIPATED BEHAVIOR.



5.3 FATE AND MICROBIOLOGICAL TESTING

Fate of Nitrate and Mercury

Sediment methylmercury ($CH3Hg^+$) production is an important source of methylmercury to the water column of Onondaga Lake. Highly reduced conditions promote methylation of mercury (Hg). Demethylation of Hg can occur either under reduced conditions (oxidative pathway) or under oxic conditions (reductive pathway) resulting in production of ionic Hg (Hg^{2+}) or Hg^{2+}/ Hg^0, respectively. Concentrations of methylmercury in the water column are the net result of methylation and demethylation processes, which are driven by the oxidation-reduction (redox) status of the sediments. The potential of Onondaga Lake sediments to methylate and demethylate Hg and knowledge of the species products of demethylation are critical to understanding the fate of methylmercury within Onondaga lake and critical also to evaluating the effectiveness of oxygenation or nitrate addition to the water column.

Preliminary results (Upstate Freshwater Institute, 2007) showed that production of methylmercury was suppressed in Onondaga Lake by the maintenance of high nitrate (NO_3^-) concentrations (~1 mg N L^{-1}) approximately 1 meter above the sediment-water interface. These results suggested that sulfate-reduction and associated methylmercury production was reduced or eliminated by the energetically favorable nitrate-reduction process. Depending on the pathway, nitrate-reduction may result in production of nitrogen, ammonia, or nitrous oxide gases. The most desirable fate of nitrate reduction would be production of inert nitrogen, while production of ammonia would be the less desirable by-product because this reduced species can exert an oxygen demand and can be toxic to aquatic organisms. The key process that results in production of inert nitrogen is denitrification, while ammonia is a product of dissimilatory nitrate reduction to ammonia (DNRA) and/or by mineralization of microbial nitrogen. A key issue in the proposed nitrate addition remediation strategy to reduce or eliminate methylation of mercury is the understanding of the ultimate fate of the added nitrate. This issue is important because knowledge of the fate of added nitrate is essential to quantify the dose of nitrate to be added to Onondaga Lake and better understand the environmental consequences of a potential nitrate treatment. Because the nitrogen cycle is complex and important processes can occur simultaneously, traditional analytical techniques are inadequate to determine the fate of nitrate. Bench-scale experiments using 15N-labelled nitrate can be used to quantify the fate of the added nitrate.

This experiment will complement and be compatible with the larger sediment incubation experiments described herein. The objective of the experiment is to quantify the fate of mercury (Hg) species and added nitrate in the sediments of Onondaga Lake under different redox conditions that are consistent with potential oxygenation and nitrate treatments. Transformations of mercury between ionic (Hg^{2+}) and organic methylmercury forms, the rate of methylmercury production, the fate of added nitrate and production of nitrogen gas species will be evaluated in a one-time experiment, as a supplement to the sediment incubation study proposed to start in the fall of 2007. Seasonal mercury and nitrogen fate experiments will not be performed.

Three different experimental conditions are to be investigated: nitrate-added, nitrate and oxygen-added, and a reference anoxic. The nitrate-added condition (Condition 1) will maintain a nitrate level determined to be optimal from the associated mercury release experiments. Nitrate and oxygen-added condition (Condition 2) will maintain optimal nitrate level as in Condition 1 and 2 milligrams per liter of oxygen. The reference condition will be anoxic (i.e., no added nitrate).

Sediment samples will be collected after fall turnover (2007) using box corer sampling device. Cores will be collected in triplicate. Initial experiments will be performed to determine the optimal incubation time of the Hg-spiked core using an experiment set-up that is consistent with the experimental apparatus to be used. Cores will be pre-incubated with 15N (a stable isotope of nitrogen) (Condition 1) and oxygen-15N (Condition 2) for 24 hours before initiating the isotope additions to allow adjustment of microbial communities. The reference core will be allowed to become anoxic. Methylmercury production and back-transformation to inorganic mercury will be assessed by using isotopes of Hg^{2+} and methylmercury. Determination of methylation and demethylation potential will be evaluated on separate cores. Water and sediment Hg and methylmercury will be determined using ELAN DRC-e LC/ICP-MS (Perkin Elmer, Inc. Walter, MA). Water samples will be analyzed for 15N-nitrate and 15N-ammonia using a modified N-diffusion technique (Stark and Hart, 1996). Acidified glass fiber disks will be used to trap ammonia volatilized in the procedure, and these disks will be packed in tin capsules, sealed and sent to the Stable Isotope Facility at the University of California at Davis. Devarda’s alloy (an alloy of aluminum, copper, and zinc) will be used to reduce nitrate to ammonia. When a solution of nitrate ions is mixed with aqueous sodium hydroxide, adding Devarda's alloy and heating the mixture gently liberates ammonia gas. The ammonia gas is then trapped and analyzed for 15N by mass spectrometry. Gas samples will be collected using a silicone diffusion chamber inserted into the headspace of the core (Jacinthe and Groffman, 2001). Gases dissolved in overlying water come into equilibrium with the air space in the chamber and are then sampled, stored in evacuated glass vials and sent to Davis for analysis of 15N2O and 15N2. The experiment will be conducted by Syracuse University. The evaluation of the fate of mercury will be assessed by Syracuse University. The evaluation of the fate of nitrate will be assessed by the independent Institute of Ecosystem Studies located in Millbrook, NY.

Microbiological Testing

This element of the study will undertake a survey of the microbial populations in the sediments of Onondaga Lake. There are currently no data available that characterize the microbial populations in Onondaga Lake sediments. Sediment cores collected during the three 2008 sediment sampling events will be used to characterize the sediment microbial populations spatially and temporally. Specifically, at least three cores will be sectioned into approximately four depths with intervals to be selected in consultation with NYSDEC based on water column and sediment porewater data, if available.. Samples will be analyzed by Microbial Insights Inc (www.microbe.com) using quantitative real time polymerase chain reaction (qPCR). This technique distinguishes between methanogens, denitrifiers, and sulfate/iron reducers using DNA primers specific to each microbial group. qPCR is used to make multiple copies of the target genes (identified by DNA primers) for each microbial group present in each sample. The target genes are fluorescently tagged and the degree of fluorescence is measured to determine the number of copies of the target gene. The number of copies is then compared to a known standard for each microbial group and the number of cells of each microbial group in the samples is thus estimated. Resulting data will provide a characterization of the relative abundance of each group of organisms with depth in the sediments. The characterization of these three groups of organisms covers the major groups of organisms involved in anaerobic carbon degradation and the potential mercury methylating organisms.

6.0 REPORTING AND SCHEDULE

Decision points that are identified in the work plan are incubation chamber turbulence representation, modeling results for determining chamber depth and incubation sample depth, results from 2007 chamber experiments, 2008 sample collection timeframes (Table 2), 2008 target sediment sample locations, 2008 incubation test conditions, numbers of replicate analyses to analyze, vertical sectioning of cores for microbiological testing, and analysis of porewater for methylmercury following the incubations.

Results from the incubations and associated testing will be used to characterize the effectiveness of adding oxygen or nitrate in terms of methylation elimination, as well as to quantify the sediment demand of each electron acceptor and the anticipated fluxes of other compounds from the sediments. Redox modeling will provide guidance as to long-term trends in the Lake and enable an assessment of potential life-cycle expenses associated with adding oxygen or nitrate. The objectives of the report will be: (1) to document data needed to design pilot tests and, (2) to document the results of the experiments and modeling. The report will also discuss uncertainties associated with the incubation efforts.

Information updates will be submitted to the NYSDEC throughout the project. In addition, an interim submittal is planned at this time for May 2008. The final report will be submitted to the NYSDEC by late October 2008 in order to determine prior to the end of 2008 whether to proceed in 2009 with either an oxygenation or nitrate addition pilot demonstration.

7.0 QUALITY ASSURANCE/QUALITY CONTROL

The sample names, QA/QC procedures, sample collection, data entry, and data validation for this portion of the work will be conducted in accordance with the Phase I PDI Work Plan (Parsons, 2005). Any deviations from these procedures will be discussed with NYSDEC prior to execution of the work or qualified in the sediment incubation report if dictated by experimental process limitations during bench studies.

Wet chemistry data generated by the laboratory, including mercury analyses, will be evaluated in accordance with the Onondaga Lake QAPP for 2007 SMU 8 work (Syracuse University and Upstate Freshwater Institute, 2007) and then validated consistent with the data evaluation and data validation performed on the 2006 data (and to be performed on the 2007 data). The data will be evaluated by the laboratory in relation to the established laboratory and project control limits for accuracy and precision with factors impacting data quality being identified in the laboratory analytical report. The data will be evaluated by the project manager as to consistency with site conditions and developed conceptual models, to determine whether field and analytical data meet the requirements for decision making. The results of the measurements will be compared to the Data Quality Objectives and considered complete and satisfied if the data are identified as usable for the intended purposes and if no major data gaps are identified.

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APPENDIX A

STANDARD OPERATING PROCEDURES (SOPs)

A.1 SOP FOR ACOUSTIC DOPPLER VELOCITY MEASUREMENTS OF *IN SITU* VELOCITIES

A.2 SOP FOR BOX CORER SAMPLE COLLECTION

A.1 SOP FOR ACOUSTIC DOPPLER VELOCITY MEASUREMENT OF *IN SITU* VELOCITIES

A.1.1 PURPOSE AND SCOPE

The purpose of this document is to define the SOP for *in situ* monitoring of water velocity in Onondaga Lake, and more generally in a lake/reservoir environment. This SOP describes the necessary equipment, field procedures, materials, and documentation procedures necessary to install the *in situ* monitoring equipment. These procedures do not cover every eventuality nor are they intended to. Instead they serve as a basic guide to be followed and adapted as deemed necessary by experienced field personnel based on site conditions, safety considerations, and measurement requirements.

A.1.2 HEALTH AND SAFETY CONSIDERATIONS

A safety briefing will be held at the beginning of each field mobilization and at each shift in personnel. The designated safety officer on the vessel shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for marine sampling -- caution deploying and retrieving heavy equipment, keeping hands and clothing out of winches and A-frame supports, and stepping in the bight of lines or cables -- apply to the field crew during sampling. Winches, lifts, cables, and lines will be used within their designed limits to avoid injury from equipment failures. Appropriate personal protective equipment will be donned prior to the start of work as described in the PSP.

A.1.3 REQUIRED EQUIPMENT

- Work Boat suitable for equipment deployment and retrieval with USCG required safety equipment,
- Personal Protective Equipment, Personal Flotation Devices, personal items (food, water, etc.),
- GPS unit to mark deployment location,
- Instrument frame,
- Ropes to attach surface marking buoy to frame,
- Anchor weight for surface buoy,
- Additional rope for deployment,
- Acoustic velocity measurement instruments (e.g. acoustic velocimeters or acoustic current profiler),
- Batteries and battery cases (if needed) for autonomous deployment,
- Instrument cable and power supply for deployment programming,

- Necessary tools and hardware for attaching surface float, instruments, and deployment
- Power winch if deemed necessary due to weight of frame and instruments,
- Measurement device (ruler, measuring tape),
- Log book
- Digital camera.

A.1.4 *IN SITU* VELOCITY MEASUREMENTS

An appropriate frame for mounting the required instruments, either one or multiple acoustic velocimeters (single measurement point), an acoustic current profiler (multiple measurement locations), or a combination of the two instrument types will be assembled on shore and moved to the boat for transport to the measurement location. The frame geometry and instrument locations should be measured prior to deployment. Pictures from multiple angles should be taken showing all aspects of the frame, close-ups of the instruments and mountings, etc. Care should be taken to note the orientation of the compasses and coordinate systems of each instrument and ensure alignment between instruments.

For a bottom mounted acoustic current profiler the frame will generally be a simple sled to which the instrument can be mounted in an upward looking orientation along with a battery case. The sled will rest on the bottom when deployed. For only acoustic velocimeters, the frame will consist of a scaffold type structure to raise the instruments to appropriate elevations above the bed. For a combination of the two instrument types, a sled may be used when an upward looking orientation profiler is used, and a tripod style frame for downward oriented, near bed profiles. In all configurations a ground line will run from the frame to a bottom anchor with a surface line running to a marking buoy.

Upon arrival at the deployment location, the appropriate lines will be attached to the frame, anchor and surface buoy. An additional line will be attached to the frame for deployment to keep the frame level and unrotated while being lowered. The frame will be moved over the side of the boat and lowered at a moderate rate to the bottom using both lines. In this way, the frame's orientation can be controlled to some degree. After the frame is on the bottom, a GPS waypoint will be taken to mark the actual instrument location. The boat will then be moved away to lay the ground line, anchor weight and deploy the surface marking buoy.

Retrieval of the instrument frame will follow the reverse of the deployment sequence. The surface line will be retrieved, followed by the anchor weight and ground line. When the frame is located, another GPS waypoint should be taken for comparison. The frame will then be lifted using hand over hand technique if weight is not an issue; or a powered winch if it is too heavy. When the frame reaches the surface, the ground line should be tied off to a support to prevent dropping the frame to the bottom. The frame will then be pulled from the water and placed in the boat.

Instruments will be removed from the frame and returned to a dry environment for data download, data quality check and battery replacement. If required, once data has been verified and batteries replaced, instruments can be re-deployed.

A.1.5 DOCUMENTATION AND DATA STORAGE

Each deployment location will have an information form created for it listing the following items.

- Deployment Date and Time
- Personnel Involved
- Deployment Location (GPS locations and datum)
- Instruments
- Sampling Setup for each instrument
- Frame Geometry and Measurements
- Deployment Notes
- Data File List
- Pictures List

The information form will be maintained in the same location as the data files (i.e., on a computer). All data, information forms, etc. will be backed up to an appropriate media (CD, DVD, or hard drive.

A.2 SOP FOR BOX CORER SAMPLE COLLECTION

A safety briefing will be held at the beginning of each field effort on the lake and at each shift in personnel. The designated safety officer on the boat shall be responsible for ensuring the safety of personnel and will be contacted immediately in the event of an emergency. The standard safety considerations for marine sampling – caution deploying and retrieving heavy equipment, keeping hands and clothing out of winches and A-frame supports, and stepping in the bight of lines or cables – apply to the field crew during sampling. Winches, lifts, cables, and lines will be used within their designed limits to avoid injury from equipment failures. Appropriate personal protective equipment will be donned prior to the start of work as described in the health and safety plan. These considerations are discussed in more detail in the project health and safety plan.

A.2.1 EQUIPMENT

- GOMEX box corer
- Winch
- Boom arm
- Sediment incubation chambers
- Sampling vessel or floating platform
- Propulsion method for sampling vessel or floating platform
- Log Book
- Labels
- Coolers
- Gloves
- Meter Wheel/Measuring device

A.2.2 SAMPLING PROCEDURE

The following steps describe the subsampling of a box core collection of undisturbed lake sediment to obtain material required for chemical flux incubation measurements. The box corer collects sediment and overlying water in a chamber approximately 23 cm by 23 cm wide by 46 cm tall. The tube portion of a sediment incubation chamber (15 cm tall by 20 cm in diameter) will be pushed into the undisturbed sediment within the box corer and sealed with a bottom plate 20 cm in diameter.

1. Select a box corer suitable for the bottom conditions expected.
2. Securely attach the box corer to a winch with cable or line of sufficient strength to accommodate the weight of the sampler and sample.
3. Set the mechanism on the box corer so the jaws are held in the open position.

4. Slowly lower the box corer using a winch and A-frame or boom arm through a moon pool or over the side of the vessel. Maintain tension on the box corer to keep the jaw mechanism from prematurely closing.
5. After the box corer contacts the sediments on the bottom, relax the tension on the box corer to allow the jaw locking mechanism to release.
6. Place tension on the cable/line and slowly lift. This should cause the sampler jaws to close trapping the sample inside.
7. Slowly retrieve the box corer.
8. Set the box corer into the bracket to hold the corer in a stable vertical position.
9. Open the top covers of the box corer.
10. Insert the tube portion of the sediment incubation chamber into the sediment within the box corer, capturing 12.5 cm of sediment and 12.5 cm of overlying water.
11. Insert the bottom plate with accompanying o-ring into the sediment, capping the bottom of the chamber.
12. Lift the bottom plate and chamber out of the box corer and rinse and wipe the outside of the device.
13. Attach the top plate and seal the device with rods and wing nuts as provided.
14. Label the outside of each core tube with the sample ID, as described in the SOP in the PDI Work Plan (Parsons, 2005) for containers, preservation, handling and tracking of samples for analysis.
15. Place the chamber in a cooler with ice.
16. Return the coolers with chambers to the laboratory, exercising care to maintain the undisturbed nature of the interface and following chain of custody procedures.

APPENDIX B

REDOX MODELING

This appendix provides an introduction to mercury cycling and oxidation-reduction (redox) processes and an introduction to redox modeling including descriptions of a water column screening model and a sediment model as applied to Onondaga Lake. These two models provide examples of approaches to modeling that are relevant to this work plan. The appendix then briefly describes three models (i.e., a diagnostic model, a sediment diagenesis model, and a coupled sediment-water column model) that will be developed during the sediment incubation work to support the design of the incubation chambers, describe sediment diagenesis, and predict electron acceptor demand and hypolimnetic methylmercury concentrations as functions of carbon fluxes, respectively.

B1. INTRODUCTION

Background

Mercury is most commonly encountered in aquatic environments in the elemental, Hg(0), mercuric, Hg(II), and methylated, MeHg, forms (Bozke et al. 2002; Ullrich et al. 2001). It is the methylated form, a product of microbial transformation, that is available for uptake by the biota (Mason 1995), leading to loss of beneficial use of aquatic resources, i.e. fish consumption advisories and bans (Anderson et al. 2004). Three redox-related processes have been implicated in the methylation of mercury (iron reduction, Fleming et al. 2006, but see also Warner et al. 2003; methanogenesis, Warner et al. 2003 and sulfate reduction). It is generally agreed that the mercury methylation is carried out largely by sulfate-reducing bacteria (Compeau and Bartha 1985; Gilmour et al. 1992), suggesting important roles for,

- dissolved or particulate inorganic mercury, as a reactant in methylation;
- labile organic carbon, as the electron donor in sulfate reduction; and
- sulfate, as the electron acceptor in sulfate reduction.

As an electron donor, labile organic carbon is the fuel for the fire that is the sulfate reduction – mercury methylation process and has been described as ‘the primary control on mercury methylation’ in estuarine sediments (Lambertsson and Nilsson 2006, p. 1822). Autochthonous production is the source of most of the organic carbon deposited to and incorporated in lake sediments. As with mercury, there are two components to the sediment profile of labile particulate organic carbon: that associated with fresh deposits at the sediment surface and that remaining in the sediment from earlier periods in the lake’s history (legacy carbon; Figure B1). Unlike mercury, labile organic carbon undergoes decomposition and is depleted over time (and depth). Source control plays an important role here, because changes in autochthonous production lead to changes in labile organic carbon flux and thus the amount of carbon available to drive sulfate reduction (mercury methylation). In addition, labile organic carbon flux mediates the depth of penetration of electron donors into the sediment relative to other elements in the methylation process (e.g. mercury and electron acceptors).

Sulfate serves as the electron acceptor in the sulfate reduction process, yielding hydrogen sulfide as a reduced species end product. Rates of mercury methylation are thought to vary with the sulfate concentration. Maximum methylation is expected between 0.2 and 0.5 millimoles per liter (mM) sulfate (Langer et al. 2001), with limitation at lower concentrations and reduction or elimination at higher levels (Gilmour et al. 1998). Onondaga Lake is naturally rich in sulfate (~1.5 mM), a result of the presence of gypsum in the watershed (Effler 1996). Thus sulfate reduction in Onondaga Lake will not be sulfate limited; there is no evidence of reduction or elimination in this system. However, sulfate reduction as a means of oxidizing carbon is thermodynamically unfavorable compared with that using oxygen or nitrate as electron acceptors. The presence of these compounds inhibits the sulfate reduction process. The interest then, from a sediment remediation perspective, becomes the role of labile carbon, oxygen and nitrate in mediating rates of sulfate reduction and the attendant interaction between that process and mercury methylation. Chemical augmentation with nitrate seeks to limit the rate of methylation by inhibiting the sister process, sulfate reduction.

Mercury Cycling, Chemical Augmentation and the Redox Sequence

The sulfate reduction – mercury methylation pathway is embedded in a family of biochemical processes termed the redox series. Here, an electron donor (labile organic carbon) participates in redox reactions with a series of alternate electron acceptors. The carbon is converted to carbon dioxide and the electron acceptors converted to reaction-specific reduced species end products (Table B1). The utilization of a given alternate electron acceptor has been shown to follow a thermodynamically-favorable progression, the redox sequence (Berner 1980). Given the geochemistry of Onondaga Lake (low in iron and manganese), the sequence may be described as oxygen → nitrate → sulfate → methanogenesis. The presence of a more thermodynamically favorable electron acceptor, e.g. oxygen, inhibits the utilization of the next most favorable species, e.g. nitrate. A water column response consistent with the redox series is clearly manifested in the hypolimnion of Onondaga Lake (Figure B2) where oxygen is depleted first, nitrate is depleted second and sulfide production (evidence of sulfate reduction) occurs last. The fact that methane evolution occurs simultaneously with these processes (Matthews et al. 2007) suggests that the region of active methanogenesis is physically segregated from (lies below) the region where oxygen, nitrate and sulfate reactions proceed.

The accumulation of methylmercury in the hypolimnion has been shown to track that of sulfide quite well (Figure B3), demonstrating the clear association of sulfate reduction and mercury methylation in this system. The underlying concept in chemical augmentation (UFI, 2006) is that maintenance of adequate nitrate levels at the sediment-water interface (B4), would support diffusion of this electron acceptor into the sediment and inhibit sulfate reduction and mercury methylation. The efficacy of this approach will depend on the extent to which electron acceptors provided through chemical augmentation penetrate the sediment relative to sulfate, labile organic carbon and mercury. The point here is that while nitrate may inhibit sulfate reduction near the surface, it is depleted with depth, leaving sulfate with an opportunity to participate in the reduction reaction. Further, the relative physical proximity of electron acceptors, labile organic carbon and mercury may vary over time due to burial and changes in carbon flux, altering rates of methylation. A redox model, supported by an integrated program of field monitoring and laboratory experimentation can serve to evaluate the feasibility of chemical augmentation in limiting water column impacts related to methylmercury.

B2. MODELING THE REDOX PROCESS

Selection of a Model Framework

The modeling discipline offers a broad spectrum of approaches for simulating environmental phenomena. The selection of a particular approach should be guided by the intended application (screening, management or research) and by the interplay amongst model reliability, model complexity, and the resources available to support the project (Figure B5). Simple models, often applied as screening tools, are of low complexity, are easy to develop and can provide insight into the perturbation-response relationships in a timely fashion.

A screening model for redox processes as manifested in the hypolimnion of Onondaga Lake is described here and applied in tracking the depletion and accumulation of chemical species participating in the those reactions. The model is also used to provide a first-cut evaluation of the impact of lake management strategies on redox processes. Next, the nature of a more complex sediment model, of the type used in research applications, is explored. Models such as this are particularly valuable in developing an improved understanding of ‘how things work’, a critical step in developing a reliable and credible predictive tool. In a subsequent section, recommendations are offered on the selection of a model framework of an intermediate complexity, one useful in examining the ‘when and to what extent’ and chemical augmentation issues relating to mercury management in Onondaga Lake.

A Water Column Screening Model

Model Framework

The screening model seeks to track changes in electron acceptors (oxygen, nitrate and sulfate) and a reduced species end product (sulfide) in the hypolimnion of Onondaga Lake over the thermally-stratified period of one season. This is a mass balance analysis performed on a control volume (the completely-mixed hypolimnion) idealized as a closed system.

The mass balance for oxygen may be written as,

$$V_h \frac{do_h}{dt} = -A_h \cdot SOD \tag{1}$$

where V_h is the hypolimnion volume (m^3), o_h is the dissolved oxygen concentration in the hypolimnion ($gO_2 \cdot m^{-3}$) , t is time (d), A_h is the area of the hypolimnion (m^2) and SOD is the sediment oxygen demand ($gO_2 \cdot m^{-2} \cdot d^{-1}$), i.e. the oxidation of labile organic carbon with oxygen as the electron acceptor,

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \qquad (2)$$

Dividing both sides of Equation (1) by V_h permits expression of the oxygen mass balance as a flux,

$$H_h \frac{do_h}{dt} = -SOD \qquad (3)$$

where H_h is the thickness of the hypolimnion (m).

When oxygen is above zero (or some other specified concentration), the SOD is assumed to be equal to the oxygen required for microbial oxidation of the labile organic carbon delivered to the sediment,

$$SOD = r_{oc} J_c \qquad (4)$$

where r_{oc} is the stoichiometric coefficient describing carbon oxidation by oxygen,

$$\frac{1\, mole\, O_2}{1\, mole\, CH_2O} \times \frac{32\, gO_2}{mole\, O_2} \times \frac{mole\, CH_2O}{12\, gC} = 2.67 \frac{gO_2}{gC} \qquad (5)$$

and J_c is the labile organic carbon flux to the sediment ($gC \cdot m^{-2} \cdot d^{-1}$).

With $o_h = o_0$ at $t = t_0$ (the initial condition), Equation (4) can be substituted into Equation (3) and the result solved for,

$$o_h = o_0 - \frac{r_{oc} J_c}{H_h}(t - t_0) \qquad (6)$$

This equation can be employed to compute the change in oxygen concentration in the hypolimnion as a function of time.

Given nonzero levels of labile organic carbon, the oxygen concentration will eventually fall to zero. This time can be computed by setting $o_h = 0$ and solving Equation (3) for,

$$t_n = t_0 + \frac{o_0 H_h}{r_{oc} J_c} \qquad (7)$$

where t_n is the time after which nitrate becomes the electron acceptor. At this point, labile organic carbon is oxidized via denitrification as in,

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O \qquad (8)$$

Using a similar approach as for oxygen, the mass balance for nitrate can be written and solved for the nitrate concentration in the hypolimnion,

$$n_h = n_0 - \frac{r_{nc} J_c}{H_h}(t - t_n) \qquad (9)$$

where n_h is the nitrate concentration in the hypolimnion (gN·m^{-3}), n_0 is the initial nitrate concentration in the hypolimnion (gN·m^{-3}) and r_{nc} is the stoichiometric coefficient describing carbon oxidation by nitrate,

$$\frac{4\ moles\ NO_3^-}{5\ moles\ CH_2O} \times \frac{14\ gN}{mole\ NO_3^-} \times \frac{mole\ CH_2O}{12\ gC} = 0.9333\ \frac{gN}{gC} \tag{10}$$

The time for nitrate to fall to zero (or some specified concentration) can be computed as,

$$t_s = t_n + \frac{n_0 H_h}{r_{nc} J_c} \tag{11}$$

where t_s is the time after which sulfate becomes the electron acceptor. In this case, organic carbon is oxidized via sulfate reduction as in,

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow HS^- + 2CO_2 + 2H_2O \tag{12}$$

The mass balance for sulfate can then be written and solved for,

$$s_h = s_0 - \frac{r_{sc} J_c}{H_h}(t - t_s) \tag{13}$$

where s_h is the hypolimnetic sulfate concentration (gS·m^{-3}), s_0 is the initial hypolimnetic sulfate concentration (gS·m^{-3}], and r_{sc} is the stoichiometric coefficient describing carbon oxidation by sulfate,

$$\frac{1\ mole\ SO_4^{2-}}{2\ moles\ CH_2O} \times \frac{32\ gS}{mole\ SO_4^{2-}} \times \frac{mole\ CH_2O}{12\ gC} = 1.3333\ \frac{gS}{gC} \tag{14}$$

If hydrogen sulfide levels in the hypolimnion are initially assumed to be negligible, the hypolimnetic concentration created by sulfate reduction can then be computed as,

$$h_h = \frac{r_{sc} J_c}{H_h}(t - t_s) \tag{15}$$

where h_h is the hydrogen sulfide concentration (mgS·L^{-1}).

Model Performance

The model was calibrated to data collected from Onondaga Lake in 1995. The equations presented above were solved in an Excel-VBA environment, yielding predicted concentrations of oxygen, nitrate, sulfate and hydrogen sulfide in the completely-mixed hypolimnion of Onondaga Lake.

Model fit to field data for a labile organic carbon flux (J_c) of 0.55 gC·m^{-2}·d^{-1} is presented in Figure B6. As this is a calibration, the excellent fit to the oxygen data is not particularly surprising. However the ability of that carbon flux and the simple framework adopted here in successfully simulating nitrate and sulfide observations is encouraging, both with respect to the similarity of depletion rates and the timing of switches between the electron acceptors that constitute the redox sequence.

It is instructive to direct some attention to the value of the labile organic carbon flux established here by calibration to be 0.55 $gC\cdot m^{-2}\cdot d^{-1}$. Stromquist (1996) applied a curve-fitting technique to sediment core measurements in determining that 40±17% of the total organic carbon reaching the bottom of Onondaga Lake was in the labile form. Applying this percentage, the calibration value for J_c would correspond to a mean particulate organic carbon flux of 1.38 $gC\cdot m^{-2}\cdot d^{-1}$ with a range of 0.97-2.40 $gC\cdot m^{-2}\cdot d^{-1}$. Effler (1996) reports average particulate organic carbon flux values for Onondaga Lake of 1.18 and 0.75 $gC\cdot m^{-2}\cdot d^{-1}$ for 1985 and 1988, with ranges of 0.41-3.65 and 0.10-1.3 $gC\cdot m^{-2}\cdot d^{-1}$, respectively. The J_c value estimated here compares quite favorably with those measured directly in the field (Figure B7). The somewhat higher flux predicted by the screening model could reflect uncertainty in the estimate of the fraction labile (not measured directly) and/or the contribution of legacy carbon not accommodated in this model framework.

Given the satisfactory performance of the screening model, it is both appropriate and instructive to apply the tool in examining some perturbation-response or management scenarios relating to the carbon-redox phenomenon and chemical augmentation.

Management Application

A consideration of an example management application can serve to illustrate key features of the natural recovery process coupled with chemical augmentation. Perhaps surprisingly, the critical element and management variable in these scenarios is the flux of labile organic carbon and, by extension, the trophic state of the water column. This was recognized by Berg et al. (2003, p. 905) who recognized labile organic carbon as 'the key driving input parameter for sediment diagenesis models.' Given the presence of mercury as a contaminant and sulfate as a natural feature of the water column, the element fueling the sulfate reduction – mercury methylation process then is carbon.

This example management case will explore the response of the redox environment (oxygen, nitrate and sulfide concentrations) to changes in the flux of organic carbon as might result from changes in the lake's primary production (trophic state). The simulations reflect not only the response to changes in carbon flux, but also impacts on the required magnitude and duration of chemical augmentation. Specific values for reductions in carbon flux are not provided here, as that step must await formal development and testing of the model.

The simulation (Figure B8) examines the impact of serial reductions (0%, X% and 2X%) in the labile organic carbon flux. In all cases, reductions in the rate of oxygen depletion are realized and paralleled by reductions in the rate of nitrate depletion. At the first level of reduced carbon flux (X%), nitrate is not sustained in the hypolimnion until turnover, sulfate reduction occurs and chemical augmentation would be required. With further reduction in the carbon flux (2X%), nitrate is maintained until turnover, sulfate reduction is blocked and chemical augmentation would not be required. This case illustrates a situation where chemical augmentation could be reduced and eventually eliminated as reductions in carbon flux are achieved. Note that legacy deposits of labile organic carbon can impact the process as well.

Lessons Learned and Issues of Uncertainty

The development and application of a simple screening model has shown that observed carbon flux rates and estimates of the fraction of that carbon present in the labile form serve well in reproducing rates and the timing of oxygen and nitrate depletion and sulfide accumulation in the hypolimnion of Onondaga Lake. Specific conclusions evolving from the exercise are,

- the sequential nature of the redox series is clearly reflected in the field data, affirming the mechanistic treatment of the process embodied in the model;
- the model successfully resolves measured rates of particulate organic carbon flux and estimates of carbon lability with observations of redox dynamics;
- model applications illustrate the role of chemical augmentation in controlling the redox sequence to inhibit sulfate reduction; and
- model simulation clearly illustrate the response of chemical species involved in redox reactions to changes in labile organic carbon flux, thus illustrating the critical linkage of nutrient and mercury management.

Albert Einstein has been credited with saying that “everything should be kept as simple as possible, but no simpler.” This is certainly true in the case of models. In that spirit, it is useful to examine the lessons learned here from a simple screening model, identifying features that could be improved to reduce uncertainty and make the framework more useful in guiding management decisions.

Some of these lessons relate to the importance of including a water column component in a more complex management tool. One reason for this is that the driving force for redox reactions, labile carbon flux, is intimately linked to water column processes, e.g. primary production. Another reason is that the proposed management action, chemical augmentation, will be applied to the water column, thus necessitating simulation and specification of water column conditions in developing an operational plan. Finally, it must be acknowledged that observations and simulations of water column conditions offer the most reliable, direct and cost-effective means of tracking sediment redox dynamics. One may conclude from this that a water column component should be included in a management model for redox dynamics in Onondaga Lake.

Mercury methylation is thought to take place at the oxic/anoxic boundary in the water column and sediment, with the relative importance of water column and sediment processes dependent on the physical and chemical structure of the lake (Watras et al. 1995). Several investigators have measured significant methylation in the water column of lakes (Henry et al. 1995; Regnell et al. 1997). Concentration gradients of oxygen, nitrate and hydrogen sulfide presented here in Figure B9 make it quite clear that the processes critical to mercury – redox interactions in Onondaga Lake (aerobic respiration, nitrate- and sulfate-reduction) are localized in the sediment. Thus it is appropriate to develop a model for sediment redox dynamics, driven by labile organic carbon flux, and to couple that sediment framework with a water column component.

Next, the simple screening model utilizes data from and performs calculations on a completely-mixed hypolimnion. Quantification of conditions directly at the sediment-water interface is required to satisfy two demands of a sediment model: (1) identification of concentrations of chemical species triggering the switch in active electron acceptors and (2) establishment of boundary conditions for diffusion-based calculations in the mass balance. Thus, it would be appropriate in a coupled, water column – sediment model to partition the water column segment into multiple layers permitting calculation of the concentration of chemical species at the interface.

Finally, the simple screening model assumes an equilibrium condition with respect to labile carbon flux. Such an assumption is not well-supported in application to sediment remediation because it neglects the role of legacy pollutants (i.e. buried labile organic carbon) and fails to accommodate the time necessary to reach that equilibrium condition. Chapra (1997) describes the time (t_{95}, years) required for a lake to experience 95% of its recovery response,

$$t_{95} = \frac{3}{\frac{Q}{V} + k} \tag{16}$$

where Q is the lake inflow ($m^3 \cdot yr^{-1}$), V is the lake volume (m^3) and k (yr^{-1}) represents decay reactions for the constituent of interest. Thus the time to steady state in the water column is a function of purging due to outflow and reaction. For a rapidly-flushing system such as Onondaga Lake, this response is very fast: on the order of several months. Conditions are decidedly different in the sediment environment,

$$t_{95} = \frac{3}{\frac{\omega}{z} + k} \tag{17}$$

where ω is the sediment burial velocity (m·yr-1) and z is the thickness of the active sediment layer (m). In the sediment, the flushing term (ω, burial) is orders of magnitude less than that for the water column and decomposition reactions (k) proceed at a much slower rate as well. The result is that the sediment recovery response may be much slower than that of the water column (Figure B10). For example, the water column response time corresponding to changes in total phosphorus loading to Onondaga Lake is on the order of several months, while that for the sediment is several decades (Lewis et al. 2007). A sediment component thus plays a critical role in a management model by quantifying the time necessary to come into equilibrium with a new loading regime (i.e. that associated with source controls). Thus, one may conclude from this exercise that a coupled, sediment - water column model holds the greatest promise for supporting management actions, including chemical augmentation to limit sulfate reduction (and therefore mercury methylation).

A Sediment Model

Models addressing carbon diagenesis and related redox reactions in the sediment lie far removed along the complexity continuum from the screening model introduced earlier. At a base level, sediment models must accommodate the role of mass transport, the varying degrees of organic carbon lability and the complex geochemical interplay of chemical constituents involved in redox reactions. In research applications, as many as six primary (relating to organic matter decomposition) and fifteen secondary (end product or metabolite) redox reactions may be involved (Berg et al. 2003). Further, these features must be simulated in time and in space, simulating the distribution of chemical species with depth in the sediment and changes in those profiles over time. While the results of such modeling efforts are conceptually satisfying and can yield rather exciting results (cf. Gilmour et al. 2003), caution must be exercised in adoption of these tools where the ability to appropriately quantify model inputs may compromise model credibility. That said it is instructive to examine this more complex approach to understanding organic carbon diagenesis and related redox reactions.

Berg et al. (2003) reviewed a suite of published model frameworks, focusing on the four numerical transport-reaction models (Boudreau 1996; Dhakar and Burdige 1996; Soetaert et al. 1996; and Van Cappellen and Wang 1996) evolving from the seminal work in early diagenesis conducted by Berner (1980). Subsequent efforts have endeavored to apply these models (Boudreau et al. 1998; Herman et al. 2001) and to simplify or extend their frameworks (Archer et al. 2002; Luff et al. 2000; Wijsman et al. 2002). The primary difference among these tools lies in their temporal resolution (steady state or dynamic), treatment of carbon diagenesis (number of carbon fractions) and number and type of primary and secondary redox reactions accommodated. Following their review, Berg et al. (2003) decided to develop a new model improving on the four numerical transport-reaction models identified above in its treatment of mass transport and redox-based reactions.

A pattern emerges here, where most modelers adopt an essentially common mass transport approach, but differ in their handling of the primary and secondary redox reactions, likely due to a combination of site-specific characteristics and individual interpretations of the underlying science. Meysman et al. (2003a, p. 291) recognized this, concluding that these tools ‘have a rigid, static and problem-specific character, leaving little autonomy for the application user’ and that ‘the resulting lack of flexibility and extensibility, and the associated need for ground-level reprogramming, constitutes a major barrier for potential model users.’ In response to this, Meysman et al. (2003a; 2003b) developed the MEDIA (Modelling Early DIAgenesis) software package that supports development of individually-tailored models of early diagenesis by extending a model template with new model components from a toolbox of available objects (elements, species, parameters, reactions). This tool may hold substantial promise for application in future efforts.

Our goal is to examine the manner in which a sediment model can improve our understanding of the interplay between labile carbon flux and redox reactions. To that end, we have selected to explore the **Ca**rbon and **N**utrient **Di**agenesis Model (CANDI; Boudreau 1996), which includes basic transport functions, multiple carbon fractions and a suite of redox reactions, as a means of illustrating that interplay. The model is available in open code which may be modified by the user for particular applications.

Model Framework

CANDI is a mechanistic model in which a mass balance is performed over a time interval Δt on a slice of the active sediment layer with a thickness Δz. Terms in the mass balance on the porewater phase (Boudreau, 1997) include diffusion, biodiffusion (mass transport due to bioturbation), advection and reaction,

$$\frac{\partial \phi C}{\partial t} = D_0 \frac{\partial}{\partial x}\left(\frac{\phi}{\theta^2}\frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial x}\left(\phi D_B \frac{\partial C}{\partial x}\right) - \frac{\partial \phi \mu C}{\partial x} + \sum Rxn \tag{18}$$

diffusion biodiffusion advection reaction

where t is time (d), C is the liquid phase concentration of a chemical species ($g \cdot m^{-3}$), D_0 is the molecular/ionic diffusion coefficient in free solution ($m^2 \cdot d^{-1}$), x is depth in the sediment (m), ϕ is the sediment porosity (dimensionless), θ is the tortuosity (dimensionless), D_B is the biodiffusion coefficient ($m^2 \cdot d^{-1}$), μ is the velocity of porewater flow ($m \cdot d^{-1}$), and ΣRxn includes all of the biogeochemical reactions ($g \cdot m^{-3} \cdot d^{-1}$).

Solid phase terms in the mass balance include biodiffusion, burial and reaction,

$$\frac{\partial (1-\phi) B}{\partial t} = \frac{\partial}{\partial x}\left((1-\phi) D_B \frac{\partial B}{\partial x}\right) - \frac{\partial (1-\phi)\omega B}{\partial x} + \sum Rxn \tag{19}$$

biodiffusion burial reaction

where B is the solid phase concentration of a chemical species (g chemical·g sediment^{-1}), ω is the sediment burial rate ($m \cdot d^{-1}$) and ΣRxn includes all of the biogeochemical reactions (g chemical·g sediment$^{-1} \cdot d^{-1}$).

For the deep littoral and profundal sediments of Onondaga Lake, where bioturbation (anoxia) and advection (groundwater flow) are negligible, the resulting porewater and solid phase contaminant profiles for a conservative substance would be well-represented by straight lines (Figure B11a). For a labile substance that decays in the sediment according to first order kinetics, particulate phase concentrations would decrease with depth, asymptotically approaching zero (Figure B11b). Liquid phase substances, e.g. those produced through diagenesis, would also be impacted by diffusion, yielding the profile illustrated in (Figure B11c).

The term diagenesis refers to the sum total of processes that bring about changes in a sediment subsequent to deposition in water (Berner 1980). The biogeochemical processes that result in diagenesis are accommodated in CANDI by the reaction term (ΣRxn in Equations 18 and 19). CANDI is a comprehensive sediment diagenesis model, treating multiple organic carbon fractions, the redox reactions outlined in Table B1, dissolved ammonia, calcium and phosphate and liquid phase-solid phase interactions for several iron and manganese minerals. Model output includes vertical profiles of the concentration of organic carbon and the redox species, the rates of reaction for members of the redox sequence and equilibrium distributions of chemical components influenced by pH. The equations may be solved as a function of time or at steady state.

Insights Gained Through Sediment Modeling

A sediment model is capable of simulating profiles of labile organic carbon over time and with changes in flux from the water column. In addition, such a model can describe variability in the depth of penetration achieved through diffusion and concentration profiles of electron acceptors (oxygen, nitrate and sulfate) in response to changes in water column levels of these species (i.e. seasonality, chemical augmentation). For example,

> *Reduced Carbon Flux* – a sediment diagenesis model tracks the concentration of labile organic carbon with depth and thus the availability of this electron donor to drive redox reactions. As shown in Figure B12, a reduction in labile carbon flux reduces the mass of carbon present as well as the depth of penetration. The rate of depletion of electron acceptors thus proceeds at a slower rate and these chemical species penetrate more deeply into the sediment. The presence of oxygen and nitrate deeper in the sediment limits the co-occurrence of sulfate and labile organic carbon, reducing the magnitude of sulfate reduction.
>
> *Chemical Augmentation* – the effect of increasing concentrations of electron acceptors is to meet the demands of labile organic carbon oxidation and to enhance the penetration of these electron acceptors into the sediment. Figure B13 compares the vertical distribution of porewater electron acceptor with and without chemical augmentation with nitrate. As with a reduced carbon flux, the effect here is to expand the region in the sediment where labile organic carbon is oxidized by oxygen and nitrate and thus limiting the region where sulfate reduction occurs.
>
> *Burial and Species Interactions* – the vertical distribution of electron acceptors is largely governed by the vertical distribution of labile organic carbon, with both of these being limited to near surface sediments.

In practice, all of these phenomena may be manifested simultaneously.

B3. REDOX MODELING FOR SEDIMENT INCUBATION WORK

As described above, models can provide important insights into understanding redox-related processes in Onondaga Lake. Thus, an important component of the sediment incubation work described in this work plan is the development of models to 1) support the design of the incubation chambers, 2) describe sediment diagenesis, and 3) predict electron acceptor demand and hypolimnetic methylmercury concentrations as functions of carbon fluxes. Models to address each of these three objectives are described briefly below. Deliverables for each of the three models will be prepared in open code (i.e., readily available software) and accompanied by appropriate documentation. Model development will be interfaced with field measurements, laboratory experimentation, and the application of electron-acceptor addition technologies to Onondaga Lake. Professor Steven Chapra of Tufts University will lead this effort.

A Diagnostic Model

By their very nature, microcosm experiments such as sediment incubations challenge scientists to develop a physical configuration and experimental protocol that appropriately represent *in situ* conditions. The methods development phase of the proposed study will be addressing questions relating to chamber dimensions, mixing phenomena, sediment depth, duration of incubation, sample volume requirements and augmentation with make-up water (feed stock). The project timeline calls for the methods development phase to be essentially complete this fall. For this reason, it is critical that chamber design and protocol development not proceed by trial and error. The diagnostic model proposed here will support this development.

The framework for the diagnostic model will be in the spirit of sediment model frameworks described by Berg (2003), Boudreau (1997) and Chapra and Reckhow (1983) and discussed in Section 2 of this appendix. The framework for the diagnostic model will focus only on selected redox-sensitive species (e.g. nitrate, oxygen and sulfide) and will be simplified to address only conditions germane to the target system (e.g. no treatment of biodiffusion or groundwater advection).

The model will generate simulated pore water profiles for each chemical species as well as predictions of their flux at the sediment-water interface. A liquid phase compartment above the sediment will represent the water column portion of the sediment chamber, permitting simulation of experimental results. In this way, the diagnostic tool can be used to examine the impact and utility of different physical chamber configurations and experimental protocols in a time- and cost-efficient fashion.

Sediment Diagenesis Model

The limitation of the diagnostic model is that it does not incorporate all of the salient diagenetic reactions and is thus not an appropriate vehicle for management simulations. This shortfall is addressed in the second modeling component. The sediment diagenesis model extends the diagnostic tool by incorporating redox processes (e.g. electron acceptors such as iron and manganese) not included in the simpler framework.

The sediment diagenesis model will be calibrated and validated using pore water chemistry data and applied to yield estimates of sediment nitrate and oxygen demand and the flux of reduced species at the sediment-water interface. Model runs will address a variety of environmental forcing conditions, e.g. water column electron acceptor levels and labile organic carbon availability. This more complete treatment of redox processes is necessary to insure that chemical flux predictions are robust.

The sediment diagenesis model will also treat biodiffusion, a process attending chemical augmentation with oxygen. This process is a serious concern associated with hypolimnetic aeration or oxygenation where diffusion of contaminants is enhanced through bioirrigation.

Finally, the diagenesis model will permit treatment of legacy materials in the sediment. Such analysis serves to resolve the roles of legacy deposits of labile organic carbon (Appendix D), quantifying changes in the magnitude of electron acceptor addition required and identifying a potential endpoint for the treatment process.

Coupled Sediment – Water Column Model

While sediments are the arena in which these biogeochemical process are played out, the driving forces for sediment phenomena and attendant ecosystem effects lie within the domain of the water column. In 2007, oxygen and nitrate levels in the hypolimnion of Onondaga Lake were sustained for the longest period in modern history. The timing of electron acceptor depletion and its relation to labile organic carbon deposition and phosphorus management at METRO may have a significant impact on the cost of electron acceptor addition, both within the annual cycle and with respect to the long-term requirement for operation. Finally, the success of a program of electron acceptor addition will likely be evaluated in terms of the level of methylmercury accumulation in the lake’s hypolimnion and epilimnion. A third component of the modeling effort will address these issues.

The objective of the coupled sediment-water column model is to compute the distribution and rate of accumulation/depletion of species in flux across the sediment-water interface. Figure B14 illustrates the framework for the coupled sediment-water column model. A modeled sediment depth of 150 cm with 0.1 cm increments has been conservatively selected. The hypolimnion will be divided into one meter segments, facilitating simulation of vertical profiles and determination of the chemical species concentrations at the sediment – water interface required for interfacial transport calculations. A mass balance will be prepared for each chemical species in each water column segment. Conditions in the upper mixed layer of the water column (i.e., the epilimnion and metalimnion) will not be simulated, but will be described through a time-variable boundary condition derived from field measurements in order to provide an upper boundary for the hypolimnion. The species addressed in the water column component will be mercury, methane, nitrate, oxygen, sulfate and sulfide. No water column processes other than diffusion are included in the model. Experimentally-determined methylmercury fluxes from the sediment incubation measurements, corresponding to various levels of electron acceptor addition, will be applied to simulate methylmercury accumulation in the water column. Mercury concentrations in the sediment will not be modeled.

In its application as a coupled model, specified labile organic carbon fluxes will generate an oxygen and nitrate demand and establish conditions of carbon diagenesis and electron acceptor consumption in the sediment. The result will be predictions of electron acceptor demand and hypolimnion methylmercury concentrations as functions of carbon fluxes.

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Table B1. Electron acceptors and associated reduced species end-products involved in the mineralization of organic carbon through the ecological redox series.

Oxygen Reduction

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

Nitrate Reduction

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 5CO_2 + 2N_2 + 7H_2O$$

Manganese Oxide Reduction

$$CH_2O + 2MnO_2 + 4H^+ \rightarrow CO_2 + 2Mn^{2+} + 3H_2O$$

Iron Oxy-Hydroxide Reduction

$$CH_2O + 4FeOOH + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 7H_2O$$

Sulfate Reduction

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$$

Methanogenesis

$$2CH_2O \rightarrow CH_4 + CO_2$$

Figure B1. The distribution of total organic carbon with depth in the sediment of Onondaga Lake illustrating exponential decay over the first 5-7 cm and the presence of legacy deposits at depth. The fraction of this carbon present in a labile form has not been determined. Measurements derived from a core collected in the south basin of the lake in 1995 and redrawn from data of Stromquist (1996).

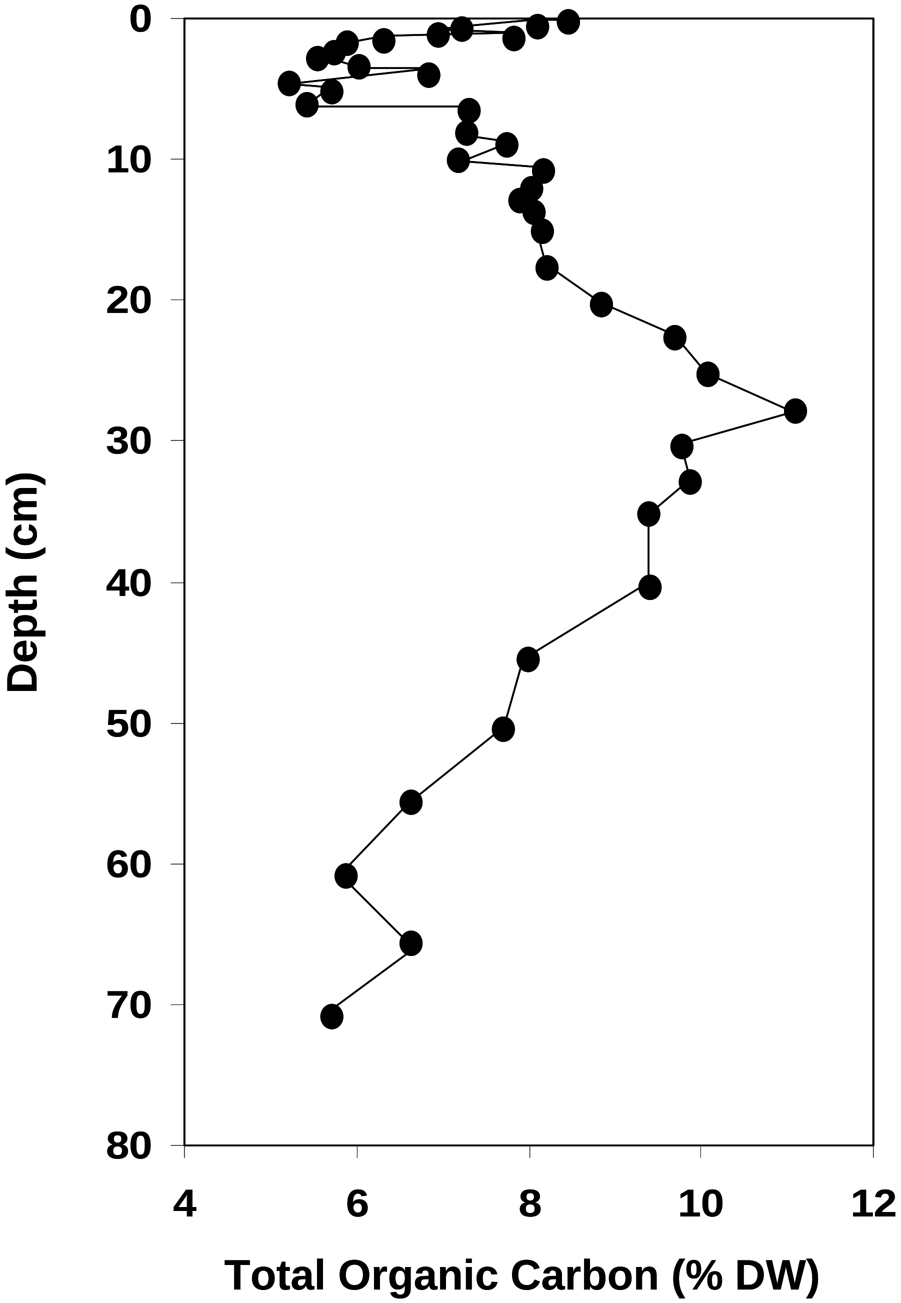


Figure B2. Temporal patterns in the concentrations of oxygen, nitrate and sulfide in the hypolimnion of Onondaga Lake illustrating conformance to the redox series. Data provided by D.A. Matthews, Upstate Freshwater Institute.

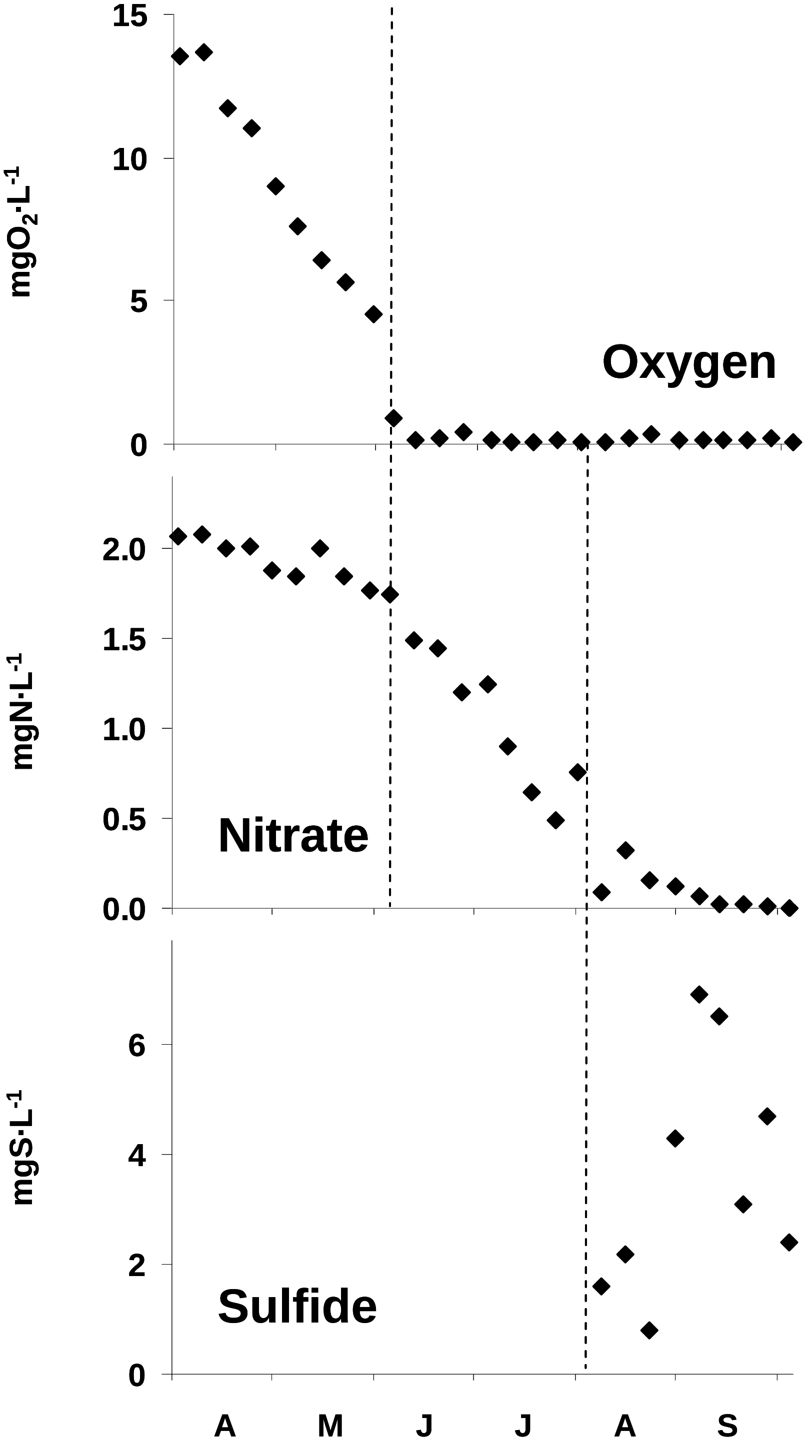


Figure B3. Temporal patterns in the concentrations of sulfide and methylmercury in the hypolimnion of Onondaga Lake for 2005 illustrating the co-occurrence of their release from the sediments. Data provided by S. Todorova and C.T. Driscoll, Syracuse, University.

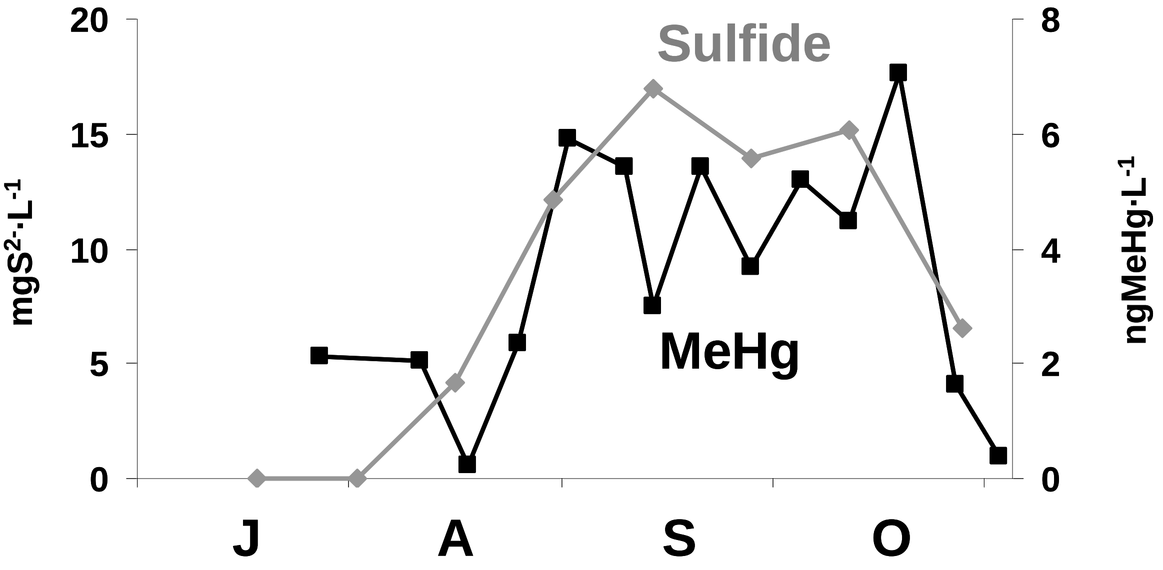


Figure B4. Temporal patterns in the concentrations of oxygen, nitrate and sulfide in the hypolimnion of Onondaga Lake illustrating the theoretical response to chemical augmentation with nitrate. Maintenance of nitrate levels in the water column sustains those in the sediment, inhibiting sulfate reduction. Data provided by D.A. Matthews, Upstate Freshwater Institute.

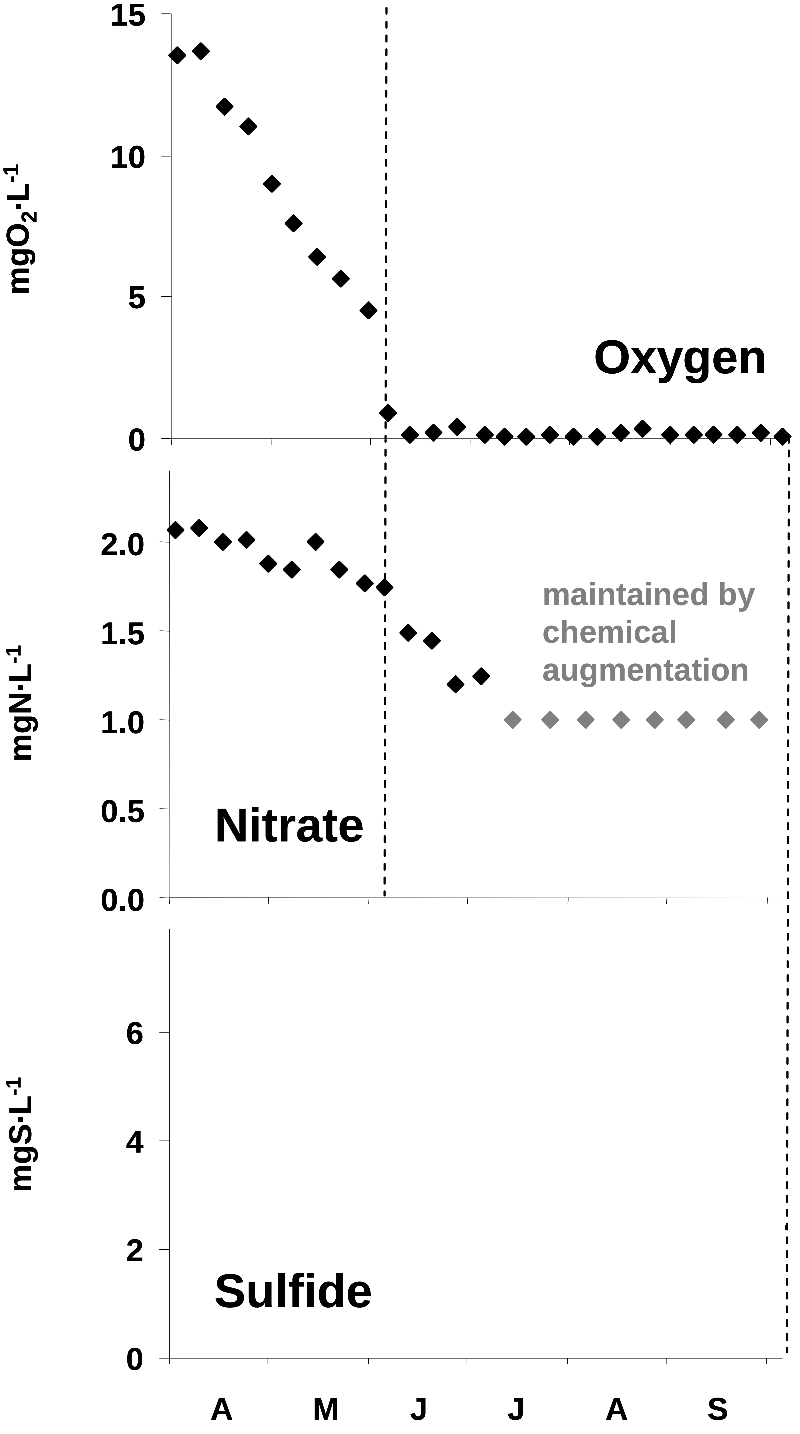


Figure B5. The relationship between model complexity, model reliability and resource availability. Given unlimited resources, all processes and coefficients may be independently derived, providing a linear relationship between complexity and reliability. More typically, resources are limited and increases in complexity may reduce model reliability at some point. The objective in developing a management model (of intermediate complexity) is to provide sufficient resources to support the requisite level of reliability.

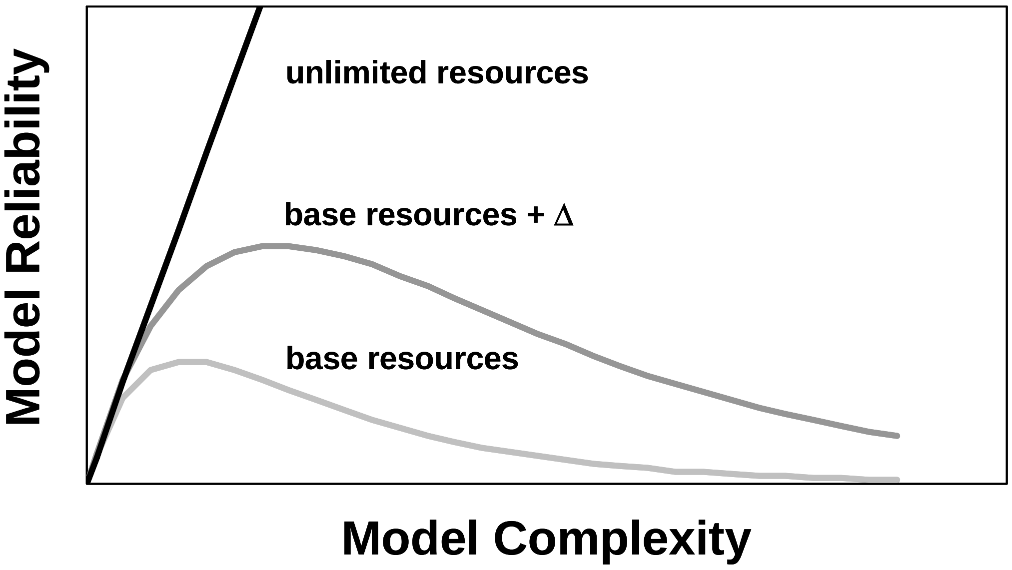


Figure B6. Model fit to field data for oxygen, nitrate and sulfide in the hypolimnion of Onondaga Lake during the thermally stratified period of 2005. The labile carbon flux yielding this plot was determined by calibration to be 0.55 gC·m^{-2}·d^{-1}.

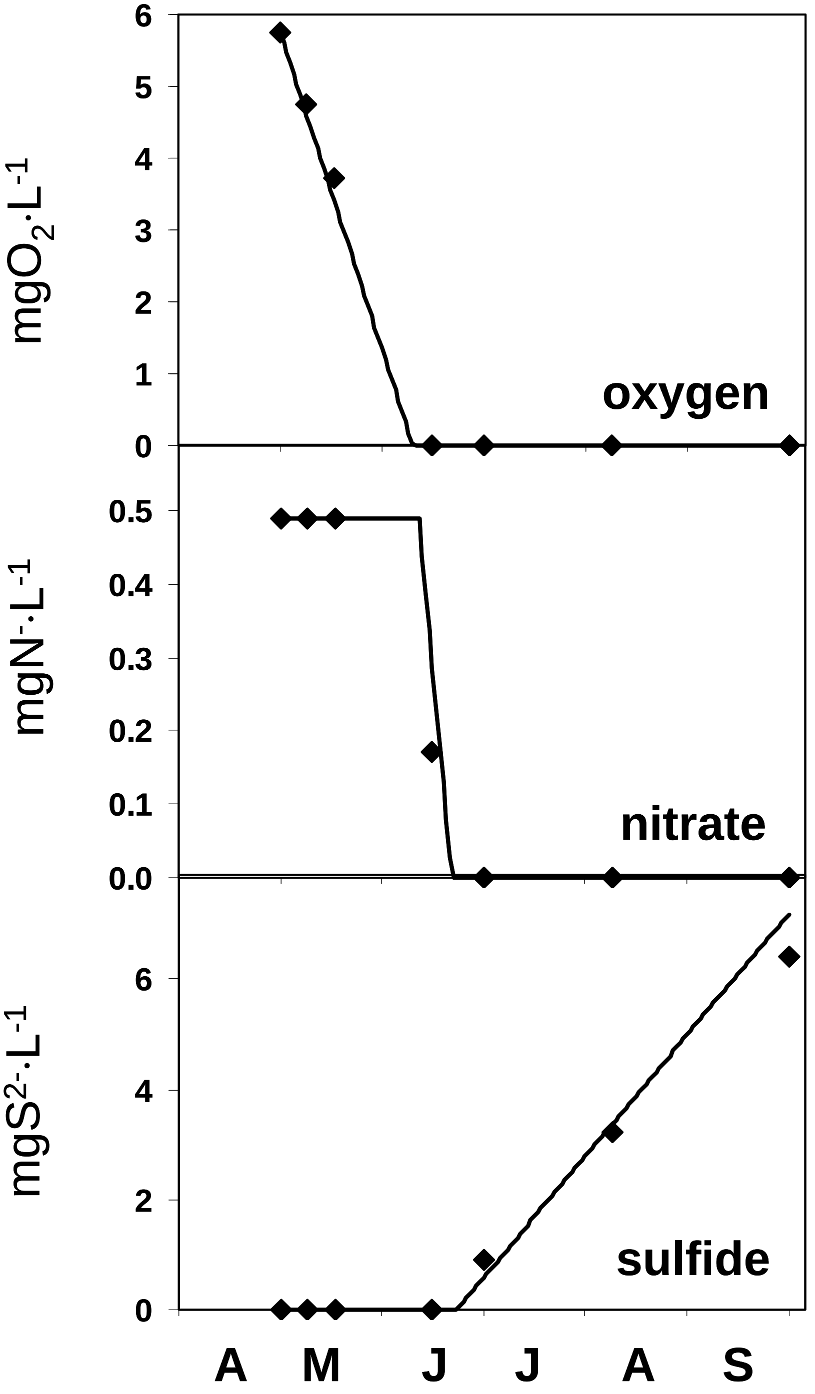


Figure B7. A comparison of the total organic carbon flux to Onondaga Lake sediments determined by model calibration with those measured directly using sediment traps in 1985 and 1988. The model calibration estimate was converted from labile to total organic carbon using a conversion factor developed by Stromquist (1996).

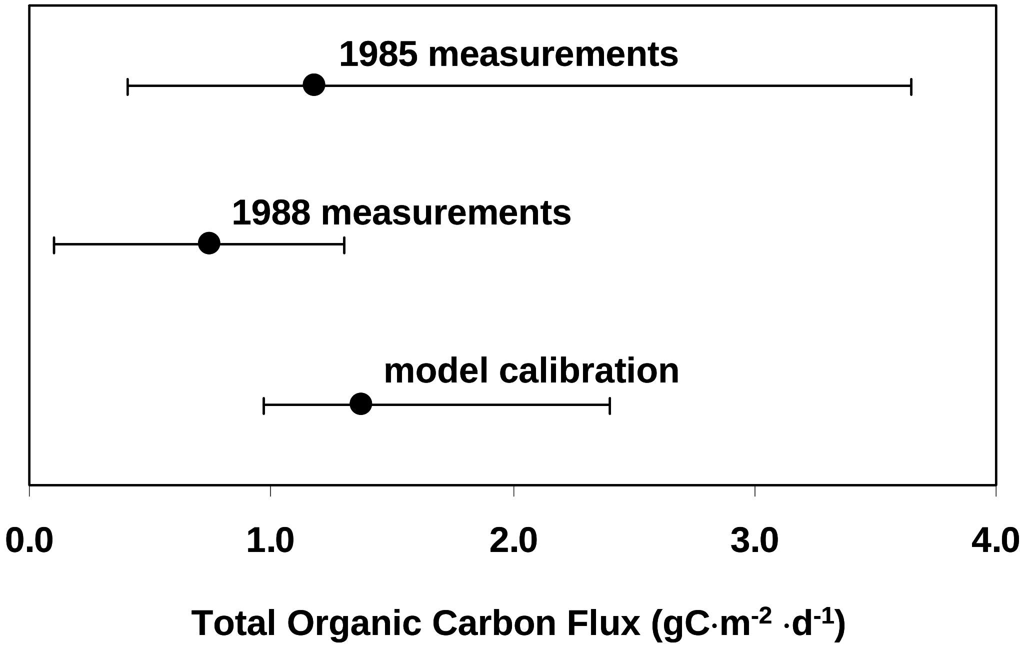


Figure B8. The results of a management simulation with 0%, X% and 2X% reductions in labile organic carbon flux to the sediment, illustrating the potential for reducing or eliminating sulfate reduction. Chemical augmentation would be required for intermediate levels of carbon flux reduction.

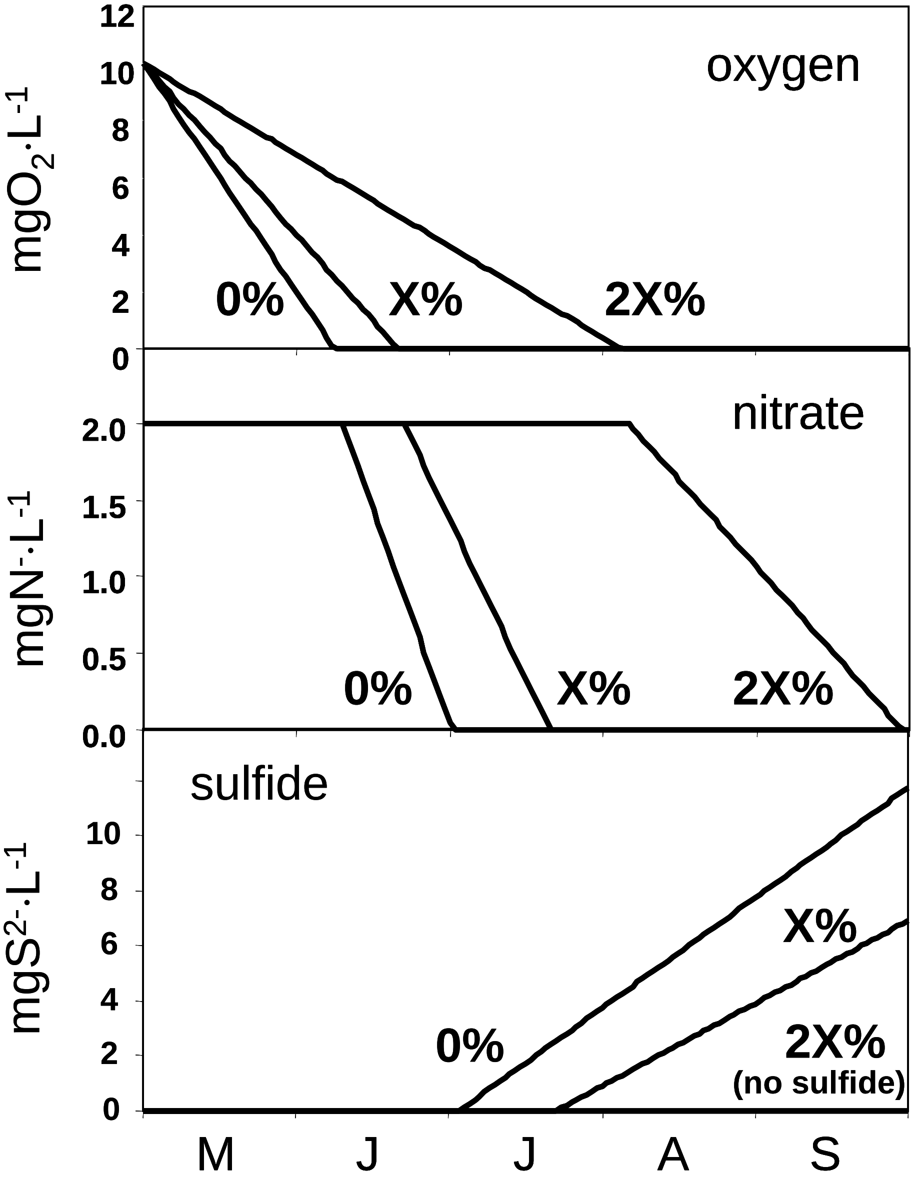


Figure B9. Vertical profiles of oxygen, nitrate and sulfide in the water column of Onondaga Lake in 2006 demonstrating the localization of redox processes in the sediment. Data provided by D.A. Matthews, Upstate Freshwater Institute.

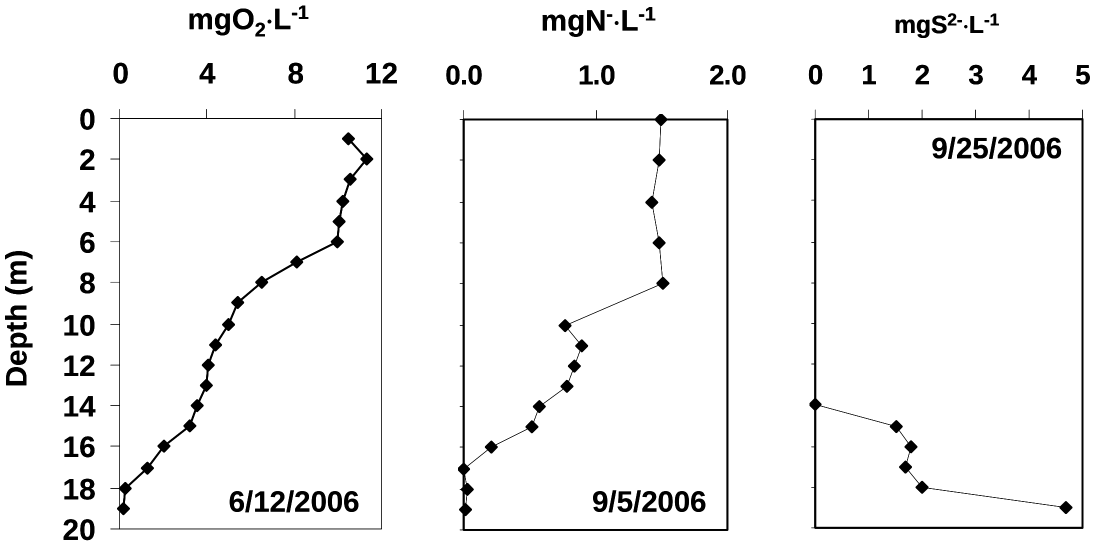


Figure B10. Idealized response of a lake to reductions in material loadings illustrating a rapid, initial response due to reaction and flushing in the water column and a slower response, retarding recovery, due to feedback from contaminated sediments.

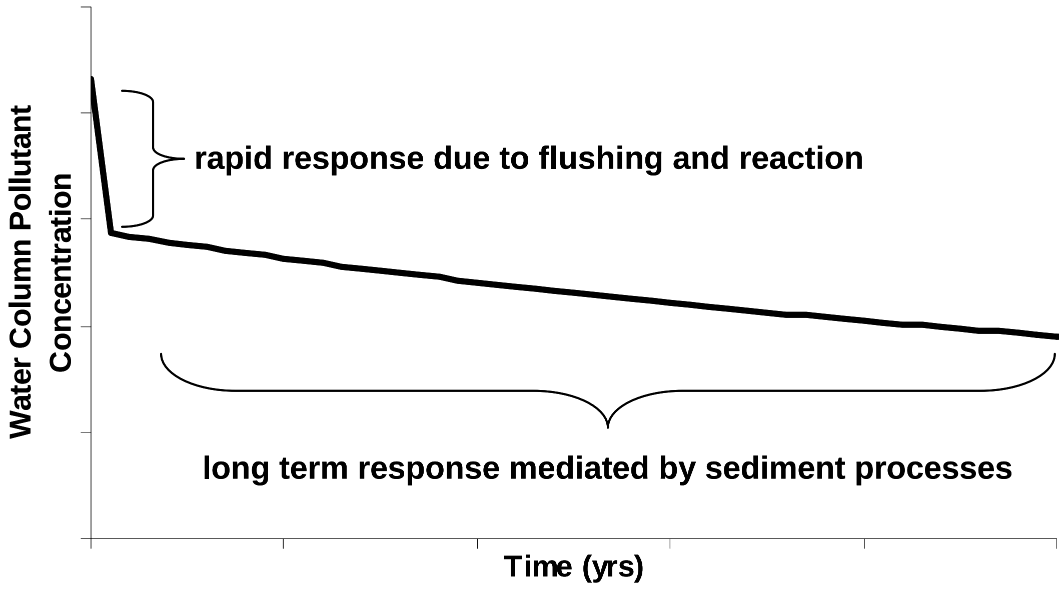


Figure B11. Concentration – depth profiles for: (a) a conservative material, (b) the particulate phase of a labile material decaying according to first order kinetics and (c) a liquid phase material produced through diagenesis.

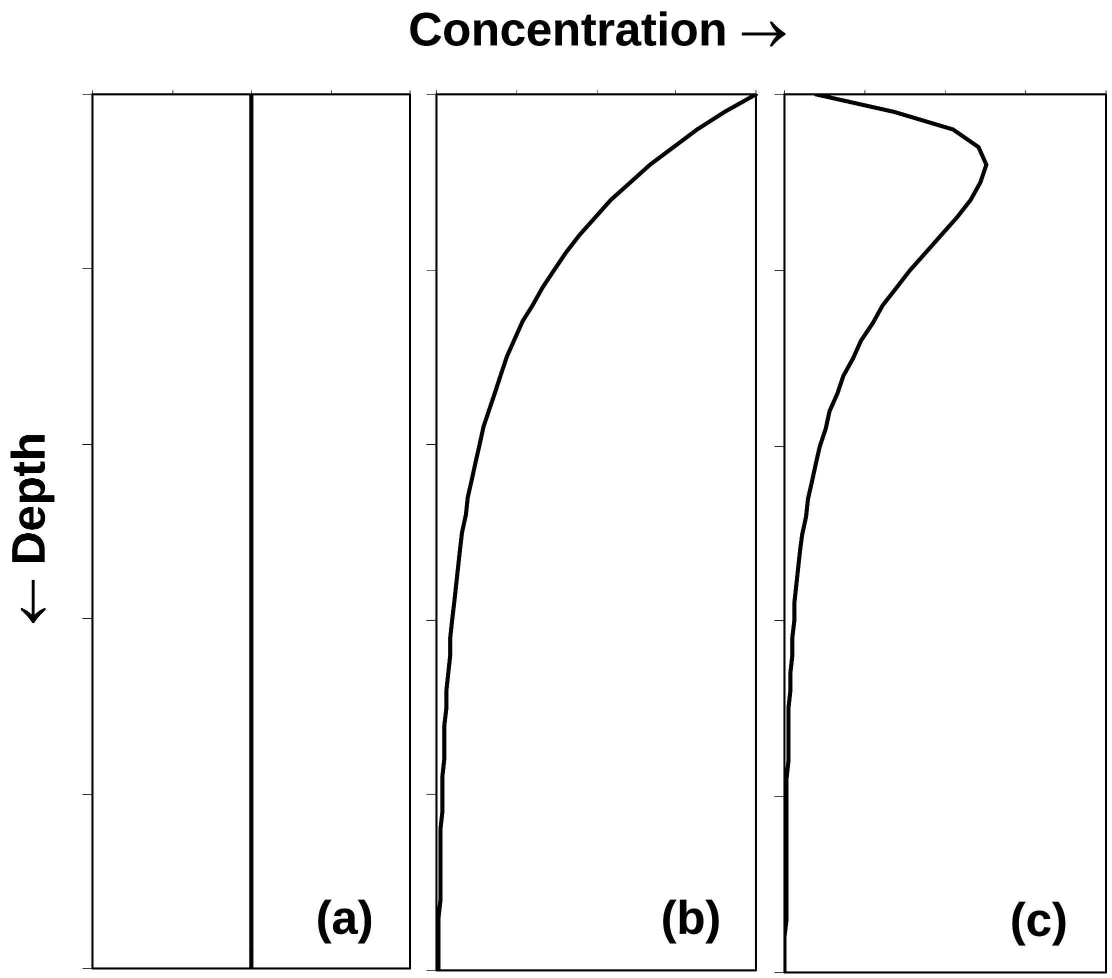
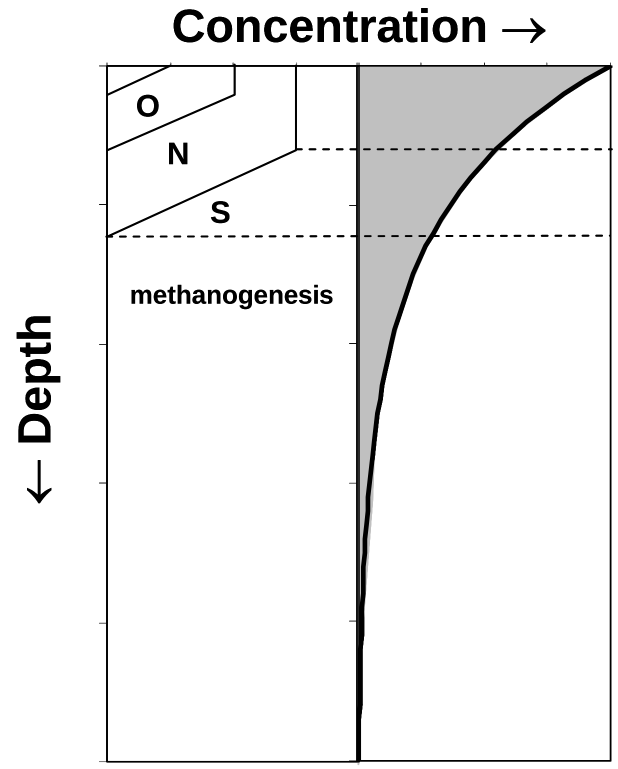


Figure B12. Profiles of labile organic carbon and electron acceptors in a sediment for (a) a high carbon flux and (b) a low carbon flux, illustrating the effect of labile carbon availability on the distribution of electron acceptors and the size of the region supporting sulfate reduction.

a. High carbon flux



b. Low carbon flux

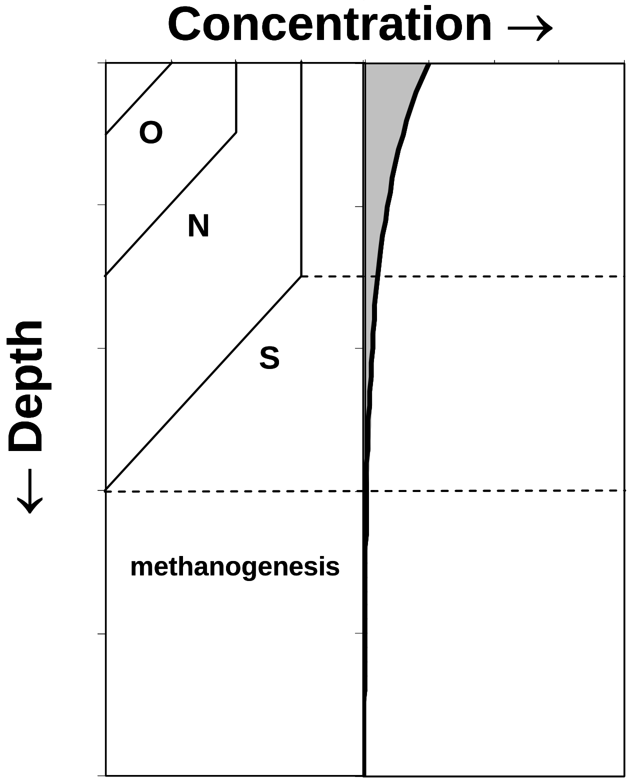
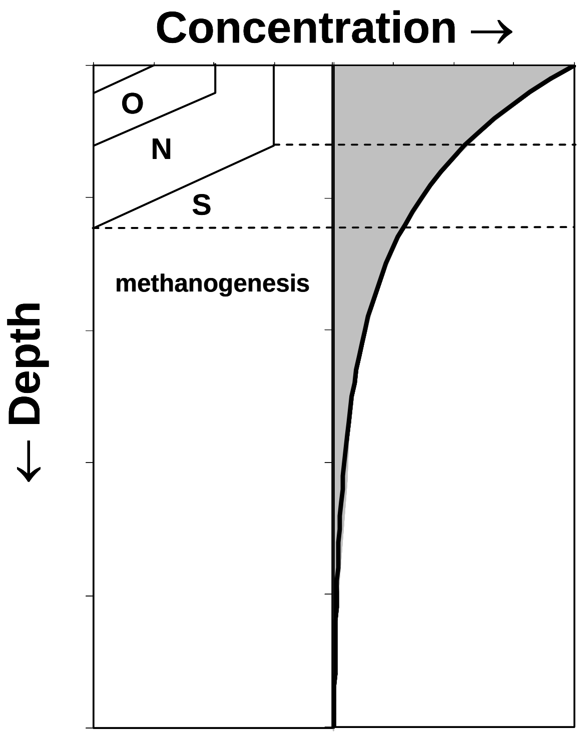


Figure B13. Concentrations of labile organic carbon and electron acceptors in a sediment for (a) ambient conditions and (b) chemical augmentation with nitrate, illustrating the effect electron acceptor availability on the distribution of electron acceptors and the size of the region supporting sulfate reduction.

a. Ambient conditions



b. With nitrate augmentation

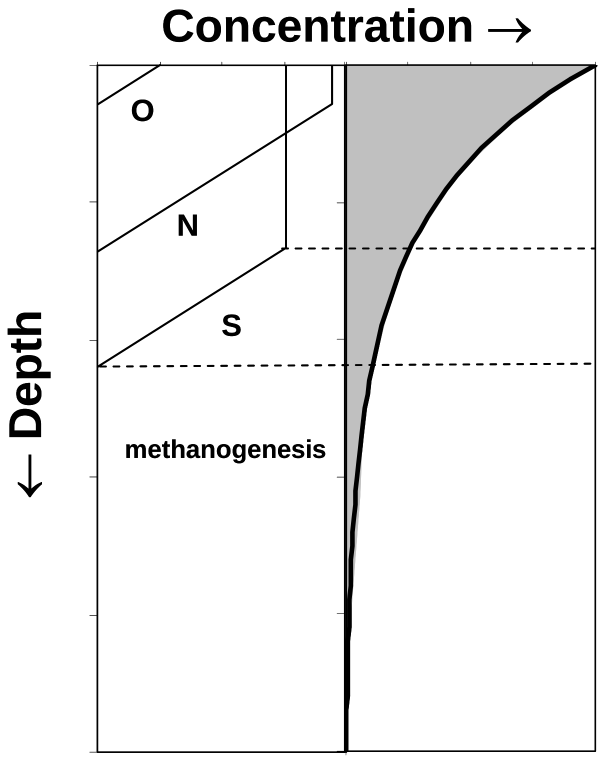
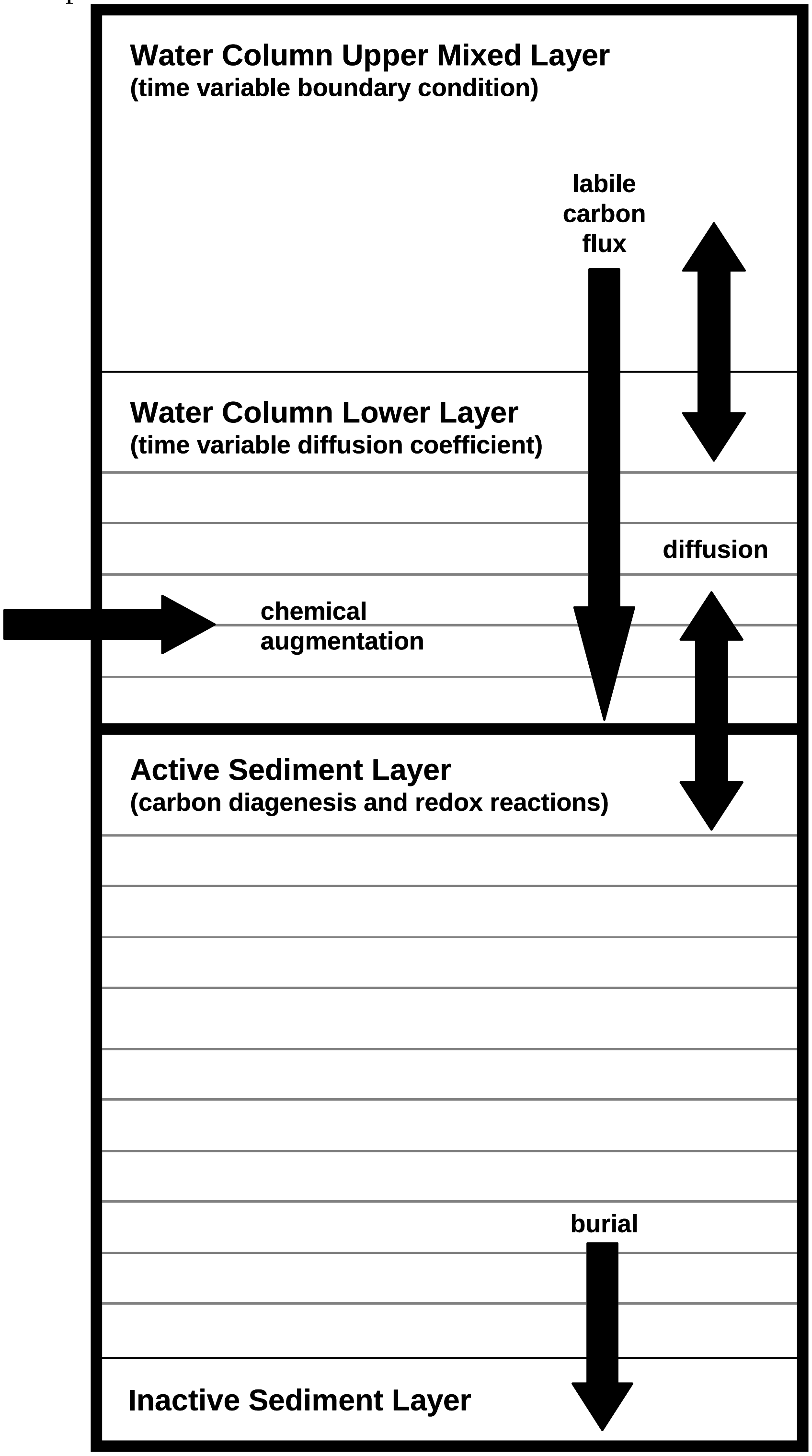


Figure B14. Framework for a linked water column – sediment model of organic carbon diagenesis and redox reactions in Onondaga Lake, illustrating model segmentation, source-sink terms and mass transport.



APPENDIX C

MAKE-UP WATER (FEED STOCK)

Make-up water is delivered to the sediment incubation chambers as a means of maintaining levels of dissolved oxygen and nitrate and, in the process, generating sample for measurement of ammonia-nitrogen, phosphorus and mercury.

Three sources/treatments of make-up water are considered:

1. Artificial lake water - ALW
2. Filtered natural lake water - FNLW
3. Unfiltered natural lake water - UNLW

The selection of a source/treatment requires consideration of features of the mercury cycle impacting the measurements, recognition of the objective of the sediment incubation study, appropriate attention to logistical concerns.

A. With respect to the CH_3Hg cycle

Five processes included in the biogeochemical cycle of mercury are germane to the design of flux measurements (Figure C1). All occur in both the sediment and the water, but under differing redox conditions. The salient reactions are:

1. Methylation (anoxic conditions)

$$Hg^{2+} \rightarrow CH_3Hg$$

Ionic mercury (Hg^{2+}) may be converted methylmercury (CH_3Hg) by microbial action. CH_3Hg formed in the sediment may be subject to demethylation there or diffuse into the water column where it is available for biotic uptake, export or demethylation.

2. Demethylation (oxic conditions)

$$CH_3Hg \rightarrow Hg^0$$

Under oxic conditions, CH_3Hg may be demethylated with an end product of elemental mercury (Hg^0). The Hg^0 so formed is lost from the system as a gas.

3. Demethylation (anoxic conditions)

$$CH_3Hg \rightarrow Hg^{2+}$$

Under anoxic conditions, CH_3Hg may be demethylated with an end product of Hg^{2+}. Hg^{2+} formed in the sediment through demethylation may once again be methylated (anoxic conditions), participate in complexation/reduction reactions or diffuse into the water column where it is available for export, methylation, complexation or reduction.

4. Reduction (oxic conditions)

$$Hg^{2+} \rightarrow Hg^{0}$$

Under oxic conditions, Hg^{2+} may be reduced photochemically or microbially to Hg^{0} with subsequent efflux to the atmosphere.

5. Complexation (oxic and anoxic conditions)

$$Hg^{2+} \rightarrow Hg^{2+}_{complex}$$

Hg^{2+} may be complexed by dissolved natural organic matter (NOM), making it unavailable for participation in methylation reactions.

It should be recognized that flux determined in sediment chamber incubations is an apparent flux, representing the net effect of the source-sink processes described above. This becomes an issue with respect to make-up water because only UNLW provides both the microbial populations and the natural organic matter necessary to support water column processes, i.e. ALW lacks both microbes and NOM and FNLW lacks microbes.

B. <u>With respect to the project objective</u>

The primary objective of this project is to identify the level(s) of nitrate and oxygen required to reduce/eliminate methylmercury production/flux in the most cost-efficient manner.

The use of ALW for make-up water has the potential to (1) underestimate that production/flux if microbe populations are insufficient to support water column methylation of Hg^{2+} originating in the sediment, (2) overestimate that production/flux if microbe populations are insufficient to support water column demethylation of CH_3Hg originating in the sediment, or (3) overestimate that production/flux because ALW lacks the NOM that would potentially complex Hg^{2+} and thus prevent methylation.

The use of FNLW eliminates the complexation issue (NOM would be present at ambient levels) but the microbial populations required to support water column methylation and demethylation would not be available unless derived from the sediment.

The use of UNLW would eliminate both the complexation and microbe issues (but note logistic concerns below).

C. <u>With respect to logistical concerns</u>

Table C1 summarizes advantages and disadvantages associated with the three make-up water sources both in regard to the science of the measurements and operational logistics.

It is noted that UNLW has been dropped from consideration due to lack of stability leading to unacceptable field sampling demands and, especially, potential problems with particle retention in the system and the release of Hg from particles at various times in the measurement.

Proposed Approach

The proposed approach evolves from a separation of the primary project objective into two parts: (1) matrix measurements to determine target electron acceptor concentrations and (2) seasonal measurements of net methylmercury flux to establish electron acceptor demand and efficacy under varying environmental conditions.

1. Matrix measurements

It is proposed ALW be used here. The objective at this point is to identify electron acceptor concentrations that will reduce or eliminate methylmercury production. The effect is intended to be manifested in both the water and the sediment and thus it does not matter if the ancillary water column processes are supported or not, i.e. shut down is shut down. Further, the use of ALW provides an unparalleled level of control (see Table C1), providing temporal consistency and fostering an accurate assessment of replicability in the measurement. Finally, this approach is logistically favorable, an important consideration with respect to the small time window available.

2. Seasonal measurements.

It is proposed that FNLW be used here. It is important that the net CH_3Hg flux determined reflect as closely as possible actual lake conditions. The smaller number of measurements (relative to the matrix objective), makes logistic concerns less burdensome.

Figure C1. Mercury Cycling

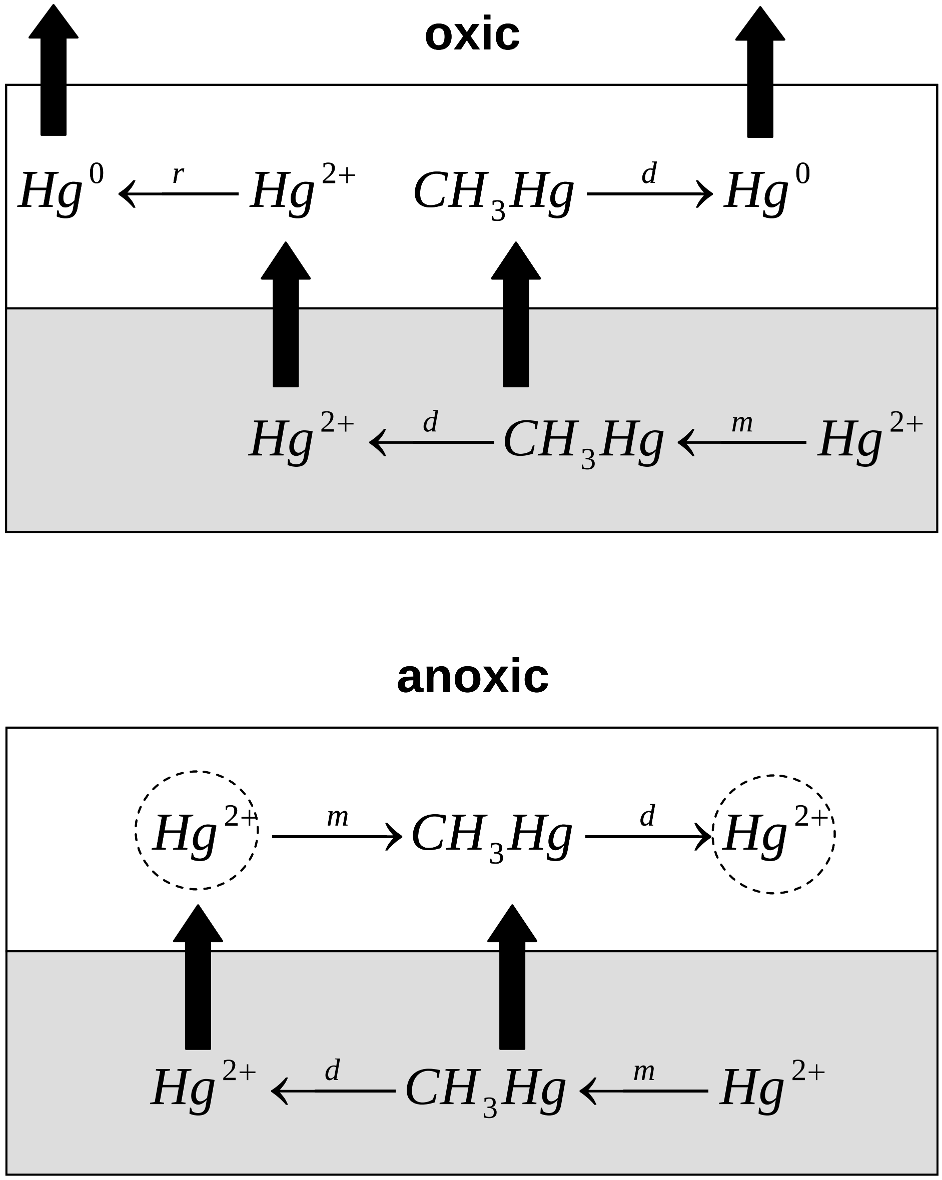


Table C1. Attributes of Various Make-up Water Sources

Characteristic	ALW	FNLW	UNLW	Comment
Field work	no	yes	yes	‘no’ minimizes logistics
Filtering	no	yes	no	‘no’ minimizes logistic, contamination concerns
Storage	no	yes	yes	‘no’ minimizes logistic, bottle effect concerns
Masking	no	yes	yes	NLW contains Hg that could mask flux
NOM	no	yes	yes	NOM can complex Hg under ambient conditions
Microorganisms	no	no	yes	Carry out methylation, demethylation, reduction
Particles	no	no	yes	Potential source of Hg leaching, contamination
Gradient	maximum	natural	natural	ALW with no Hg offers maximum diffusion gradient
Consistency	high	natural	natural	NLW matrix could change day to day

APPENDIX D

LEGACY DEPOSITS

Professor Martin T. Auer of Michigan Technological University will lead this effort.

Labile organic carbon is ‘the primary control on mercury methylation’ (Lambertsson and Nilsson 2006, p. 1822). As such, it is critical that the magnitude and lability of the labile organic carbon pool be appropriately described. The magnitude of the organic carbon flux to the sediment has been quantified through sediment trap collections made by Upstate Freshwater Institute. The demand associated with labile organic carbon reaching the sediment surface in years past (legacy deposits) will be determined through a stratigraphic analysis of sediment cores.

Determination of carbon lability is problematic, but critical to meeting project goals. It is the lability of this carbon that governs the rate of redox reactions and the attendant dynamics of electron acceptors and reduced species end products. By definition, lability must be determined through a bioassay. While it may later be related to sediment characteristics more amenable to chemical analysis (e.g. COD), it must first be examined from the perspective of the microbes that mediate the reaction. While there is no ‘standard’ method for measurement of carbon lability, researchers have typically followed the depletion of the reactant (organic carbon) or the generation of product (carbon dioxide, methane) through long term incubations. The sophisticated analytical measures and length of the incubation period required here represent potential barriers to the routine application of this approach.

Here we propose an alternative approach for determination of lability that is shorter in duration and potentially simpler analytically. A 50 cm core would be collected and sectioned into intervals of consistent length (i.e., likely one centimeter). Sediment samples from each interval would be resuspended in artificial lake water, amended with nitrate or oxygen and incubated on a rotary mixing device at 35°C for 30 days. Samples would be collected at various time intervals and the electron acceptor concentration noted. Additional electron acceptor would then be added, maintaining levels sufficient to support aerobic respiration or denitrification, and the container would be returned to the incubator. Over time, as labile organic carbon is consumed, the rate of consumption of electron acceptor would decrease and eventually reach an asymptote (see Figure D1 for an example illustration).

The mass of electron acceptor utilized, adjusted for the stoichiometry of the reaction, would provide an estimate of the labile organic carbon content of the sample. This value, when divided by the total organic carbon content of the sample, establishes the fraction of the organic carbon that is present in the labile form. By integrating the labile organic content over the length of the core, the magnitude of legacy deposits may be determined. Similar experiments, conducted with incubations at ambient sediment temperatures, can supply rates constants for carbon diagenesis with freshly deposited (highly labile) and legacy (less labile) carbon.

Figure D1. Results from preliminary carbon lability bioassay, illustrating the rate of consumption of nitrate in laboratory incubations.