SECTION 5

CONCLUSIONS

This report documents the results of sediment incubations and other studies undertaken to assist in the evaluation of nitrate addition and oxygenation as required in the Record of Decision for the Onondaga Lake Bottom Subsite and the Statement of Work appended to the Consent Decree. The objectives of the work were to establish the efficacy of oxygen and nitrate addition in blocking methylmercury production, the quantities of nitrate and oxygen required to meet sediment demand, and the interplay between conditions in the water column and sediment dynamics.

5.1 METHYLmercury Flux FROM THE Sediments OF Onondaga Lake, New York as Determined Using Flow-Through Sediment Microcosms

Three experimental treatments, roughly corresponding to the sequential depletion of electron acceptors of Onondaga Lake, were examined: high oxygen – high nitrate, low oxygen plus nitrate and no oxygen – no nitrate. The development of porewater profiles for oxygen, nitrate, sulfide and methylmercury supported the theory of depletion of electron acceptors with depth in the sediment following the pattern oxygen $\rightarrow$ nitrate $\rightarrow$ sulfate. Below the zone of sulfate reduction, methanogenesis would be the operative process for organic carbon diagenesis.

The profiles for methylmercury and total sulfide support the hypothesis of co-occurring production within the sulfate reduction zone. The distributions of oxygen and nitrate were consistent with the operating hypothesis that methylmercury produced within the layer of sulfate reduction is sorbed or demethylated within the oxygen and nitrate bands near the sediment surface.

Baseline methylmercury flux from Onondaga Lake sediments to overlying water were estimated using three techniques: hypolimnetic accumulation, porewater gradient calculation and microcosm measurement. The results did not differ significantly from one another. Experiments conducted with zero nitrate and oxygen concentrations ranging from 0.2 – 12.2 mgO₂·L⁻¹ indicated a 92 percent reduction in methylmercury flux from the baseline (no oxygen – no nitrate) condition. There was no trend in flux with increasing oxygen levels, suggesting that the simple maintenance of an aerobic environment is sufficient to control methylmercury flux.

Experiments were conducted with zero oxygen and nitrate concentrations of 0.3 and 1.0 mgN·L⁻¹ indicated a 65 percent reduction in methylmercury flux from the baseline (no oxygen – no nitrate) condition. As with the case for oxygen amendment, there was no apparent benefit from the maintenance of increasing nitrate concentrations.

The results of the sediment incubation studies support the concept of oxygen and/or nitrate addition to the hypolimnion of Onondaga Lake to control methylmercury accumulation in the hypolimnion. These results, however, will need to be interpreted in conjunction with water column observations from the ongoing baseline monitoring program as well as results from the nitrate application field trial being conducted during 2009.
5.2 THE FATE OF MERCURY AND NITROGEN IN THE WATER AND SEDIMENTS OF ONONDAGA LAKE

This study provided information on the fate of mercury and nitrogen in the surficial sediments of Onondaga Lake under three different oxidation-reduction regimes: oxic, anoxic, and anaerobic. Methylmercury was produced in the zone of sulfate reduction, as evidenced by maximum porewater methylmercury concentrations and percent mercury as methylmercury in this region. In the oxic treatment, the sulfate reduction zone was below the nitrate reduction zone which was at 0 to 2 cm (0 to 0.8 inch) sediment depth. Under anoxic conditions, when nitrate was still present in overlying water, the nitrate reduction zone occupied the 0 to 1 cm (0 to 0.4 inch) sediment depth interval while both the maximum methylmercury concentrations and the maximum percent mercury as methylmercury were observed between 1 and 2 cm depth, in the zone of sulfate reduction.

Anaerobic conditions (i.e., conditions without oxygen or nitrate) in the overlying water promoted the extension of the sulfate reduction zone to the sediment-water interface and into overlying water. Under these conditions, the average concentration of methylmercury in overlying water was approximately a factor of 10 greater than under oxic and anoxic conditions. Almost 50 percent of mercury was methylmercury in overlying water in the anaerobic treatment compared to nine and five percent, respectively, in the oxic and anoxic treatments. Unlike overlying water, the average methylmercury concentrations in porewater in the anaerobic treatments were not statistically different from the average concentrations observed in the oxic and anoxic treatments.

Regarding the fate of nitrogen in the lake, most nitrate reduction was in the form of complete denitrification to nitrogen gas, with no trend towards increased nitrous oxide or ammonium production even at ten times ambient nitrate concentrations.

5.3 MICROBIOLOGICAL ANALYSES OF SMU 8 SEDIMENT

The microbiological analyses in SMU 8 sediment support the observations made during the sediment incubations and the mercury and nitrogen fate studies. During stratification when the hypolimnion was anaerobic and nitrate was still present in water overlying the sediment, denitrifiers predominated in surface sediments indicating active nitrate reduction occurring in this zone. When nitrate was depleted, iron/sulfate reducers increased in abundance in surface sediment. Methanogens were most abundant when redox potential was low, following oxygen and nitrate depletion. There appears to be a lag time of at least several weeks before sediment re-equilibrates with oxic conditions in overlying water.
APPENDIX A

TESTING AND CALIBRATION OF TURBULENCE LEVELS WITHIN A SEDIMENT OXYGEN DEMAND CHAMBER

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Testing and Calibration of Turbulence Levels within a Sediment Oxygen Demand Chamber

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Abstract

Turbulence at the sediment-water interface can significantly alter the flux of oxygen or other scalars by sharpening gradients in the concentration boundary layer. Prior work examining sediment oxygen demand (SOD) in the hypolimnion of a reservoir in California (Beaulé et al., 2007) demonstrated this effect in the laboratory but did not provide any quantitative data on the turbulent intensity of the turbulence. Importantly, the applied turbulence field came from a simple Gaussian random field, a turbulence model which was not calibrated to levels typically found in the reservoir bottom boundary layer (BBB). Simple jets are known to produce strong mean flows that may contribute to, or even dominate, the sediment-water interface exchange. To reproduce calibrated turbulence in a typical laboratory SOD chamber, the randomly actuated cycle of the BBB was adapted to a provided SOD chamber. Turbulence is generated by randomly changing the direction of three periodic pumps, with the between-time changes selected from a Gaussian distribution with user controllable mean and standard deviation. Particle Image Velocimetry (PIV) is used to measure the mean and turbulent velocities in the chamber and calibrate pump rotation rate to turbulence intensity. A more thorough investigation of the turbulence structure details some major shortcomings of the order system, particularly at low target turbulence levels, primarily due to the limited number of degrees of freedom. Despite these shortcomings, the turbulence generation system is capable of producing the range of expected turbulence levels in the Chorntit Lake and provides a necessary and important tool for the investigation of transport processes at the sediment-water interface.

Chamber Design and Control

The turbulent SOD chamber tested is constructed of six inch outer diameter acrylic pipe with acrylic top and bottom plates to allow excellent optical access. An array of six ports is spaced symmetrically on the top plate around the chamber center, approximately 5 cm from the center, 5 cm from nearest neighbors, and 2.5 cm from the outer wall (Figure 1). Three periodic pumps (MasterFlex Model 7526-70) are plumbed to the chamber using flexible Tygon tubing, with the ends attached to opposing ports on the chamber top plate. Using the Sunburst algorithm detailed in Variano and Cowen (2008), the pump direction is changed randomly, with the time between direction changes selected from a Gaussian distribution with user controllable mean and standard deviation. Each pump is set to the same rotation rate as a means of controlling the turbulence intensity. The pump control software permits the inclusion of a flushing cycle during which the pumps do not change direction for a specified amount of time, with the flushing cycle occurring at a user specified interval. For the present case, this was prescribed by the end-user group at Michigan Technological University for two minutes of randomization and one minute of flushing.

Basic Results - A Calibration Curve

After processing, vertical profiles of RMS turbulent intensities were plotted against elevation where an assumption of homogeneity was invoked and the statistics are averaged in time and space. Variano and Cowen (2008) discuss three regions in their facility, a jet merging region, a homogenous region, and a surface overflow influenced region. There are similar regions in the SOD chamber (Figure 5) particularly at the 50 and 75 RPM pump speeds, where there is a constant turbulence intensity region lying between z = 30 and 40 cm and thewall influenced region occurring for z < 30 cm. The mean value of u'rms ∼ 10 – 20 mm/s is used for the initial calibration presented here.

Figure 2: An example instantaneous velocity field determined by the PIV algorithm. Note the small eddies in the bottom left corner of the image.

Velocity Data Collection and Analysis

Velocity data are collected using Particle Image Velocimetry (PIV). PIV provides two velocity components, a radial and vertical velocity, on a 2-D plane located on a diameter of the chamber. Image acquisition, system timing, and pump control were all controlled through the Mathworks MATLAB Data Acquisition Toolbox. Image pairs were processed using custom code based on cross-correlation of images Cowen and Merriman, 1987 and including the anti-aliasing spatial continuous window technique of Lien and Cowen (2005) on a 32 x 32 pixel grid, resulting in ∼250 velocity points in the chamber for each image pair. Because of the periodic nature of the flushing and randomization cycle of the pumps, a single phase decomposition was performed to the velocity time series, where the randomization and flushing portions were treated separately for averaging and turbulent decomposition. (u', v') = (u, v) + (u', v'), where u, v is the measured velocity, u', v' is the phase dependent random or flushing time averaged velocity and u'' and v'' represents the fluctuation from the mean. The turbulence intensities are represented as root-mean-square (RMS) values of the fluctuations and all velocities are reported in mm/s.

Figure 3: The chamber was placed in a small fish tank to correct distortion caused by the curved walls. The camera is being scanned from left to right in ∼ 6 ms. The camera can be seen in the background, with the imaging plane parallel to the light sheet.

Figure 5: z' = u'rms velocity profiles averaged horizontally in space and temporally as a function of elevation in the chamber for 6, 10, 50 and 75 RPM (top left to bottom right). Black lines are for the randomized portions of the cycle, red lines for the flushing portion of the cycle.

Turbulence Verification

Temporal spectra are calculated at each interrogation point using the fluctuating velocities (n ≥ 3 subintervals), then spatially averaged at each elevation across the chamber. These spectra provides information on the lower frequency motions in the chamber. At low RPM, these spectra show energy peaks at 120, 180, and 360 Hz and higher frequencies, which is the spectral signature of a wave-like behavior (Figure 6). We believe these low frequency rates the system is responding to a transition between periodic and one unidirectional. Looking at the spectra the flow is not turbulent at modest to higher frequencies nor at any wavenumber (Figure 7).

Spatial spectra are calculated for each data set at vertical levels and averaged in time (Figure 8). Spatial spectra provide information on the high frequency motions in the tank. Here the spectra are much steeper due to the increased availability of temporal data for averaging. While the 6 and 10 RPM spectra appear to show some, only the energy level is decades lower than the 50 and 75 RPM case suggesting that this is not turbulence capable of stirring. At higher RPM a clear inertial band rolls off into the dissipative range is present.

Figure 6: z' = u'rms, a ratio of the mean and turbulent energy in the tank, versus pump speed. This value is computed by averaging spatially over z = 50 – 100 cm and all u using temporally averaged mean flow values and the RMS fluctuations. At higher pump speeds this ratio stabilizes but is still high. The outlier for the randomized data at 10 RPM is due to the persistence of the individual jet forcing and its bias mean of the to higher values.

Figure 7: Spatial spectra at 6, 10, 50 and 75 RPM (top left to bottom right). The solid black line has a slope of -5/3, indicative of the inertial subrange. At higher RPM, the flow is turbulent and a roll off into the dissipative range is present.

References

APPENDIX B

ELECTRON ACCEPTOR ADDITION AND THE REGULATION OF AMMONIA AND PHOSPHORUS FLUX
APPENDIX B

ELECTION ACCEPTOR ADDITION AND THE
REGULATION OF AMMONIA AND PHOSPHORUS
FLUX

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Electron Acceptor Addition and the Regulation of Ammonia and Phosphorus Flux
From The Sediments of Onondaga Lake, New York

Addendum to Data Report: Sediment Incubations and Supporting Studies for Onondaga
Lake Sediment Management Unit (SMU) 8

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SECTION 1

SUMMARY AND CONCLUSIONS

A series of intact sediment core incubations were performed using flow-through sediment flux chambers to evaluate the efficacy of electron acceptor augmentation with oxygen and nitrate on the release of ammonia and phosphorus from Onondaga Lake sediments. Electron acceptor concentrations were maintained at the levels (2 mg nitrate-nitrogen (NO₃-N) per liter and 2 mg of oxygen (O₂) per liter) used in companion studies of methylmercury release (Exponent et al., 2009). Neither electron acceptor had a significant impact on ammonia flux, with the observed fluxes being comparable to those for unamended control incubation. Oxygen likely did not have an effect because levels were too low to support active populations of nitrifying bacteria, the primary mechanism for eliminating ammonia flux. There is no known mechanism for inhibition of ammonia flux by augmentation with nitrate. Both electron acceptors were effective in inhibiting phosphorus flux, yielding negligible rates of release. The mechanism here, in both cases, is believed to be related to mediation of redox levels and the attendant response of the ferrous-ferric iron system. Phosphorus release was initiated following cessation of electron acceptor augmentation, reaching or approaching flux levels observed in the unamended control incubation. This demonstrates that the cores in which inhibition was observed displayed the potential to yield unrestricted release of phosphorus. It is concluded that, when oxygen and nitrate levels both decline to near zero, electron acceptor amendment with either nitrate (at 2 mg NO₃-N per liter) or oxygen (at 2 mg O₂ per liter) will effectively inhibit phosphorus release. Neither amendment would be expected to impact ammonia release.
SECTION 2

ELECTRON ACCEPTOR AMENDMENT AND THE REGULATION OF CHEMICAL FLUX

The addition of electron acceptors (nitrate and/or oxygen) to the hypolimnion of lakes has been identified as a means of controlling the flux of methylmercury as needed from the sediments of mercury-contaminated Onondaga Lake. Methylmercury is produced in the sediment at locations supporting active microbial sulfate reduction. The operative principle for controlling methylmercury flux from sediment to overlying water is to maintain the presence of sediment microlayers rich in nitrate or oxygen where the biogeochemical processes (e.g. demethylation and sorption) inhibiting transport of methylmercury to the sediment-water interface are favored. Several of the biogeochemical processes associated with organic carbon diagenesis are influenced by redox conditions and it is thus reasonable to expect that fluxes other than methylmercury, e.g. ammonia and phosphorus, may be influenced by maintaining electron acceptor levels through amendment. The purpose of this report addendum is to quantify effects of electron acceptor addition on ammonia flux and phosphorus flux from the sediment when oxygen and nitrate levels in overlying hypolimnetic waters approach zero. Work reported herein is part of the sediment incubation work conducted for Honeywell by Michigan Technological University, Upstate Freshwater Institute, and Syracuse University in accordance with a work plan approved by the New York State Department of Environmental Conservation (Parsons et al., 2007) and as part of pre-design work for the Onondaga Lake Bottom remediation effort.
SECTION 3

THE BIOGEOCHEMICAL BASIS FOR REGULATION OF AMMONIA AND PHOSPHORUS FLUX

Although both ammonia and phosphorus fluxes are potentially impacted by redox conditions, the underlying biogeochemistry differs considerably for the two processes. Ammonia is introduced to the sediment pore water through the diagenesis of particulate organic nitrogen (PON) reaching the lake bottom through sedimentation. In highly productive systems such as Onondaga Lake, most of the PON deposited at the sediment-water interface is in the form of detrital algae. Concentrations of ammonia are typically higher at depth within the sediment than at the sediment-water interface where mixing with hypolimnetic waters reduces ammonia levels. The result is a concentration gradient which promotes ammonia diffusion from the sediment to the water, i.e. an ammonia flux (see Wickman, 1996). When the sediment surface microlayer contains oxygen concentrations sufficient to support nitrifying bacteria, the ammonia diffusing to the surface is converted to nitrite and then nitrate (nitrification) which may subsequently participate in reactions within the microlayer or diffuse from the sediments (Pauer and Auer 2000). In the absence of an oxic surface microlayer, nitrifying bacteria are absent and the ammonia simply diffuses across the sediment-water interface and accumulates within the hypolimnion. Ammonia in the water column is a nutrient supporting algal growth, can be toxic to aquatic life and, when oxidized, consumes oxygen. Thus management of ammonia and its release from the sediments is often an objective of water quality restoration efforts.

In contrast to the microbially-mediated case of ammonia, the flux of phosphorus across the sediment-water interface is chemically controlled through the interplay of redox conditions and iron chemistry. The mobility of phosphorus in lake sediments is governed by the presence of hydrous iron oxides possessing solid surfaces that adsorb phosphorus (Penn et al., 2000). The environmental chemistry of these oxides is such that their formation is greatly favored under oxidizing redox conditions where ferric (Fe$^{3+}$) iron predominates. Oxide formation is not favored under reducing conditions where ferrous (Fe$^{2+}$) is dominant and, as a result, soluble phosphorus accumulates in the porewater. Phosphorus and ferrous iron gradients developing in the porewater support a flux of these chemical species across the sediment-water interface (i.e., from sediment to overlying water). The redox conditions, through the ferric-ferrous iron couple, serve as a gatekeeper for phosphorus flux from the sediments. Internal loads of phosphorus, generated in this manner, have been known to retard efforts to restore lakes impacted by eutrophication.

Given the biogeochemical foundation of ammonia and phosphorus fluxes, i.e. their association with redox conditions, it is reasonable to suggest that their flux across the sediment-water interface may be amenable to control through electron acceptor augmentation.
SECTION 4

TASK SPECIFIC OBJECTIVES AND APPROACH

The objective of this work is to evaluate the utility of electron acceptor augmentation, at the levels required to achieve the desired effect on methylmercury flux, in controlling the flux of ammonia and phosphorus across the sediment-water interface. This work was accomplished using bench-scale sediment microcosms. Specifically, the objective was to:

- Quantify the flux of ammonia and phosphorus from the sediments of Onondaga Lake under conditions of electron acceptor augmentation (2 mg O₂ per liter, 2 mg NO₃-N per liter) for control of methylmercury flux and to compare those fluxes with the rates characteristic of an un-augmented environment (0 mg O₂ per liter, 0 mg NO₃-N per liter).

This objective was accomplished through a continuous, long-term incubation simulating in-lake conditions where electron acceptors are sequentially maintained: (a) in abundance, (b) at augmentation levels and (c) in the depleted state.
SECTION 5

METHODS AND MATERIALS

Sediments were collected from the South Deep depositional basin of Onondaga Lake in May 2009 with a box corer (Model 1260, Ocean Instruments, Inc., San Diego, CA). The South Deep basin (maximum depth, 19 meters or 62 feet) is considered to be representative of conditions in the remainder of the lake’s profundal zone (Effler, 1996) and was the site for collections supporting previous studies of ammonia (Wickman, 1996) and phosphorus (Auer et al., 1993; Penn et al. 2000) flux. Teflon containers (10 centimeters (4 inches) in diameter by 30 cm (12 inches) tall; Savillex Corporation) were used to subsample the box core, yielding approximately 7 centimeters (3 inches) of hypolimnetic water over 12 centimeters (5 inches) of sediment. Upon collection, sediment samples were placed in an ice chest and transported to the laboratory for storage at 4 °C until used. Particular care was taken to minimize disturbing the sediment-water interface during box coring and transportation to the laboratory.

A microcosm approach to laboratory determination of flux across the sediment-water interface using a completely-mixed flow reactor was applied here as described in Parsons et al. (2007). The sediment microcosm consisted of a cylindrical Teflon container, 10 cm (4 inches) in diameter by 30 cm (12 inches) tall, outfitted with opposing inlet-outlet ports located approximately 2 centimeters (1 inch) below the top rim (Figure B.1). The microcosm was filled with 7 centimeters (3 inches) of hypolimnetic water over 12 centimeters (5 inches) of sediment, leaving approximately 11 centimeters (4 inches) of headspace. A friction fit TeflonR bottom provides a seal against leakage following sample collection. A threaded Teflon top is outfitted with six peripheral ports to provide mixing and a single, central port where gas may be introduced.

Artificial lake water (ALW), with an ionic composition similar to that of Onondaga Lake (Exponent et al., 2009), served as feed stock to the reactor with the rate of input regulated by a peristaltic pump. In its unamended state, the artificial lake water does not contain ammonia, nitrate or phosphorus, and gases are at levels dictated by the ambient environment. The impact of nitrate on chemical flux was examined by adding nitrate to the feed stock and then adjusting the feed stock flow rate until the desired nitrate concentration was achieved. Gas was bubbled into the microcosm as a means of regulating redox conditions. Air (for oxygen saturation), a mixed gas (nitrogen gas with 5 percent hydrogen and 1,600 parts per million (ppm) carbon dioxide; for anoxic conditions) or an air-mixed gas combination (to establish 2 mg O2 per liter; digital gas mixer Mix 1000 model, Applied Analytics, Inc.) were utilized depending on the desired condition. Mixing in the microcosm was provided by three re-circulating channels (Teflon tubes; six ports) attached to a computer-controlled peristaltic pump. The pump was set at a re-circulating rate that provided random mixing at a turbulence level comparable to that observed at the sediment-water interface of Onondaga Lake (Exponent et al., 2009, Appendix A). All experiments were conducted in a temperature-controlled room or incubator maintained at 8°C, a representative hypolimnetic temperature for Onondaga Lake. Ammonia and phosphorus flux
were determined in three single incubations: (a) in the absence of nitrate and oxygen, (b) with nitrate only added and (c) with oxygen only added. Where experimental conditions required the absence of oxygen, experiments were conducted in an anaerobic chamber (mixed gas; Coy Laboratory Products). The maintenance of anoxic conditions within the chamber was confirmed through daily monitoring.

The theory of microcosm operation establishes that chemical flux may be calculated once the system has reached steady state, i.e. chemical conditions in the effluent stream are unchanged with respect to time. The achievement of steady-state conditions was established by monitoring of nitrate (Thermo Fisher Scientific Inc., Model 9707BNWP Ionplus® Nitrate Combination Electrode) and oxygen (Hach Model LBOD 10101 luminescent dissolved oxygen probe) in the chamber effluent. Once effluent conditions indicated steady state condition, effluent samples were collected daily for five days and composited. Subsamples were collected and filtered (0.45 micron disc filter, Vipor Inc.) daily, placed in glass (phosphorus) or plastic (ammonia) vials and stored temporarily at 4ºC. Daily subsamples collected over a 5-day interval were composited to yield a weekly sample and frozen prior to shipment to Upstate Freshwater Institute for analysis (ammonia by U.S. EPA, Method 350.1 Rev. 2.0, O’Dell 1993 and phosphorus by Standard Methods, 20th Edition, Method 4500-PE, APHA 1998).

Chemical fluxes are calculated by assuming that the sediment microcosm is a completely-mixed flow reactor. The mass balance on that reactor may be given as,

\[ V \cdot \frac{dC}{dt} = Q \cdot C_{in} - Q \cdot C + J \cdot A \]  

where:
- \( V \) = microcosm volume, m³
- \( Q \) = feed stock flow rate, m³·d⁻¹
- \( C \) = microcosm ammonia-nitrogen (NH₃-N) or phosphorus (P) concentration, mg per cubic meter
- \( C_{in} \) = influent NH₃-N or P concentration, mg·per cubic meter
- \( J \) = NH₃-N or P flux, mg·per square meter per day
- \( A \) = area of the sediment surface, square meters

Given that the ammonia and phosphorus concentrations in the influent (i.e., the artificial lake water) are zero and that, at steady-state, \( dC/dt = 0 \), Equation 1 becomes,

\[ J = QC_{ss} / A \]  

Thus, at steady state, the ammonia or phosphorus flux may be calculated as a function of the flow, the steady state effluent ammonia or phosphorus concentration (Cₘₐₓ) and the sediment surface area of the reactor.
SECTION 6

RESULTS AND DISCUSSION

6.1 BASELINE CONDITIONS – NO NITRATE OR OXYGEN ADDED

The reactor not receiving electron acceptor augmentation, colloquially termed the ‘nono’ condition provides a baseline with which to compare the efficacy of nitrate and oxygen addition in reducing ammonia and phosphorus flux. The baseline condition simulates the interval of anaerobic conditions in the hypolimnion anoxia of the lake, i.e. where both oxygen and nitrate have been depleted and ammonia and phosphorus diffuse readily from the sediment. The sediment flux chamber used for the baseline condition was incubated in the anaerobic chamber and fed with artificial lake water containing neither nitrate nor oxygen. Concentrations of nitrate and oxygen in this chamber dropped rapidly over a 30-day equilibration period approaching the limit of detection well before flux sampling commenced. Once strongly reducing conditions were established, interferences prevented additional nitrate monitoring. However, given knowledge that nitrate had been depleted from this reactor and that no nitrate was added over the course of the experiment, it is reasonable to conclude that the system remained nitrate-free. Oxygen concentrations remained at zero mg O$_2$ per liter over the course of the incubation (Figure B.2a). Flows were reasonably constant (0.4 to 0.5 liter per day) over the course of the incubation (Figure B.2a).

The baseline ammonia and phosphorus fluxes, averaged over the 7 weeks of incubation (Figures B.2b and B.2c), were 18.0±3.0 mg NH$_3$-N per square meter per day and 5.2±1.6 mg P per square meter per day, respectively. As points of reference, these fluxes are significantly less than those measured for Onondaga Lake sediments by Wickman (1996; 78.0 mg NH$_3$-N per square meter per day in 1995), Auer et al. (1993; 13.3 mg P per square meter per day in 1987) and Penn et al. (2000; 10.0 mg P per square meter per day in 1992). These reduced fluxes are consistent with the projected response of the system to reduced phosphorus loadings and attendant rates of primary production and organic matter deposition.

6.2 ELECTRON ACCEPTOR AUGMENTATION – NITRATE ADDITION

The reactor simulating electron acceptor augmentation with nitrate was operated at a steady state nitrate concentration of 2.0±0.2 mg NO$_3$-N per liter (Figure B.3a). This level is comparable to that present in the hypolimnion of Onondaga Lake at the onset of thermal stratification and was one of the nitrate levels tested in examining the impact of electron acceptor augmentation on methylmercury flux (Exponent et al. 2009). Following 4 weeks of incubation, nitrate addition was discontinued and the system allowed to assume a steady state equivalent to that of the no nitrate – no oxygen baseline reactor. Oxygen was absent from the reactor (Figure B.3a) and flows remained relatively constant, ranging from 0.5 to 0.6 liter per day, over the course of the incubation (Figure B.3a).
The ammonia flux in the nitrate-added reactor (Figure B.3b) averaged 25.8±2.5 mg NH₃-N per square meter per day for the 4 weeks during which nitrate was added and 24.2±7.4 mg NH₃-N per square meter per day during the 3 weeks simulating no nitrate – no oxygen conditions. The ammonia flux in the nitrate added reactor (Figure B.3b) was significantly (p<0.001) higher than that observed in the no nitrate-no oxygen reactor (Figure B.2b). It is concluded from this that electron acceptor augmentation with nitrate, at a nominal concentration of 2 mg N per liter has no inhibitory effect on ammonia flux from Onondaga Lake sediments (as expected because there is no candidate biogeochemical sink for achieving such an effect). The fact that nitrate addition (Figure B.3b) yielded fluxes higher than the no nitrate-no oxygen control (Figure B.2b) suggests an additional source of ammonia such as dissimilatory nitrate reduction (DNRA, NO₃ → NH₃). The fact that the ammonia flux in the nitrate-added reactor fell, when nitrate addition was discontinued, to levels comparable to those observed for the no-nitrate – no oxygen reactor, suggests the DNRA ammonia source was lost after this step (Figure B.3b). The lag in the DNRA response (weeks 5 and 6 in Figure 3b) is similar to that noted in other sediment microcosm incubations.

The average phosphorus flux in the nitrate-added reactor for the 4-week period of electron acceptor augmentation was 0.2±0.1 mg P per square meter per day (Figure B.3c), significantly (p<0.001) lower than the no nitrate – no oxygen flux. This flux is considered negligible and reflects essentially complete inhibition of phosphorus flux. Over the 3 weeks following cessation of nitrate addition, the phosphorus flux increased from 0.1 to 1.9 mg P per square meter per day. It is anticipated that the phosphorus flux would have continued to increase had the incubation period been extended, approaching the flux attained in the no nitrate-no oxygen reactor. It is concluded from these results that electron acceptor augmentation with nitrate, at a nominal concentration of 2 mg N per liter, is effective in inhibiting phosphorus flux from the sediments of Onondaga Lake.

6.3 ELECTRON ACCEPTOR AUGMENTATION – OXYGEN ADDITION

The reactor simulating electron acceptor augmentation with oxygen was operated at saturation for the first week, spent a week in transition and stabilized at a steady state oxygen concentration of 2.0 mg O₂ per liter, remaining there for two weeks (Figure B.4a). Saturation concentrations are comparable to levels present in the hypolimnion of Onondaga Lake at the onset of thermal stratification, while the steady state concentration corresponds to one of the oxygen levels tested in examining the impact of electron acceptor augmentation on methylmercury flux (Exponent et al. 2009). Following four weeks of incubation, oxygen addition was discontinued and the system allowed to assume a steady state equivalent to that of the no nitrate – no oxygen baseline reactor. Flows remained relatively constant, ranging from 0.3 to 0.4 liter per day, over the course of the incubation (Figure B.4a).

The ammonia flux in the oxygen-added reactor averaged 9.4±4.4 mg NH₃-N per square meter per day for the four weeks of oxygen augmentation and 20.9±3.1 mg NH₃-N per square meter per day for the three weeks simulating no nitrate – no oxygen conditions (Figure B.4b). The ammonia flux was low initially, but climbed steadily over the course of the incubation, reaching a plateau with a rate in the last two weeks (Figure B.4b) comparable to that achieved in
the no nitrate-no oxygen reactor. It is inferred from this response that nitrifying bacteria were initially present (flux less than 5 mg NH₃-N per square meter per day), but were not sustained at the level of oxygen augmentation used here. Beutel (2006) observed that oxygenation at concentrations of 7 to 8 mg O₂ per liter (M. Beutel, personal communication) successfully inhibited ammonia release. The conclusion here, however, is that electron acceptor augmentation with oxygen, at a nominal concentration of 2 mg O₂ per liter, is not capable of sustaining the microbial populations required to reduce ammonia flux from Onondaga Lake sediments.

The average phosphorus flux in the oxygen-added reactor for the 4-week period of oxygen augmentation was 0.1±0.05 mg P per square meter per day (Figure B.4c), significantly (p less than 0.001) lower than the no nitrate-no oxygen flux. This flux is considered negligible and reflects essentially complete inhibition of phosphorus flux. Over the three weeks following cessation of oxygen addition the phosphorus flux increased from 0.3 to 5.7 mg P per square meter per day (Figure B.4c), a rate little different from the average for the no nitrate-no oxygen reactor (5.2 mg P per square meter per day). It is concluded from these results that electron acceptor augmentation with oxygen, at a nominal concentration of 2 mg O₂ per liter, is effective in inhibiting phosphorus flux from the sediments of Onondaga Lake.
SECTION 7

LITERATURE CITED


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APPENDIX C

INDUCED OXYGEN DEMAND AND ELECTRON ACCEPTOR AMENDMENT IN ONONDAGA LAKE, NEW YORK
APPENDIX C

INDUCED OXYGEN DEMAND AND ELECTRON ACCEPTOR AMENDMENT IN ONONDAGA LAKE, NEW YORK

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INDUCED OXYGEN DEMAND AND ELECTRON ACCEPTOR AMENDMENT IN ONONDAGA LAKE

EXECUTIVE SUMMARY

Onondaga Lake has been identified as a candidate for electron acceptor amendment (with nitrate or oxygen) as a means of reducing the flux of methylmercury from its sediments. Past experience at other sites indicates that such amendments may influence electron acceptor demand by altering the turbulence regime of the hypolimnion and by increasing concentration gradients at the sediment-water interface. Where the induction effect is significant, augmentation systems may be under-designed, with engineering and economic consequences. This research presents the results of experiments characterizing the relationship between hypolimnetic turbulence and electron acceptor (nitrate and oxygen) demand. Measurements of ambient turbulence in the lake’s hypolimnion are applied in assessing the vulnerability of the system to induced demand. It is concluded that the anticipated induced demand effect would be modest for Onondaga Lake, ranging from 1-4% for sediment oxygen demand and 5-10% for sediment nitrate demand (SND). It is believed that the projected lack of sensitivity to induced demand evolves from the lake’s orientation with respect to prevailing winds and attendant seiche activity; i.e. ambient hypolimnetic turbulence naturally places the system near the upper turbulent intensity threshold for the induction phenomenon. A second component of induced demand would arise if the augmentation system increased the average bulk water concentrations above that used for quantifying baseline demand. Experiments, where higher SND was observed, involved nitrate concentrations approximately double those of average concentrations during the historical depletion periods and double the proposed target nitrate concentration for the pilot test (1 mgN/L at 18m). Such conditions are highly unlikely in the field and, therefore, it is not anticipated that induced demand generated by concentration increases would be significant. It is recommended that projections of a modest induced electron acceptor demand effect be accommodated in the design of a pilot system.

Acronyms Used In This Report

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHOD</td>
<td>Areal hypolimnetic oxygen deficit</td>
</tr>
<tr>
<td>MT</td>
<td>Metric ton</td>
</tr>
<tr>
<td>DBL</td>
<td>Diffusive boundary layer</td>
</tr>
<tr>
<td>SND</td>
<td>Sediment nitrate demand</td>
</tr>
<tr>
<td>SOD</td>
<td>Sediment oxygen demand</td>
</tr>
<tr>
<td>VOD</td>
<td>Volumetric oxygen demand</td>
</tr>
</tbody>
</table>

1.0 HYPOLIMNETIC AERATION/OXYGENATION AND INDUCED OXYGEN DEMAND

Hypolimnetic oxygen depletion is one manifestation of the eutrophication of lakes. Where nutrient enrichment yields rates of organic matter delivery to the sediment in excess of the system’s capacity to mineralize those materials, legacy deposits accumulate. Decomposition of contemporary and legacy deposits of organic matter leads to oxygen depletion with attendant...
extirpation of the benthic invertebrate and fish communities and the release of a variety of chemical species from the sediments (ammonia, iron and manganese, methane, mercury, phosphorus and sulfide; Penn et al. 2000; Beutel 2006; Beutel et al. 2008b; Matthews et al. 2008). The long-term solution to this problem is to reduce phytoplankton growth and attendant organic matter deposition by managing nutrient inputs. The result is that legacy deposits of labile organic matter undergo diagenesis over time, the system comes into equilibrium with contemporary rates of organic matter deposition and the demand on hypolimnetic oxygen resources is reduced to levels where depletion does not lead to water quality problems. As a short-term solution, or where the requisite level of load management is infeasible, hypolimnetic aeration (introduction of air) or oxygenation (introduction of pure oxygen) may be employed to maintain oxygen resources (McQueen and Lean 1986; Beutel and Horne 1999) and limit the flux of chemical species from the sediment (Gemza 1997; Beutel 2006; Beutel et al. 2008b).

Hypolimnetic aeration/oxygenation systems are designed based on a knowledge of the sediment oxygen demand (\(SOD\), gO\(_2\)·m\(^{-2}\)·d\(^{-1}\)), i.e. the flux of oxygen from the hypolimnion into the sediment. Estimates of \(SOD\) may be derived in several ways, e.g. through a flux-gradient approach using sediment porewater oxygen microprofiles (Sweerts et al. 1989), through laboratory incubations using intact sediment cores (Gelda et al. 1995) and by calculation of the areal hypolimnetic oxygen deficit (\(AHOD\), gO\(_2\)·m\(^{-2}\)·d\(^{-1}\); Matthews and Effler 2006). In this last case, a volume-weighted hypolimnetic oxygen concentration is determined at intervals over the stratified period and the \(AHOD\) is calculated based on sediment surface area and hypolimnetic volume, corrected for inputs from vertical mass transport. Of these three methods, \(AHOD\) is the approach most commonly applied in design of aeration/oxygenation systems (Ashley 1985; Moore et al. 1996; Beutel 2003; Beutel et al. 2007).

It has been noted in practice, however, that pre-implementation determinations of oxygen demand may underestimate the oxygen supply later required to maintain target concentrations in the hypolimnion, a phenomenon termed induced oxygen demand (Smith et al. 1975; Taggart and McQueen (1982); Ashley 1983; McQueen et al. 1984; Ashley et al. 1987; Soltero et al. 1994; Moore et al. 1996; Beutel 2003; Beutel et al. 2007; Gantzer et al. 2009). The degree of underestimation can be significant, with post-implementation \(SOD\) values increasing by 57% (Moore et al. 1996) and factors of 2 (Soltero et al. 1994), 2-3 (Smith et al. 1975), 2-4 (Beutel 2003; Beutel et al. 2007) and 2-6 (depending on aeration rate, Gantzer 2009), and leading to design failures with both engineering and economic implications. Induced oxygen demand effects have led designers to include a safety factor in the sizing of hypolimnetic aeration systems (Cooke et al. 2005). The induced oxygen effect is thought to result from an increase in mixing within the hypolimnion (post-implementation turbulence effect; Moore et al. 1996; Gantzer et al. 2009) and from an increase in the bulk liquid oxygen concentration, i.e. the driving force for diffusion at the sediment-water interface (Jørgensen and Revsbech, 1985; Cai and Sayles 1996; Moore et al. 1996; Beutel 2003; Beutel et al. 2007; but see also Gantzer et al. 2009; the review by Hall et al. 1989 and the theoretical development presented in the following section).

2.0 THE MECHANISTIC BASIS FOR INDUCED OXYGEN DEMAND

The phenomenon termed induced demand is a manifestation of changes in mass transport and thus has application to any chemical species exchanged at the sediment-water interface. The
mechanistic basis for the phenomenon is developed here using oxygen as an example. Sediment oxygen demand refers to the process through which oxygen is consumed in the conversion of ammonia to nitrate, dissolved organic carbon to carbon dioxide and selected reduced species end products of organic carbon diagenesis (Mn$^{2+}$, Fe$^{2+}$, S$^{2-}$ and CH$_4$) to their oxidized counterparts.

2.1 Fate, Transport and the Physical Environment

The physical environment hosting and interacting with this phenomenon includes the bulk liquid, the diffusive boundary layer and the sediment (Figure C.1a). Assuming that turbulent diffusion dominates, i.e. advection and horizontal gradients are negligible in this system, a steady-state, one-dimensional mass balance for oxygen can be written as,

$$0 = D \cdot \frac{d^2C}{dz^2} - k \cdot C$$

where:

- $C$ is concentration, g·m$^{-3}$
- $t =$ time, d
- $D$ is the diffusion coefficient (layer-specific), m$^2$·d$^{-1}$
- $z$ is depth measured downward, m
- $k$ is a first order decay coefficient, d$^{-1}$

The first term to the right of the equal sign describes diffusive mass transport and the second represents consumption of oxygen resulting from the diagenesis of organic matter. In the absence of oxygen consumption, the oxygen profile ($C = f(z)$) will be linear and vertical through all three layers, with oxygen extending indefinitely into the sediment (Figure C.1b). Profiles in the presence of sediment oxygen consumption vary among the three layers.

Mass transport in the bulk liquid is dominated by turbulent diffusion. Oxygen consumption within the bulk liquid is assumed to be negligible and Equation 1 reduces to,

$$0 = D \cdot \frac{d^2C}{dz^2}$$

This equation states that the profile within the bulk liquid will be linear (i.e., the second derivative of a straight line is zero). In addition to being linear, the profile in the bulk liquid will be vertical (Figure C.1c) because intense turbulent mixing tends to eliminate vertical concentration gradients.

The bulk liquid and sediment are separated by the diffusive boundary layer (DBL). In this region the internal friction (viscosity) of the water creates a laminar film that does not participate in the general circulation of the bulk liquid (Vogel 1981) and mass transport is by molecular diffusion (Santschi et al. 1983). It is assumed that no oxygen consumption occurs within the film. Adopting as a top boundary condition the bulk liquid oxygen concentration and as a bottom boundary condition the concentration at the sediment-water interface, the oxygen profile for the
DBL (Figure C.1c) will again be linear as described by Equation 2. However, for the case where sediment oxygen demand causes the sediment porewater concentration to be lower than the bulk concentration, the resulting profile will be non-vertical (as required by the boundary conditions).

In the sediment, mass transport is by molecular diffusion (as modified by porosity and tortuosity effects); here the reaction term is significant and Equation 1 applies. As a consequence, the resulting oxygen profile (Figure C.1c) is non-linear (as in Equation 1, the second-derivative is non-zero) and non-vertical (as required by the lower boundary condition; that is, that oxygen eventually goes to zero with depth).

The DBL, existing as a thin (~1 mm or less in thickness; Santschi et al. 1983; Jørgenson and Revsbech 1985; Gunderson and Jørgenson 1990) layer above the sediment, constitutes a significant barrier to the exchange of chemical species into (oxygen, nitrate) and out of (nutrients, metals, reduced species end products) the sediment (see Gunderson and Jørgenson 1990). The conceptual treatment of fate and transport within the bulk liquid – DBL – sediment environment provided here offers a basis for quantifying SOD and its relationship to the rate of organic matter diagenesis, the thickness of the DBL and the bulk liquid oxygen concentration.

2.2 Factors Mediating Sediment Oxygen Demand

Sediment oxygen demand is appropriately quantified as a flux across the sediment-water interface, equal to the product of the diffusion coefficient and the concentration gradient between the sediment and the overlying water well described by Fick’s 1st Law,

\[ J_{O_2} = -D \frac{dC}{dz} \]  \[ [3] \]

where: \( J \), a generic representation of SOD, is the diffusive flux, g·m⁻²·d⁻¹

At steady state, the flux of oxygen at the sediment-water interface and the flux across the DBL are equal. As described above, because of the absence of significant oxygen depleting reactions, the oxygen profile within the DBL is well described by a linear representation which links the dependence of flux (SOD) to the bulk liquid oxygen concentration and the thickness of the DBL,

\[ \frac{dC}{dz} = \frac{C_{bulk} - C_{swi}}{z_{DBL}} \]  \[ [4] \]

where: \( C_{bulk} \) is the bulk liquid oxygen concentration, gO₂·m⁻³

\( C_{swi} \) is the oxygen concentration at the sediment-water interface, gO₂·m⁻³

\( z_{DBL} \) is the thickness of the diffusive boundary layer, m

Models developed by Bouldin (1968) and Hall et al. (1989) provide a means of quantifying these relationships. Bouldin (1968) introduced the concept of volumetric oxygen demand (VOD),
an intrinsic property representing the carbon undergoing diagenesis with oxygen as the electron acceptor. \( VOD \) may be estimated from measurements of three parameters typically included in sediment studies: \( SOD \), \( D \) and \( C_{bulk} \),

\[
VOD = \frac{SOD^2}{2 \cdot D \cdot C_{bulk}}
\]

where: \( VOD \) is the volumetric oxygen demand, gO₂·m⁻³·d⁻¹

As an intrinsic property, \( VOD \) does not exhibit short term changes in response to environmental conditions and thus proves useful in calculating other features of sediment oxygen dynamics. Hall et al. (1989) extended Bouldin’s (1968) development, accommodating the presence of a diffusive boundary layer and permitting calculation (for specified values of \( D \) and \( VOD \)) of sediment oxygen demand,

\[
SOD = VOD \cdot \left[ \sqrt{\frac{2D_{sed} \cdot C_{bulk}}{VOD} + \left( \frac{D_{sed}}{D_{DBL}} \cdot z_{DBL} \right)^2} - \frac{D_{sed}}{D_{DBL}} \cdot z_{DBL} \right]
\]

the maximum depth of oxygen penetration (\( z_{ox} \)),

\[
z_{ox} = \sqrt{\frac{2D_{sed} \cdot C_{bulk}}{VOD} + \left( \frac{D_{sed}}{D_{DBL}} \cdot z_{DBL} \right)^2} - \frac{D_{sed}}{D_{DBL}} \cdot z_{DBL}
\]

and the attendant oxygen profile (\( C(z) \)),

\[
C(z) = \frac{VOD}{2 \cdot D_{sed}} \cdot \left[ \sqrt{\frac{2D \cdot C_{bulk}}{VOD} + \left( \frac{D_{sed}}{D_{DBL}} \cdot z_{DBL} \right)^2} - \frac{D_{sed}}{D_{DBL}} \cdot z_{DBL} \right] \cdot \frac{VOD}{2 \cdot D} \cdot z^2
\]

as functions of \( C_{bulk} \) and \( z_{DBL} \).

Illustrative applications of Equations 6-8 are presented here with values of \( VOD \) (2900 gO₂·m⁻³·d⁻¹) and \( D \) (8.64×10⁻⁵ m²·d⁻¹) representative of Onondaga Lake sediments. The response of the oxygen profile to changes in \( C_{bulk} \) in the absence of a DBL (\( z_{DBL} = 0 \)) is presented in Figure C.2a. Note that as \( C_{bulk} \) increases, the depth of oxygen penetration and the slope of the
profile (~$SOD$) both increase. The role of the DBL in mediating $SOD$ is considered for two cases ($z_{DBL} = 1.0$ mm and 0.1 mm) in Figure C.2b. Here, the driving force for $SOD$ is not $C_{bulk}$, but rather $C_{swi}$ (the oxygen concentration at the base of the DBL). Reducing the DBL thickness leads to a higher value of $C_{swi}$, an increased depth of oxygen penetration and a greater slope (~$SOD$). This effect is illustrated in model-predicted oxygen profiles for a range of sediment-water interface oxygen concentrations in Figures 3a (without a DBL) and 3b (with a DBL). It can be seen here that increasing $C_{swi}$ increases both the depth of oxygen penetration and the slope of the profile (~$SOD$).

Thus model-predicted $SOD$ is seen to be a function of an intrinsic $VOD$, the oxygen concentration in the bulk liquid (and thus at the sediment-water interface, Figure C.4a) and the thickness of the diffusive boundary layer (Figure C.4b). The combined effect of the two factors is illustrated in Figure C.4c. These relationships are consistent with the observations of Moore et al. (1996), Beutel (2003), Beutel et al. (2007) and Beutel et al. (2008a) that induced oxygen demand is mediated by both $C_{bulk}$ and mixing conditions, but stands in contrast to the conclusion of Gantzer et al. (2009) and several studies summarized by Hall et al. (1989) that hypolimnetic oxygen consumption is independent of $C_{bulk}$.

It is clear that, for given values of $VOD$ and $C_{bulk}$, $SOD$ decreases with increasing boundary layer thickness. Thus it may be appropriate to consider $SOD$ for a minimum $z_{DBL}$ (unburdened by mass transport limitations) as a maximum value and $SOD$ as $z_{DBL}$ increases to be apparent or realized values.

### 3.0 MOTIVATION, OBJECTIVES, AND APPROACH

Sediments at the study site, Onondaga Lake, are contaminated with mercury as a result of industrial discharges, leading to production of methylmercury and attendant ecosystem impacts. Remediation at upland and nearshore in-lake locations is expected to significantly reduce mercury inputs to the lake’s depositional basins with attenuation of methylmercury formation as legacy deposits become buried and overlain by uncontaminated sediment. It has been observed here that methylmercury flux from the sediments is initiated once oxygen and nitrate have been depleted from the hypolimnion (Todorova et al. 2009). Electron acceptor augmentation with nitrate or oxygen is thus being considered as a means of controlling methylmercury flux as the sediments approach equilibrium with contemporary conditions of deposition (United States District Court 2007).

An examination of the potential response of chemical flux at the sediment-water interface of Onondaga Lake to changes in turbulence levels, i.e. induced demand, is an appropriate pre-condition to field-scale testing of the electron acceptor augmentation technology. The objectives of this study are to:

(a) quantify the relationship between $SND/SOD$ and turbulence for Onondaga Lake sediments;

(b) place that relationship within the context of the bottom boundary layer turbulence measured for Onondaga Lake; and

(c) apply those results in assessing the sensitivity of the system to the induced demand following implementation of electron acceptor augmentation.
Sediment nitrate and oxygen demand were measured using sediment flux chambers designed to provide varying levels of isotropic turbulence at the sediment-water interface. Rates of SND and SOD were measured over a range of turbulences and plotted to provide the desired relationship. A quantitative characterization of the bottom boundary layer turbulence for Onondaga Lake (Rusello and Cowen 2010) is used to place ambient conditions within the context of the turbulence – SND/SOD relationship. Evaluation of that result permits estimation of the degree to which induced electron acceptor demand will be manifested following implementation of electron acceptor augmentation.

4.0 METHODS

4.1 Sediment Core Collection and Handling

Sediments were collected from the South Deep station in the south depositional basin of Onondaga Lake on 4 dates between 12 June 2008 and 26 April 2009, supporting 12 measurements of sediment nitrate demand and 13 measurements of sediment oxygen demand. The South Deep station (maximum depth, 19m) is considered representative of sediment conditions in the depositional basins of Onondaga Lake (Effler 1996). Sediment was collected using a stainless steel box corer (Model 1260, Ocean Instruments, Inc., San Diego, CA). The box core was sub-sampled using 15 cm (6-inch) diameter polycarbonate reactor housings and capped with friction-fit tops and bottoms. The sealed cores were placed on ice and transported to the laboratory where they were stored at 4 °C. Particular care was taken to minimize disturbance of the sediment-water interface during box coring and transportation to the laboratory.

The organic matter content of sediments in nature decreases over time with exposure to electron acceptors (see Gantzer et al. 2009). This is also the case with the organic matter in sediment cores when stored or utilized in sediment flux chambers (incubations; see Sundby 1986), altering the associated SND/SOD. We observed that our cores had a ‘shelf life’ of about 3 months, i.e. values of SND/SOD began to decline after this period. Where measured values of SND_{max}/SOD_{max} declined significantly (due to length or storage or utilization in measurements) the core was discarded and a fresh core utilized.

4.2 Sediment Flux Chamber Design

A sediment flux chamber (i.e. completely-mixed flow reactor) has identifiable sources and sinks of chemical mass and, when operating at steady state, supports determination of an unknown source/sink when the other source/sink terms and physical conditions (area, volume and flow) are known. The application of this approach and detailed calculations are provided in Section 4.5 below.

The chambers were specifically designed to support quantification of chemical flux at the sediment-water interface by:

- Housing an intact sediment core
- Providing an inlet for addition of feed stock
- Permitting establishment of specified turbulence levels
- Maintaining isotropic mixing conditions
- Providing an outlet for sample collection.
Chambers consisted of a cylindrical Plexiglas container, 15 cm diameter by 25.4 cm tall, outfitted with opposing inlet-outlet ports located approximately 1.3 cm below the top rim. When filled, chambers contained ~13 cm of sediment and ~12 cm of overlying water. Plexiglas top and bottom pieces, inlaid with flexible gaskets and placed within clamping devices sealed the system against gas penetration and leakage of liquid. The chamber top had six peripheral jet ports where the liquid content of the chamber water was circulated via peristaltic pumps to provide mixing and control turbulence. The system was operated with zero head space.

### 4.3 Regulation of Turbulence

The objective of this work, quantification of the effect of turbulence on the thickness of the diffusive boundary layer and thus chemical flux, demands particular attention to characterization and regulation of that turbulence. Direct field measurement of these effects is challenging due to the small length scales associated with boundary layers. Sediment flux chambers provide an alternative approach, but yield estimates representative of the ambient environment only when natural boundary conditions are reproduced (Boynton et al. 1981; Hall et al. 1989). It is necessary to overcome several challenges in order to meet this criterion.

The first challenge is to insure that turbulent flux dominates within the chamber (i.e. mean advective flux is eliminated). Mass transport in the hypolimnion of lakes and attendant chemical renewal at the sediment-water interface occurs primarily through vertical turbulent mixing. Horizontal advective flux in the hypolimnion (spatial scale of 100s of meters) does not serve to renew conditions at the interface, but rather moves water of a relatively constant chemical composition over the bed. In chambers (spatial scale of centimeters), however, horizontal advective transport quickly moves water to the boundary (chamber wall), setting up a circulation pattern that provides chemical renewal at the sediment-water interface. Thus it is the goal of chamber design to establish isotropic conditions, i.e. no net flow. To meet this challenge, a novel chamber was developed based on proven isotropic turbulence generation techniques (Rusello and Cowen 2010). The chamber design minimizes advective horizontal transport by utilizing an array of jets arranged symmetrically on the chamber top and oriented with the jet axes perpendicular to the sediment bed. The jets are driven by peristaltic pumps which randomly change direction, generating nearly isotropic turbulence that is horizontally homogenous with very low mean flows.

The second challenge is to quantitatively characterize turbulence within the chamber. Particle image velocimetry (PIV) was used for this purpose, characterizing chamber turbulence under various forcing conditions (pump speeds; Figure C.5). Vertical turbulent intensity, calculated as the root mean square difference between the instantaneous and mean velocities, was selected as the metric representing turbulence in the chamber. The turbulent intensity is a common turbulence statistic and provides a measure of the strength of the turbulence readily comparable to field measurements. With appropriate assumptions it can also be used for comparison to other systems where turbulence statistics are not reported. The third challenge is to scale chamber turbulence to that of the ambient environment. Vertical turbulent intensity, the metric adopted for laboratory chambers, is readily measured in the field and its use in characterizing turbulence in the ambient environment facilitates direct comparison of conditions. Measurements in the bottom boundary layer of Onondaga Lake (Rusello and Cowen 2010) showed classic turbulent boundary layer conditions, although with weaker mean flows than...
expected. Because of the slow mean flows, measurement noise dominates the horizontal turbulence statistics, leaving the vertical turbulence measurements (which have significantly lower measurement noise) as the most reliable estimates of in-situ turbulence conditions. Turbulent intensities and turbulent dissipation rates in the chamber were compared to estimates from the field measurements with good agreement at a representative turbulent intensity of 1-2 mm/s. Chamber turbulence conditions were calibrated to the pump speed in RPM, yielding a vertical turbulent intensity appropriate for modeling scalar flux at both current in-situ conditions and with enhanced turbulence as may be imparted through electron acceptor augmentation. Vertical turbulent intensity can also be scaled to yield the friction velocity (u*, a common boundary layer parameter) to facilitate comparison of our findings with those from other systems where direct turbulence measurements have not been performed.

In this application, the top of the chamber was outfitted with six jets that were flush with the reactor/water interface. Tygon tubes were run from these jets through 3 peristaltic pumps (Masterflex L/S Computerized Drive; Masterflex Easy Load II Model #77202-50). The pumps were programmed (MATLAB) to randomly reverse the recirculation direction to achieve isotropic conditions. The degree of turbulence was varied by adjusting the pump speed (Figure C.5). At intervals of 60 minutes, the pumps operated in a single direction for several minutes to flush the tubing system. Velocities employed here (~0-4.5 mm/s, pump speeds of 0-50 RPM) reflect the range of ambient fluid velocities observed near the sediment-water interface of Onondaga Lake. Higher velocities (25 and 50 RPM) represent a minimum DBL thickness and thus an appropriate condition for determination of SODmax/SNDmax. Above 50 RPM, sediment resuspension occurred. Given that implementation of electron acceptor amendment would be designed to prevent sediment resuspension, this range of velocities also represents expected conditions should the technology be utilized.

4.4 Chamber Operation and Monitoring

The continuous-flow sediment flux chamber and supporting system components are described schematically in Figure C.6. Incubations were performed in a constant temperature room (8°C; mimicking ambient hypolimnetic conditions) with two reactors (one SND and one SOD) operated simultaneously at turbulent intensities of 0.07 – 4.57 mm·s⁻¹. Artificial lake water (Table C.1), with an ionic composition similar to that of the lake, served as feed stock to the reactor with the rate of input regulated by metered gravity flow or a peristaltic pump. Feed stock for the oxygen reactor (measurement of SOD) was continuously bubbled with an air-nitrogen mixture (Mix-1000 Digital Gas Mixer/Blender) to achieve the desired oxygen concentration. Feed stock for the nitrate reactor (measurement of SND) was augmented with potassium nitrate (~4-6 mgNO₃-N·L⁻¹) and continuously bubbled with nitrogen gas to purge oxygen from the system.

It is necessary that the bulk liquid nitrate/oxygen concentration be controlled, as this represents a driving force for diffusion (Jørgensen and Revsbech 1985; Moore et al. 1996). Further, by controlling the bulk liquid electron acceptor concentration, turbulence (DBL thickness) is isolated as the sole factor mediating realized SND/SOD. Target bulk liquid concentrations (nominally, 2-4 mgNO₃-N·L⁻¹ and 2-4 mgO₂-L⁻¹) were those proposed for control of MeHg flux through electron acceptor amendment (Auer et al. 2009). Target concentrations were maintained at steady-state levels of 2.2±0.8 mgNO₃-N·L⁻¹ (n = 12) and 3.0±1.9 mgO₂-L⁻¹.
(n = 13) through regulation of feed stock inflow (rotameters and gravity feed, initially, and peristaltic pumps, later). Feed stock nitrate (Orion Thermo Scientific Nitrate Sensor 9700B NWP) and oxygen (HACH HQ 40d LDO probe) concentrations were monitored daily. Effluent nitrate concentrations were monitored four times daily using the ion-specific electrode. Effluent oxygen levels were monitored continuously using a Unisense in-line oxygen microprobe (50 and 100 μm tip diameter). The LDO and nitrate probes were calibrated daily, while the in-line oxygen microprobe was calibrated only at the beginning and end of the incubation to avoid disturbing the system. Effluent concentrations were monitored for several days after placing the core at 8°C and flux measurements initiated once the system stabilized, i.e. achieved steady state (Figure C.7). The stabilized sediment flux chambers were then monitored for 2-4 days and the average concentration applied in calculating $SND$ and $SOD$ as described below.

### 4.5 Flux Calculation

The sediment reactors were run to steady state and the effluent concentration noted. The flux ($J = SND, SOD$) was then calculated by conducting a mass balance on the electron acceptor concentration ($C$) in the reactor,

$$V \cdot \frac{dC}{dt} = Q \cdot C_{in} - Q \cdot C - J \cdot A$$

where:

- $V$ is the liquid volume in the sediment flux chamber, m$^3$
- $Q$ is the reactor flow rate, m$^3$/d$^1$
- $C_{in}$ is the influent electron acceptor concentration, g·m$^{-3}$
- $A$ is the reactor surface area, m$^2$

At steady state, the change in concentration (dC/dt) is zero, and Equation 9 becomes,

$$0 = Q \cdot C_{in} - Q \cdot C - J \cdot A$$

The flux may be solved for by rearranging Equation 10,

$$J = \frac{Q \cdot (C_{in} - C)}{A}$$

The values for $Q$, $C_{in}$, $C$, and $A$ are all known or measured during the conduct of the experiment.

The fluxes generated by this calculation were obtained using sediment cores collected at various times of the year and thus reflecting a range of sedimentation fluxes (Soltero 1994) and carbon content and lability. These differences manifest themselves in variation in the maximum value of $J$, i.e. that associated with a minimal DBL thickness. Thus, fluxes determined for a
particular core were normalized to their respective maxima ($SND_{\text{max}}$ and $SOD_{\text{max}}$) value before being placed within the pool of data used to define the demand/turbulence relationship.

### 5.0 RESULTS AND DISCUSSION

Sediment flux chambers containing Onondaga Lake sediment were exposed to controlled environments characterized by turbulent intensities ranging from 0.07 – 4.57 mm·s⁻¹. Chambers were operated and monitored for several days until the effluent electron acceptor concentration reached a steady state condition (Figure C.7). Effluent oxygen and nitrate concentrations were then monitored for 2-4 days and the average concentration applied in calculating $SND$ and $SOD$ according to Equation 11.

#### 5.1 Maximum Rates of Sediment Nitrate and Oxygen Demand

A total of 12 incubations were conducted with nitrate as the electron acceptor, yielding $SND_{\text{max}}$ values ranging from 0.079 - 0.258 gN·m⁻²·day⁻¹ with an average of 0.17±0.07 gN·m⁻²·day⁻¹ (Table C.2). These values are roughly double those of contemporary rates of hypolimnetic nitrate depletion observed for Onondaga Lake (0.07 and 0.09 gN·m⁻²·day⁻¹ for 2008 and 2009, respectively; Upstate Freshwater Institute unpublished). In-lake nitrate depletion rates are expected to be less than those observed in flux chambers due to differences in bulk liquid nitrate concentrations, i.e., in-lake levels are depleted over the stratified interval and thus are, on average, less than those utilized in experiments where concentrations are held constant. (It should also be noted that the target concentration to be maintained during the pilot test at 18m is 1 mgN/l, approximately half the value used in the experiments.) $SND_{\text{max}}$ values observed here compared favorably with those determined for sediment from Lake Perris, California (0.04-0.17 gN·m⁻²·day⁻¹; Beutel et al. 2008a) for similar bulk liquid nitrate concentrations (1-5 mgN·L⁻¹).

A total of 13 incubations were performed with oxygen as the electron acceptor, yielding values of $SOD_{\text{max}}$ ranging from 1.01 to 1.25 gO₂·m⁻²·day⁻¹ and averaging 1.09 ±0.11. gO₂·m⁻²·day⁻¹ (Table C.3). The average value for $SOD_{\text{max}}$ compares favorably with that determined for Onondaga Lake as $AHOD$ (1.02 gO₂·m⁻²·day⁻¹ for both 2008 and 2009; Upstate Freshwater Institute, unpublished); exact correspondance is not expected due to differences in $C_{\text{bulk}}$. An increase in SOD corresponding to maintenance of oxygen levels was not observed, perhaps because the average condition in the lake reasonably approximated that used in the measurements. The range observed for $SOD_{\text{max}}$ in Onondaga Lake falls between that reported in chamber studies by Beutel (2003) for nine California reservoirs (0.1–0.8 gO₂·m⁻²·day⁻¹) and by Arega and Lee (2005) in primarily semi-artificial cores (2-6 gO₂·m⁻²·day⁻¹).

#### 5.2 Turbulence and Induced Electron Acceptor Demand

Determinations of $SND_{\text{max}}$ and $SOD_{\text{max}}$ were made at mixing pump speeds of 25 and 50 rpm, yielding turbulent intensities associated with a minimum DBL thickness. Additional measurements were made at lesser turbulent intensities (pump speeds of 2, 6, 10 and 17.5 rpm) to explore the induced demand effect. Here, $SND$ and $SOD$ values for each turbulent intensity were normalized to the $SND_{\text{max}}$ or $SOD_{\text{max}}$ value for their particular collection and plotted as a function of turbulent intensity (Figure C.8). In each case, the relationship between turbulent intensity (mm·s⁻¹) and electron acceptor demand (gO₂·m⁻²·day⁻¹) was well described by a rectangular hyperbola.
\[ J_i = \alpha \cdot J_{i,\text{max}} \cdot \frac{i}{\beta + i} \]  \hspace{1cm} [12]

where: \( J_i \) is the normalized flux, i.e. at turbulent intensity \( i \),

\( J_{i,\text{max}} \) is the maximum flux, 1.0 for the normalized case,

\( \alpha, \beta \) are dimensionless fitting parameters

The model represented in Equation 12 was fit to the normalized SND and SOD data (Figures 8a and b) using Microsoft Excel Solver yielding values of the fitting parameters \( \alpha \) and \( \beta \) were 1.05 gNO\textsubscript{3}-N·m\textsuperscript{-2}·d\textsuperscript{-1} and 0.15 mm·s\textsuperscript{-1} for SND and 1.05 gO\textsubscript{2}·m\textsuperscript{-2}·d\textsuperscript{-1} and 0.09 mm·s\textsuperscript{-1} for SOD. The root mean square errors for fits to the SND and SOD results were 0.07 gNO\textsubscript{3}-N·m\textsuperscript{-2}·d\textsuperscript{-1} and 0.27 gO\textsubscript{2}·m\textsuperscript{-2}·d\textsuperscript{-1}. The relationship embodied in Equation 12 may then be applied for measured ambient and projected future (post amendment) turbulent intensities to quantify the system’s sensitivity to the induced demand effect.

5.3 Management Application: Induced Electron Acceptor Demand in Onondaga Lake

The motivation for this research was to enhance the reliability of an electron acceptor augmentation design for Onondaga Lake by quantifying the sensitivity of the system to the induced demand effect. The theoretical and experimental development presented above demonstrates that induced demand occurs in response to increased turbulence (decreased boundary layer thickness) and increased bulk liquid electron acceptor levels.

The turbulent intensity-electron acceptor demand relationship presented as Figure C.8 provides a means of assessing the sensitivity of a system to the phenomenon. Ambient turbulent intensities for Onondaga Lake measured in late September and October of 2007 ranged from 1.0 – 1.5 mm·s\textsuperscript{-1} (Rusello and Cowen 2010). Application of Equation 12 for this range of ambient velocities using the electron acceptor-specific coefficients \( \alpha \) and \( \beta \) (as illustrated in Figure C.9) indicates that an increase in turbulent intensity at the sediment water interface yielding \( J_{\text{max}} \) values would increase SND by 5-9% and SOD by 1-4%. Assuming a sediment surface area of 6.75 km\textsuperscript{2} for the Onondaga Lake profundal, this would correspond to an additional requirement of 5-10 MT-NO\textsubscript{3}-N and 7-27 MT-O\textsubscript{2} over a stratified interval of 100 days.

These projected induced demand effects are modest in comparison to those reported for other systems (e.g., increases by a factor of 2-4; see Section 1.0). It is surmised that this lack of projected sensitivity involves both of the factors believed to mediate the induced demand effect. First, the major axis of Onondaga Lake is oriented in the direction of prevailing westerly and northwesterly winds. Exposure to this energy source promotes seiche activity in the lake (Effler 2004), the primary driving force for turbulence in the hypolimnion. Elevated turbulent intensities would reduce the DBL thickness, enhancing diffusive mass transport and increasing ambient \( J_{\text{max}} \). Thus Onondaga Lake would potentially lie further to the right (i.e. SOD → SOD\textsubscript{max}) along the velocity-demand continuum presented as Figure C.9 than would some other systems and would be less sensitive to further increases in turbulence imparted by electron acceptor addition.
However, differences in the bulk liquid concentration play a role as well. Flux chamber measurements conducted here for Onondaga Lake sediments utilized $C_{\text{bulk}}$ levels averaging 2.2 mgNO$_3$-N·L$^{-1}$ and 3.0 mgO$_2$·L$^{-1}$. The theoretical development summarized in Figure C.4a and the findings of Moore et al. (1996) suggest that SOD may increase by a factor of 2-3 for an increase in the bulk concentration from 2 to 6 or 8 mgO$_2$·L$^{-1}$. The maintenance of electron acceptor levels through chemical conditioning may thus be expected to induce demand compared with contemporary in-lake rates where bulk concentrations fall over the stratified period due to microbial consumption. A prediction of induced demand due to concentration effects under an augmentation regime requires a comparison of average bulk water concentrations over the historical nitrate depletion periods (starts at 2.0 mgN/l, ends at 0 mgN/l, averaged approximately 1 mgN/l) to concentrations maintained during the experiments (2.2 mgN/l), to proposed concentrations during the pilot test (1 mgN/l). Thus for the ambient mixing conditions determined for Onondaga Lake by Rusello and Cowen (2010) and the bulk concentrations proposed for augmentation, the prospect of a modest induced electron acceptor demand effect seems reasonable. It is recommended that projections of an induced electron acceptor demand effect be accommodated in the design of a pilot system.

6.0 REFERENCES


Table C.1. Composition of artificial lake water (ALW), mimicking the ionic composition of Onondaga Lake water.

a. Components as salts.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration (mM)</th>
<th>Concentration (mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂.2H₂O</td>
<td>5.84</td>
<td>858.83</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>4.24</td>
<td>356.20</td>
</tr>
<tr>
<td>(Na)₂SO₄</td>
<td>1.67</td>
<td>237.21</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.21</td>
<td>187.45</td>
</tr>
<tr>
<td>MgCl₂.6H₂O</td>
<td>0.99</td>
<td>200.87</td>
</tr>
<tr>
<td>KCl</td>
<td>0.44</td>
<td>32.43</td>
</tr>
<tr>
<td>NaF</td>
<td>0.02</td>
<td>1.01</td>
</tr>
</tbody>
</table>

b. Components as ions and ion balance.

<table>
<thead>
<tr>
<th>Cations</th>
<th>(meq·L⁻¹)</th>
<th>(mM)</th>
<th>(mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>11.68</td>
<td>5.84</td>
<td>234.14</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.44</td>
<td>0.44</td>
<td>17.01</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>1.98</td>
<td>0.99</td>
<td>24.03</td>
</tr>
<tr>
<td>Na⁺</td>
<td>10.81</td>
<td>10.81</td>
<td>248.57</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>24.908</strong></td>
<td><strong>24.908</strong></td>
<td><strong>24.908</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Anions</th>
<th>(meq·L⁻¹)</th>
<th>(mM)</th>
<th>(mg·L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>17.303</td>
<td>17.303</td>
<td>611.54</td>
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<tr>
<td>HCO₃⁻</td>
<td>4.241</td>
<td>4.241</td>
<td>258.64</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3.340</td>
<td>1.670</td>
<td>160.42</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.024</td>
<td>0.024</td>
<td>0.46</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>24.908</strong></td>
<td><strong>24.908</strong></td>
<td><strong>24.908</strong></td>
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</table>
Table C.2. Summary of results from measurements of nitrate and oxygen demand as a function of turbulence for Onondaga Lake sediments.

a. Sediment nitrate demand, non-normalized values ($SND_{\text{max}}$ in **bold**)

<table>
<thead>
<tr>
<th>Date</th>
<th>Pump Speed (rpm)</th>
<th>Turbulent Intensity (mm·s⁻¹)</th>
<th>$SND$, mean gN·m⁻²·d⁻¹</th>
<th>$SND$, s.d. gN·m⁻²·d⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-12-2008</td>
<td>2.0</td>
<td>0.07</td>
<td>0.023</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.24</td>
<td>0.052</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.44</td>
<td>0.063</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>4.57</td>
<td><strong>0.079</strong></td>
<td>0.006</td>
</tr>
<tr>
<td>10-16-2008</td>
<td>25.0</td>
<td>1.55</td>
<td><strong>0.176</strong></td>
<td>0.003</td>
</tr>
<tr>
<td>4-28-2009</td>
<td>2.0</td>
<td>0.07</td>
<td>0.096</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>1.55</td>
<td>0.252</td>
<td>0.028</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>4.57</td>
<td><strong>0.258</strong></td>
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<tr>
<td>7-29-09</td>
<td>10.0</td>
<td>0.44</td>
<td>0.123</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
<td>0.93</td>
<td><strong>0.181</strong></td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>4.57</td>
<td><strong>0.158</strong></td>
<td>0.006</td>
</tr>
</tbody>
</table>

**Grand Mean, $SND_{\text{max}}$**

|          |                  |                               | 0.168                   | 0.073                   |

b. Sediment nitrate demand, average normalized values (data source for Figure C.8a)

<table>
<thead>
<tr>
<th>Pump Speed (rpm)</th>
<th>Turbulent Intensity (mm·s⁻¹)</th>
<th>n</th>
<th>$SND$, mean gN·m⁻²·d⁻¹</th>
<th>$SND$, s.d. gN·m⁻²·d⁻¹</th>
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</thead>
<tbody>
<tr>
<td>2.0</td>
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<td>0.06</td>
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<tr>
<td>6.0</td>
<td>0.24</td>
<td>0.66</td>
<td></td>
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</tr>
<tr>
<td>10.0</td>
<td>0.44</td>
<td>0.79</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>1.55</td>
<td>0.98</td>
<td>0.00</td>
<td></td>
</tr>
<tr>
<td>50.0</td>
<td>4.57</td>
<td>1.00</td>
<td>0.00</td>
<td></td>
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Table C.3. Summary of results from measurements of oxygen demand as a function of turbulence for Onondaga Lake sediments.

a. Sediment oxygen demand, non-normalized values ($SOD_{\text{max}}$ in bold)

<table>
<thead>
<tr>
<th>Date</th>
<th>Pump Speed (rpm)</th>
<th>Turbulent Intensity (mm·s$^{-1}$)</th>
<th>$SOD$, mean gO$_2$·m$^{-2}$·d$^{-1}$</th>
<th>$SOD$, s.d. gO$_2$·m$^{-2}$·d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-8-2008</td>
<td>2.0</td>
<td>0.07</td>
<td>0.50</td>
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<td></td>
<td>6.0</td>
<td>0.24</td>
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<td>0.01</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>0.24</td>
<td>0.84</td>
<td>0.02</td>
</tr>
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<td></td>
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<td>1.55</td>
<td>1.01</td>
<td>0.02</td>
</tr>
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<td>1.55</td>
<td>1.07</td>
<td>0.01</td>
</tr>
<tr>
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</tr>
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<td>1.25</td>
<td>0.01</td>
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<td>4-14-2009</td>
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<td></td>
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<td>1.55</td>
<td>1.37</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
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<td>1.01</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>4.57</td>
<td>1.01</td>
<td>0.01</td>
</tr>
<tr>
<td>7-28-2009</td>
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<td>0.63</td>
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</tr>
<tr>
<td></td>
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<td>0.93</td>
<td>0.97</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>4.57</td>
<td>1.03</td>
<td>0.00</td>
</tr>
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</table>

Grand Mean, $SOD_{\text{max}}$ 1.09 0.11

b. Sediment oxygen demand, average normalized values (data source for Figure C.8b)

<table>
<thead>
<tr>
<th>Pump Speed (rpm)</th>
<th>Velocity (mm·s$^{-1}$)</th>
<th>n</th>
<th>$SOD$, mean gO$_2$·m$^{-2}$·d$^{-1}$</th>
<th>$SOD$, s.d. gO$_2$·m$^{-2}$·d$^{-1}$</th>
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</thead>
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<td>2.0</td>
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<td>1</td>
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</tr>
<tr>
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<td>2</td>
<td>0.76</td>
<td>0.03</td>
</tr>
<tr>
<td>10.0</td>
<td>0.44</td>
<td>3</td>
<td>0.66</td>
<td>0.06</td>
</tr>
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<td>17.5</td>
<td>0.93</td>
<td>1</td>
<td>0.94</td>
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<td>25.0</td>
<td>1.55</td>
<td>3</td>
<td>0.98</td>
<td>0.03</td>
</tr>
<tr>
<td>50.0</td>
<td>4.57</td>
<td>3</td>
<td>1.00</td>
<td>0.00</td>
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</table>
Figure C.1. Sediment oxygen demand and the diffusive boundary layer: (a) the physical environment; (b) oxygen profile with no consumption in the sediment; (c) oxygen profile with consumption in the sediment.
Figure C.2. The effect of changes in (a) the bulk liquid concentration and (b) the diffusive boundary layer thickness on sediment oxygen demand. In Panel A, a doubling of the bulk liquid oxygen concentration increases the profile slope (and thus the SOD) by a factor of 1.4. In Panel B, a 10-fold reduction in the thickness of the DBL increases the profile slope (and thus the SOD) by a factor of 2.4.
Figure C.3. Model-predicted oxygen profiles (a) without and (b) with a diffusive boundary layer. The bulk liquid oxygen concentration ($C_{\text{bulk}} = 2\rightarrow10 \text{ gO}_2\cdot\text{m}^{-3}$) is the same in both cases. In the absence of a DBL, the oxygen concentration at the sediment-water interface ($C_{\text{swi}}$) equals that of the bulk liquid ($C_{\text{bulk}}$). In the presence of a DBL (see Figure C.2b), $C_{\text{swi}}$ is less than $C_{\text{bulk}}$, reducing the concentration gradient and thus the SOD.
Figure C.4. Illustrating the role of (a) the bulk liquid concentration and (b) the diffusive boundary layer thickness in mediating model-predicted SOD separately and (c) together.
Figure C.5. Sediment flux reactor turbulence calibration.

\[
\text{intensity} = 0.0012 \cdot \text{rpm}^2 + 0.0319 \cdot \text{rpm} + 0.0064
\]
Figure C.6. Schematic drawing of the sediment flux chamber and supporting apparatus.
Figure C.7. Approach to steady state in the sediment flux chamber for (a) SOD and (b) SND.
Figure C.8. Relationship between normalized electron acceptor flux and turbulent intensity for (a) SND and (b) SOD.
Figure C.9. Management application of the turbulent intensity – electron acceptor flux relationship.