

FINAL TECHNICAL REPORT

**Lake Erie Protection Fund
Small Grants Program
Project Number: 347-08**

IMPROVED ESTIMATES OF SEDIMENT OXYGEN DEMAND

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Introduction/Background/Rationale

During the 1960s, Lake Erie experienced significant cultural eutrophication resulting in huge algal blooms, low oxygen waters, and fish kills (Snodgrass 1987). Research on Lake Erie played a major role in the limiting nutrient debate and in identifying phosphorus control as the best means of controlling eutrophication. The phosphorus was being released from wastewater treatment plants, as well as non-point sources such as agricultural runoff (DePinto et al. 1986). Study of these problems led to an ecosystem approach and the recognition of the relationship between nutrients and water quality and the implementation of the Great Lakes Water Quality Agreement (GLWQA) (Burns and Ross 1972; 1972 US/Canada Water Quality Agreement; IJC 1978). The basic approach was to synthesize process-oriented eutrophication research into complex mathematical models which relate nutrient loads to eutrophication symptoms. These ecosystem models were then used to set target P loads for each lake or major embayment, and the International Joint Commission (IJC) recommended programs that would achieve those loads. After the P loads were reduced to target levels, the models were post-audited and in general found to be "right on" in their predictions of the degree to which eutrophication symptoms would be decreased (DePinto et al. 1986). Twenty years later this process has been heralded as one of humankind's greatest environmental success stories and since then it has been copied and implemented in numerous other locations throughout the world.

Regular ship-board monitoring of oxygen in the hypolimnion of Lake Erie by the United States Environmental Protection Agency Great Lakes National Program Office (GLNPO) has been established to monitor the status of the lake and determine if the water quality is meeting the terms of the Great Lakes Water Quality Agreement (GLWQA). Their annual water quality monitoring reveals that in spite of reductions in phosphorus loadings over the past 20 years spring total phosphorus concentrations are as high as in the 1970s, Lake Erie bottom waters have gone anoxic in the late summer months and the areal extent of the anoxia has increased during recent years (Figure 1; Rockwell and Warren 2003). These observations can be termed 'The Lake Erie Trophic Paradox' (Matisoff and Ciborowski 2005). In essence, the traditional eutrophication model predicts that a decrease in phosphorus loading will result in a decrease in phosphorus concentration which will result in a decrease in algal production which will result in less hypolimnion oxygen depletion. This is exactly what was observed in Lake Erie during the 1970-1990 time period. Decreasing loadings of phosphorus during the 1970s to the 1990s were accompanied by decreases in phosphorus concentrations in the water column, decreases in the chlorophyll (algal) concentrations and decreases in the hypolimnetic oxygen depletion rate. However, since then these systems all appear to be disconnected. Although phosphorus loadings have remained at about the target loadings of 11,000 metric tons/year, phosphorus concentrations have increased to levels as high as in the 1970s while chlorophyll concentrations have dropped to the lowest values observed and oxygen depletion rates appear to have increased. It is not clear why these changes have occurred and they are the subject of much current research.

Oxygen in the hypolimnion decreases throughout the summer because of bacterial respiration and chemical oxidation reactions in the water and sediment and because of a limited resupply of oxygen from the atmosphere due to seasonal stratification. The rate of this seasonal decrease in the oxygen concentration is termed the 'hypolimnion oxygen depletion rate'. However, lake-wide monitoring is expensive and there is a difference of opinion on whether

dissolved oxygen depletion rate is a good indicator of the condition of Lake Erie. For example, changes to the ecosystem such as an increase in deep hypolimnetic or benthic primary production will supply oxygen to the hypolimnion even if other indicators (i.e., phosphorus concentrations) suggest that water quality conditions are poor. Conversely, nuisance algal blooms in the near shore regions of the Lake may be occurring independently of hypoxia in the deeper waters.

Clearly, the Lake Erie ecosystem has undergone significant and complex changes since P load control efforts achieved TP and chlorophyll *a* targets in the mid-1980s, including the introduction of dreissenid mussels, reduced lake water levels, enhanced water temperatures, and potentially enhanced non-point source inputs of P (Richards 2006). Each of these changes, individually and in combination, may affect the extent and magnitude of hypoxia. These findings indicate that there is a need to better understand carbon and energy flow in Lake Erie and how the current trophic system affects oxygen concentrations in lake water. This relatively small project employed a modeling approach to provide improved estimates of sediment-oxygen demand.

Although earlier water quality and ecosystem models recognize the importance of nutrients and sediment water exchange on the water quality of Lake Erie, they did not incorporate a very sophisticated description of the chemical exchange process and some did not incorporate internal chemical loading to the lake water. Early models focused on estimating internal phosphorus loadings because phosphorus was considered to be the limiting nutrient for primary production. The Army Corps 3-Basin Model (Rumer 1977) included a phosphorus regeneration term that assumed that the flux from the sediment is proportional to the phosphorus concentration in the sediment. Although that model has not been calibrated to current conditions in Lake Erie, results from the earlier work suggest that as much as half of the phosphorus loading to Lake Erie may be from diffuse internal sediment loading. More complex water quality models (Di Toro and Connolly 1980) also described chemical exchange between sediment and water as a simple proportionality to the concentration in the sediment. For example, for ammonia nitrogen, their model assumes that the chemical flux from the sediment is proportional to the organic nitrogen concentration in the sediment; the phosphorus flux is assumed to be proportional to the ammonia flux. These early models did not consider any linkages between oxygen, carbon, nitrogen, phosphorus, iron or manganese.

Although these earlier water quality and ecosystem models recognized the importance of nutrients and sediment water exchange on the water quality of Lake Erie, they did not incorporate a very sophisticated description of the chemical exchange process. A more sophisticated model of sediment organic matter and nutrient diagenesis (Berner 1974) described organic matter degradation as a steady-state diffusion-advection-reaction model of sulfate reduction in marine sediments (G-model) in which organic matter is oxidized (and nutrients released) in direct proportion to its own concentration. Models of this type can be considered ‘uncoupled, single electron acceptor’ models. Modifications to this basic model have included time dependence, multiple organic matter types, dependency on the oxidant concentration, seasonality and temperature dependency, bioturbation, pore water irrigation, age-dependent decay kinetics, inhibition of oxidants, and reintroduction of reduced byproducts. These individual modifications, while relatively sophisticated, still modeled the system as a single, uncoupled electron acceptor and therefore suffered from a lack of oxygen-nutrient coupling.

Recently, significant progress has been made in sediment chemical model development (Van Cappellen and Wang 1995; Soetaert et al. 1996; Wang and Van Cappellen 1996; Boudreau 1996; DiToro 2001). These newer models consider sequential and/or simultaneous electron acceptors that couple organic matter degradation with sediment oxygen consumption, nitrate reduction, the dissolution and reduction of manganese dioxide and ferric hydroxide, and sulfate reduction which results in the release of phosphate, ammonia, sulfide, dissolved manganese, dissolved iron, carbonate and methane. The models also consider the oxidation of upwardly mobile reduced substances (secondary redox reactions), and bioturbation and irrigation of bottom sediments. However, these models were developed for marine systems. When compared to Lake Erie, marine systems exhibit significantly lower sedimentation rates and organic matter, and significantly more sulfate and methane fermentation. Mechanisms for oxygen removal in sediments include diffusion and consumption by reaction. Oxygen in pore waters may be removed by microbial respiration (Van Cappellen and Wang 1995), reaction with a counter-diffusing reductant (Bouldin 1968), reaction with reduced solids (Boudreau 1996), and in the case of supersaturation the upward movement of gas bubbles. Adams et al. (1982) suggest that counter-diffusing ammonium and methane account for half of the SOD in Lake Erie. The mechanisms of metabolic reactions are extremely complex and most likely the consumption of oxygen is the result of many biologic and abiologic reactions.

Therefore, although the structure of these newer models can be used to describe sediment-water chemical exchange, the models need modification and calibration to be useful in freshwater environments and need to be linked to the water quality and physical models being developed by other researchers. Of particular value is that once these models are developed they can be readily applied to virtually any environment provided they are properly calibrated. The proposed work will do this for Lake Erie, but the model can easily be applied to other systems. This is especially useful in meeting the stated NOAA and Sea Grant program goals of developing models that can be used by resource managers to assess relative management strategies and make informed decisions regarding hypoxia in US coastal waters.

Objectives:

The project had four objectives:

1. Assemble a data set of sediment chemistry and sediment pore water chemistry suitable for use in model calibration.
2. Develop a relationship between available spatial chemistry data and sediment oxygen demand that will permit use of spatially-variant SOD in more complex models.
3. Apply and calibrate existing biogeochemical models of sediment oxygen demand (Matisoff and Neeson, 2005) in Lake Erie sediments.
4. Apply and calibrate the more complex Biogeochemical Reaction Network Simulator (BRNS) model (Wang and Van Cappellen 1996; Regnier et al. 2002) to provide predictions of the sediment oxygen demand and internal chemical loading to the hypolimnion of Lake Erie (Smith and Matisoff 2007). Link this model to the ECOFORE water quality framework.

Methodology

The proposed work plan consisted of 4 tasks:

1) All models require a calibration data. The ECOFORE physical model uses a 2 km grid spacing. While it is not possible to have chemistry and SOD data at such a high spatial resolution, any spatial resolution in these parameters will improve significantly the current hypoxia forecasts. In this task, existing data on pore water chemistry, sediment solids chemistry, and sedimentation rates were compiled from each of the basins in Lake Erie to generate a calibration data set. Unfortunately, sufficient data do not exist to generate a calibrated model for each basin. Data were derived from the PIs own pore water and chemistry data dating back 30 years, from the EPA monitoring cruises, from periodic collection of cores for other purposes such as those collected by John Robbins and Brian Eadie for sedimentation rate studies or those collected by Claire Schelske and Gene Stoermer for silica and diatom analysis, and more recent data collected by the GLERL IFYLE project, such as the Klump et al. (2005) report. These data were used to constrain model fitting parameters, recognizing that they were not collected at the same time from the same locations, so that the model calibrations may be somewhat limited.

2) The concentration of dissolved oxygen at a given depth is controlled by a suite of fluxes or processes, including the addition of oxygen to the upper water column due to photosynthesis and re-aeration, utilization of oxygen due to phytoplankton respiration, sediment oxygen demand (SOD), and CBOD (carbonaceous biochemical oxygen demand), and physical transport processes including vertical mixing and re-aeration. Both phytoplankton and detrital solids can settle from the water column to sediments. Sediment oxygen demand will be driven by the flux of organic carbon to the sediments. P flux from the sediments to the water column will be dependent on the TP in the sediments and the oxygen level in the bottom layer.

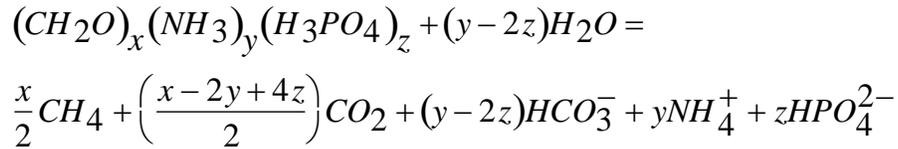
Although some SOD and pore water chemistry data exists, it is limited both spatially and temporally. It is also difficult to obtain, so model forecasts and future improvements, such as finer spatial resolution will be limited. In this task we developed a relationship between available chemistry data and sediment oxygen demand that enables higher spatial resolution SOD modeling and hence better hypoxia predictions. This was accomplished by conducting a suite of simulations and a sensitivity analysis using a range of values in the key variables in the diagenetic and SOD models to develop approximations between sedimentation rate, carbon flux SOD and the bioirrigation rate. In this manner, more abundant data, such as sedimentation patterns or sediment carbon concentrations may be correlated with SOD to improve SOD spatial resolution.

3) Link the Matisoff and Neeson (2005) SOD model to the Level 1 ECOFORE water quality model. This task was not completed as it was determined that the model calibration data set did not have sufficient spatial resolution to enable significant improvements in the ECOFORE modeling results.

4) SOD may be calculated as Fickian diffusion directly from the oxygen profile as was done by Matisoff and Neeson (2005) or may be calculated as the sum of all oxygen consumption reactions in the sediment, including secondary reactions such as reduced iron phase oxidation as

was done by Matisoff, Rodríguez Aguilera and Thullner (2004) and Smith and Matisoff (2007). In this work, the BRNS model code was generated in such a way to output a format that readily permitted calculating SOD. FORTRAN code was generated to permit linkage to the ECOFORE water quality model.

This work used the Biogeochemical Reaction Network Simulator (BRNS) (Regnier et al. 2002) to calculate the sediment oxygen demand (SOD). The BRNS model is a computationally modified version of the biogeochemical model STEADYSED1 (Van Cappellen and Wang 1995, Wang and Van Cappellen 1996) but with modified Monod kinetics. The BRNS model fully incorporates reaction couplings among C, O, N, S, Fe and Mn in pertinent biogeochemical reactions to calculate coupled solid phase and solute sediment diagenetic reactions. The BRNS uses a MAPLE pre-processor for automatic code generation, a numerical engine that links the solving routines of transport equations to nonlinear equations generated from the pre-processor, and a web interface. The underlying biogeochemical model is a multicomponent early diagenetic reactive transport model that accounts for solute transport by molecular diffusion, porewater irrigation, and sediment burial advection and particulate transport by bioturbation and advective burial. In the model organic matter is mineralized by specific modified Monod kinetic reaction pathways that include the 6 primary redox reactions: oxic mineralization, denitrification, oxidation by manganese and iron oxyhydroxides, dissimilatory sulfate reduction, and methanogenesis. For example, organic matter degradation by methane fermentation, the last reaction in the sequence, may be described as



The rate of this reaction is given by

$$R_{CH_4} = \left(\frac{R_{CH_4\max} [CH_4]}{K_{CH_4} + [CH_4]}\right) \cdot \left(\frac{K'_{SO_4}}{K'_{SO_4} + [SO_4]}\right) \cdot \left(\frac{1}{1 + \frac{K'_{Fe(III)}[Fe(III)]}{[Fe(III)]_o}}\right) \cdot \left(\frac{1}{1 + \frac{K'_{MnO_2}[MnO_2]}{[MnO_2]_o}}\right) \cdot$$

$$\left(\frac{K'_{NO_3}}{K'_{NO_3} + [NO_3]}\right) \cdot \left(\frac{K'_{O_2}}{K'_{O_2} + [O_2]}\right)$$

Similar degradation and kinetic reactions can be written for each degradation pathway. This kinetic formulation insures that exhaustion of the terminal electron acceptor causes the corresponding pathway for organic carbon oxidation to come to a halt and permits vertical overlap between successive metabolic pathways. It also avoids the *a priori* assignment of a depth interval to each pathway considered. The components are coupled through the reaction terms and through organic carbon. The overall rate of organic matter degradation is equal to the sum of the individual pathway degradation rates.

The BRNS model can be used to provide an estimate of the sediment oxygen demand, where SOD is equal to the sum of the depth integrated rates of each of the metabolic pathway reactions. Model coefficients are constrained by matching pore water profiles of O_2 , NO_3^- , NH_4^+ , HCO_3^- , SO_4^{2-} , Fe^{2+} , and Mn^{2+} and solid phase profiles of Fe and Mn. Additional input data includes the organic carbon profile, the CH_4 profile, and the HPO_4^{2-} pore water profile which were obtained from previous our previous work. The values for the temperature dependency (α) and molecular diffusion coefficients (D_o) of all species examined were taken from VanCappellen and Wang (1995). Rate parameters for the six primary redox reactions are derived by the BRNS and are combined to obtain an overall SOD.

Results and Discussion

The BRNS model was calibrated against the compiled sediment and pore water data sets and modified to calculate the SOD. This was accomplished by using two different pools of organic matter of different reactivities (one highly reactive representing fresh organic matter and one more refractory representing older organic matter), adding in secondary and equilibrium reactions (see Table 1), and calculating SOD as the depth integrated sum of reactions that consumed oxygen. Table 1 also includes some physical model parameters.

In addition to the reactions and physical parameters given in Table 1 the model requires input for compound specific parameters that describe the molecular diffusion coefficient and its temperature dependency, and upper and lower boundary conditions. The values used in the calibrated model are given in Table 2.

Sensitivity analysis of the BRNS model revealed that the two most sensitive parameters are the concentration of organic matter and the SOD required to match the observed O_2 concentration profile in the porewaters (Smith and Matisoff 2008). The BRNS model results were constrained by sediment solid, pore-water, and microprofile concentration data. In most cases the model was able to reproduce similar trends as those seen in the data and was able to very accurately reproduce the dissolved oxygen concentration profiles and were used to calculate an SOD.

Simulated pore water and sediment solids concentrations and the comparable data compiled from the various data sources are given in Figures 1-9 for oxygen, methane, ferrous iron, solid phase iron, dissolved manganese, solid phase manganese, ammonium, nitrate, and sulfate. The calculated SOD for this simulation is $SOD = 22.5 \text{ mmol/m}^2/\text{yr}$. While it is possible to improve the model fits for one parameter, for example, for iron, such improvement usually comes at the expense of another parameter, such as oxygen or sulfate. For example, Figure 10 illustrates a better model fit for iron. Only one set of methane pore water concentrations could be found in the literature, and it was published in 1981.

One additional set of simulations were conducted to evaluate the effect of bioirrigation on SOD. This simulation assumed a likely range of bioirrigation coefficients based on a literature review. Mayflies and other burrow-dwelling benthic organisms have become more abundant due to

Table 1. Primary, secondary, acid-base, and adsorption reactions and physical parameters used in the model.

Reactions	Physical Domain	Value Units	Source	Reaction Network Parameters	Value	Source
Primary Reactions	Porosity	0.8	Smith and Matisoff (2007)	KsFeS	6.30E-03	default BRNS value
Denitrification Refrac	Burial Velocity	0.197 cm/y	Smith measured	Kfemno2	1.00E+05	Canavan (2006)
Denitrification*25	Bioturbation	$D_b=2.5\text{erfc}(x-8) \times \text{in cm}$		kfe02	5.00E+05	within Canavan (2006) range
Fe(III) Reduction Refrac	Biot at Boundary	1		kfesprecip	1.50E+03	Canavan (2006)
Fe(III) Reduction	Bio depth	8		kfesreox	2.00E+06	Canavan (2006)
Methanogenesis Refrac	Bio attenuation coeff	1		kfox	1.08E+00	calculated based on Boudreau (1997)
Methanogenesis	No Bioirrigation			kfoxref	2.30E-03	calculated based on Boudreau (1997)
Mn(IV) Reduction Refrac	Redfield Ration	106:16:1	Smith estimated	kmethox1	1.00E+10	Canavan (2006)
Mn(IV) Reduction	Temperature	12 oC	Smith measured	kmethox2	1.00E+05	within Canavan (2006) range
Oxic Degredation Refrac	Salinity	0.01 0/00	Smith and Matisoff (2007)	kmfeoh3	2.00E-04	Canavan (2006)
Oxic Degredation*100	Solid Phase Density	2.5 g/cm ³	Smith and Matisoff (2007)	kmno2	1.60E-05	Canavan (2006)
Sulfate Reduction Refrac				kmno3	1.00E-05	Canavan (2006)
Sulfate Reduction				kmnox	3.50E+05	within Canavan (2006) range
				kmo2	8.00E-06	Canavan (2006)
				kms04	1.00E-04	Canavan (2006)
Secondary Reactions	Acid/Base Reactions			knh4ads	1.40E+00	Canavan (2006)
FeS Precipitation	Bicarbonate Dissociation			knit	2.00E+03	model fit
FeS re-oxidation via O ₂	Carbonic Acid Dissociation			ksulfox1	1.00E+05	model fit (slightly below range given in Canavan (2006))
Methane Reoxidation (O ₂)				ksulfox2	7.50E+03	Canavan (2006)
Methane Reoxidation (SO ₄)	Adsorption Reactions			ksulfox3	2.50E+03	Canavan (2006)
Mn re-oxidation via O ₂	Ammonia Adsorption					
Nitrification (O ₂)						
Sulfide Dissociation						
Sulfide Oxidation (Fe(OH) ₃)						
Sulfide oxidation (MnO ₂)						
Sulfide Oxidation (O ₂)						

Table 2. Compound specific parameters such as the molecular diffusion coefficient and its temperature dependency, and upper and lower boundary conditions used in the calibrated model.

ch20	molecular diffusion coeff	0
	temp depend	0
	Upper boundary condition	ff 3.94e-4
	lower boundary condition	fg 0.0
ch20 ref	initial condition	2.00E-03
	molecular diffusion coeff	0
	temp depend	0
	Upper boundary condition	ff 9.85e-5
ch4	lower boundary condition	fg 0.0
	initial condition	5.00E-04
	molecular diffusion coeff	263.935
	temp depend	5.20E-02
co2	Upper boundary condition	fc 0.0
	lower boundary condition	fg 0.0
	initial condition	0
	molecular diffusion coeff	320.04
co3	temp depend	6.00E-02
	Upper boundary condition	fc 1.73 e-5
	lower boundary condition	0
	initial condition	1.73E-05
fe2	molecular diffusion coeff	176.086
	temp depend	4.70E-02
	Upper boundary condition	fc 1e-20
	lower boundary condition	fg 0.0
feoh3	initial condition	1.00E-20
	molecular diffusion coeff	136.242
	temp depend	4.40E-02
	Upper boundary condition	fc 2.0e-5
fes	lower boundary condition	fg 0.0
	initial condition	2.00E-05
	molecular diffusion coeff	0
	temp depend	0.00E+00
h2s	Upper boundary condition	ff 1.97e-6
	lower boundary condition	fg 0.0
	initial condition	1.00E-05
	molecular diffusion coeff	0
h2s	temp depend	0.00E+00
	Upper boundary condition	ff 0.0
	lower boundary condition	fg 0.0
	initial condition	0.00E+00
h2s	molecular diffusion coeff	331.608
	temp depend	6.00E-02
	Upper boundary condition	fc 1e-20

	lower boundary condition	fg 0.0
	initial condition	0.00E+00
hco3	molecular diffusion coeff	217.216
	temp depend	4.80E-02
	Upper boundary condition	fc 9.88e-4
	lower boundary condition	fg 0.0
	initial condition	9.88E-04
hplus	molecular diffusion coeff	2273.7
	temp depend	2.60E-02
	Upper boundary condition	fc 3.98e-8
	lower boundary condition	fg 0.0
	initial condition	3.98E-08
hpo4	molecular diffusion coeff	112.3577
	temp depend	5.40E-02
	Upper boundary condition	fc 12.353e-6
	lower boundary condition	fg 0.0
	initial condition	1.24E-05
hs	molecular diffusion coeff	392.01
	temp depend	3.10E-02
	Upper boundary condition	fc 1.7e-19
	lower boundary condition	fg 0.0
	initial condition	1.70E-19
mn2	molecular diffusion coeff	123.289
	temp depend	5.00E-02
	Upper boundary condition	fc 1.2e-5
	lower boundary condition	fg 0.0
	initial condition	1.20E-05
mno2	molecular diffusion coeff	0
	temp depend	0.00E+00
	Upper boundary condition	ff 7.5e-7
	lower boundary condition	fg 0.0
	initial condition	3.80E-06
nh4	molecular diffusion coeff	395.87
	temp depend	4.10E-02
	Upper boundary condition	1.34E-04
	lower boundary condition	fg 0.0
	initial condition	1.34E-04
nh4ads	molecular diffusion coeff	0
	temp depend	0.00E+00
	Upper boundary condition	ff 0.0
	lower boundary condition	fg 0.0
	initial condition	0.00E+00
no3	molecular diffusion coeff	394.5878
	temp depend	3.80E-02
	Upper boundary condition	fc 9.5e-5
	lower boundary condition	fg 0.0

o2	initial condition	9.50E-05
	molecular diffusion coeff	380.4495
	temp depend	6.00E-02
	Upper boundary condition	fc 1.41e-4
	lower boundary condition	fg 0.0
so4	initial condition	1.41E-04
	molecular diffusion coeff	172.92
	temp depend	4.50E-02
	Upper boundary condition	fc 1.4e-4
	lower boundary condition	fg 0.0
	initial condition	1.40E-06

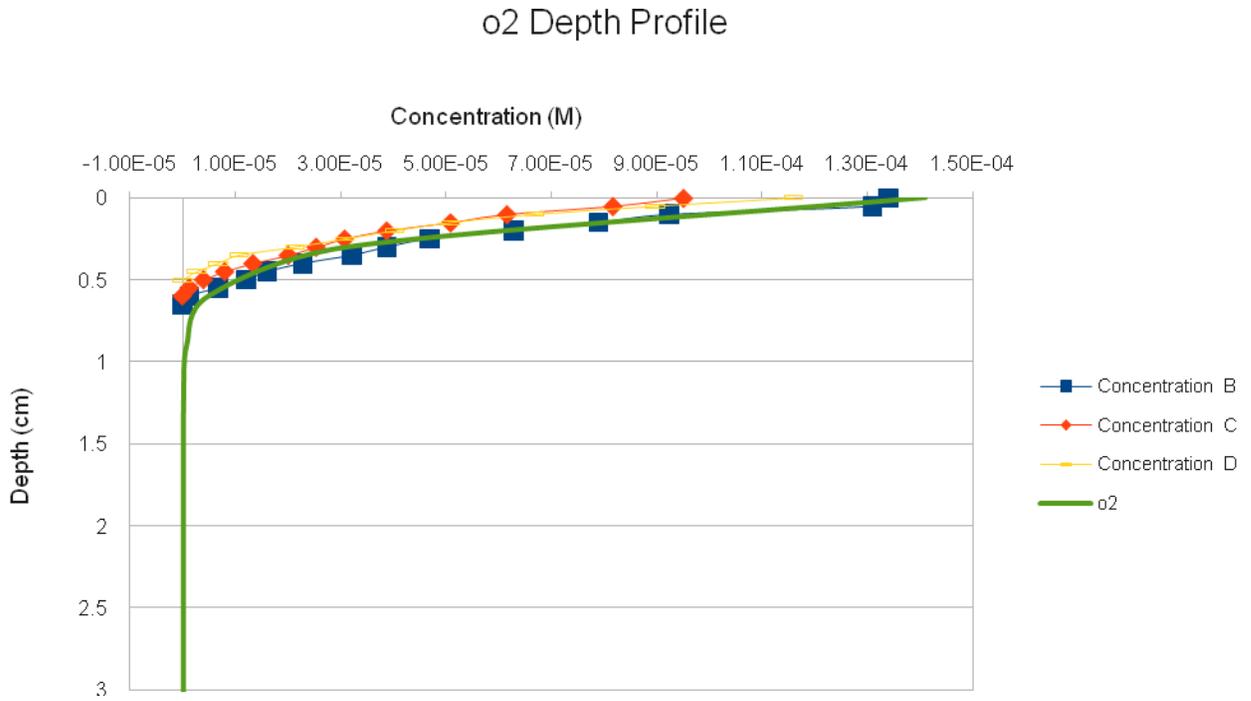


Figure 1. Model simulation of pore water oxygen concentrations along with three pore water profiles of oxygen concentrations.

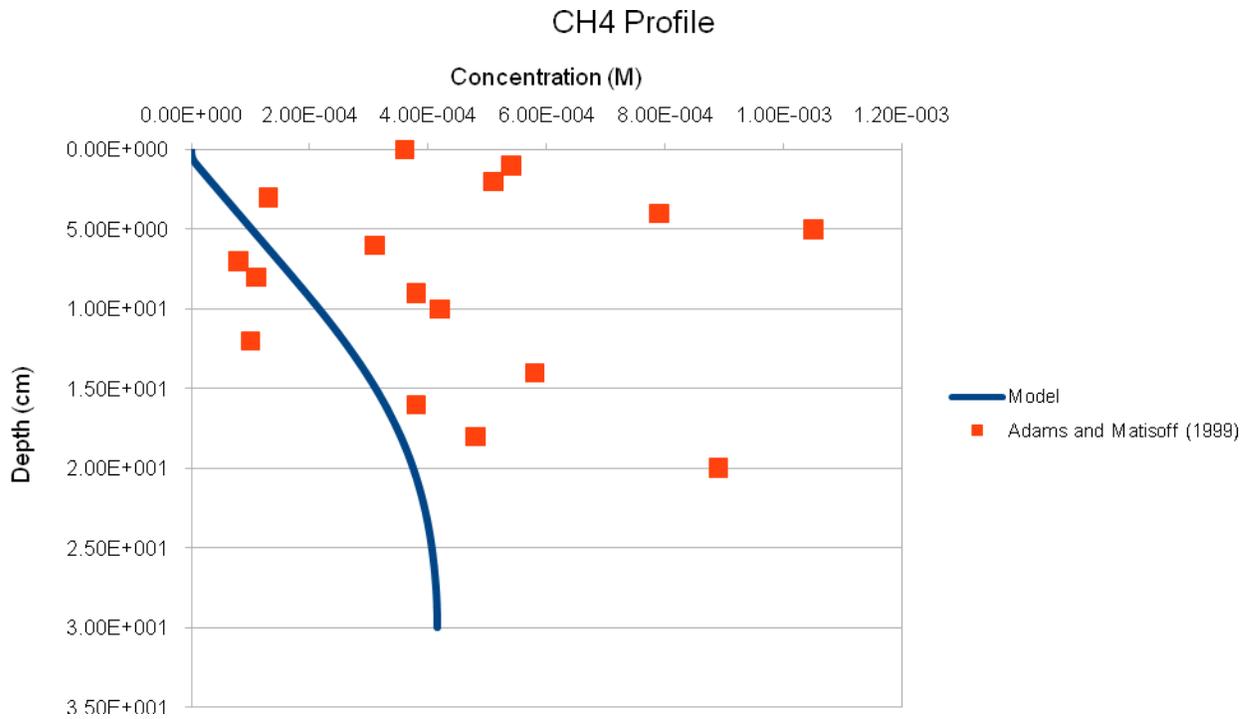


Figure 2. Model simulation of pore water methane concentrations along with pore water concentration profiles of methane concentrations.

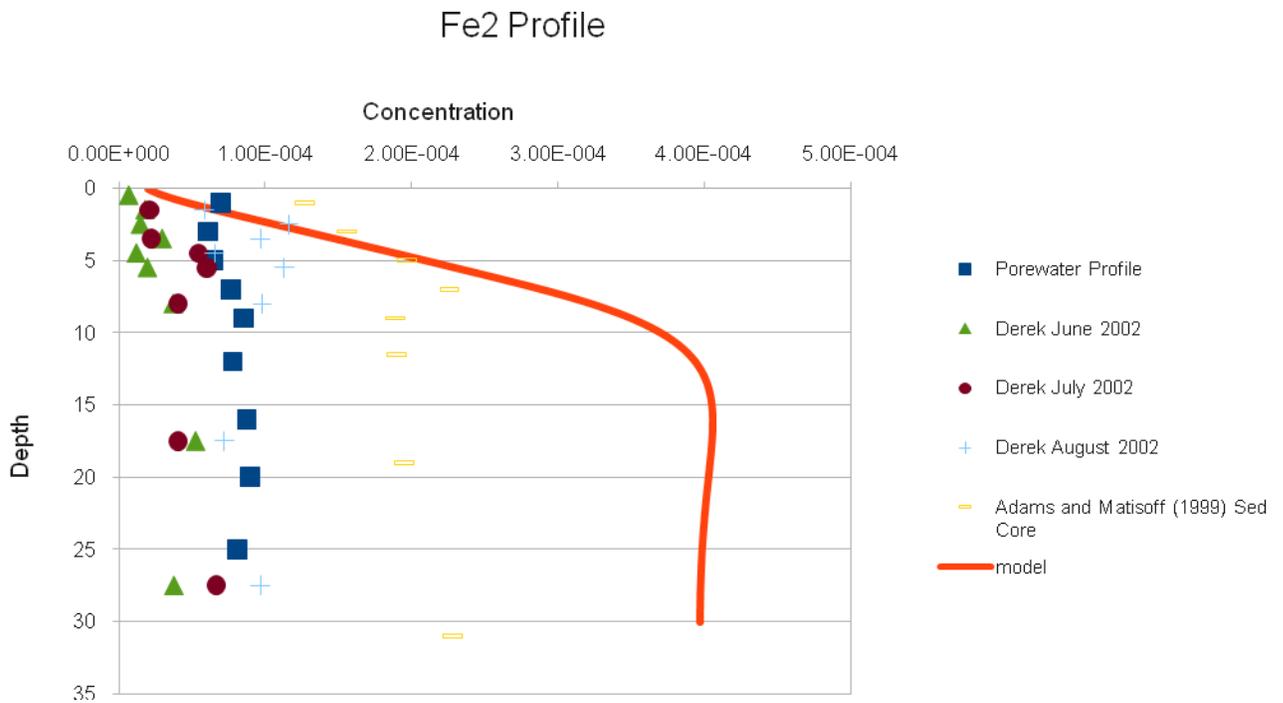


Figure 3. Model simulation of pore water ferrous iron concentrations along with pore water concentration profiles of iron concentrations in cores collected in 1981 and 2002.

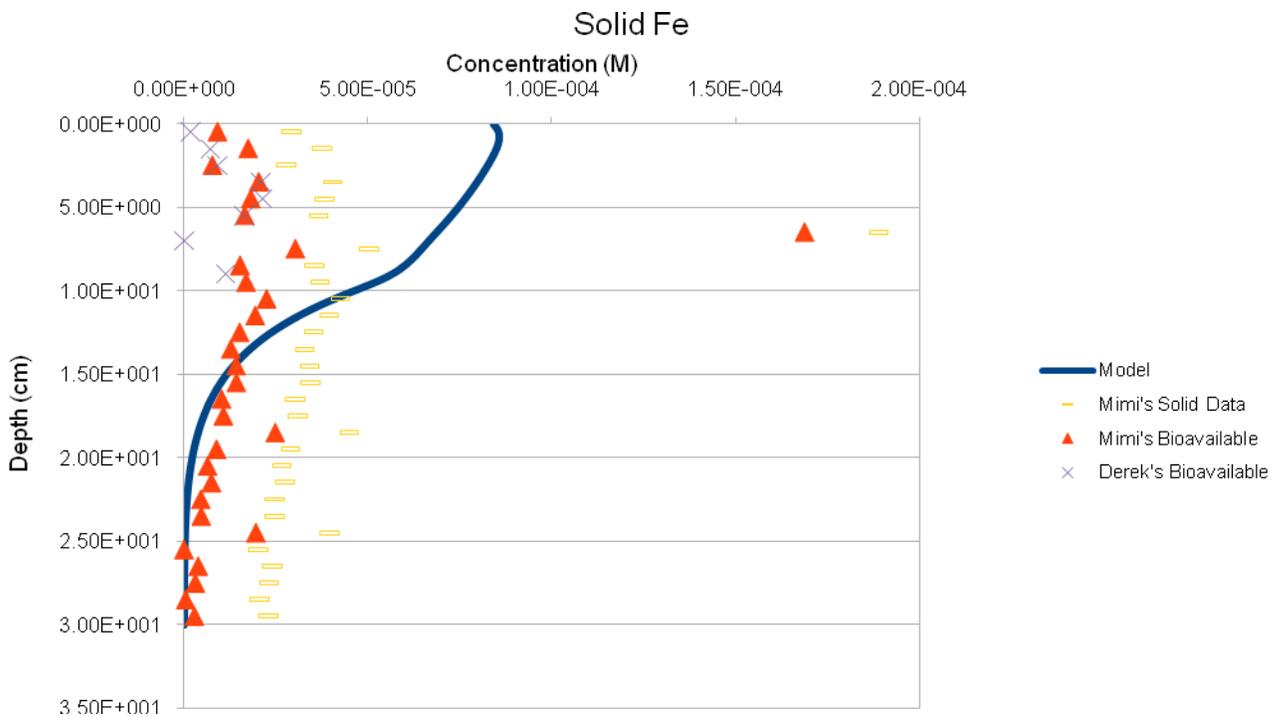


Figure 4. Model simulation of solid phase iron concentrations along with extractable iron concentration profiles in cores collected in 2002 and 2007.

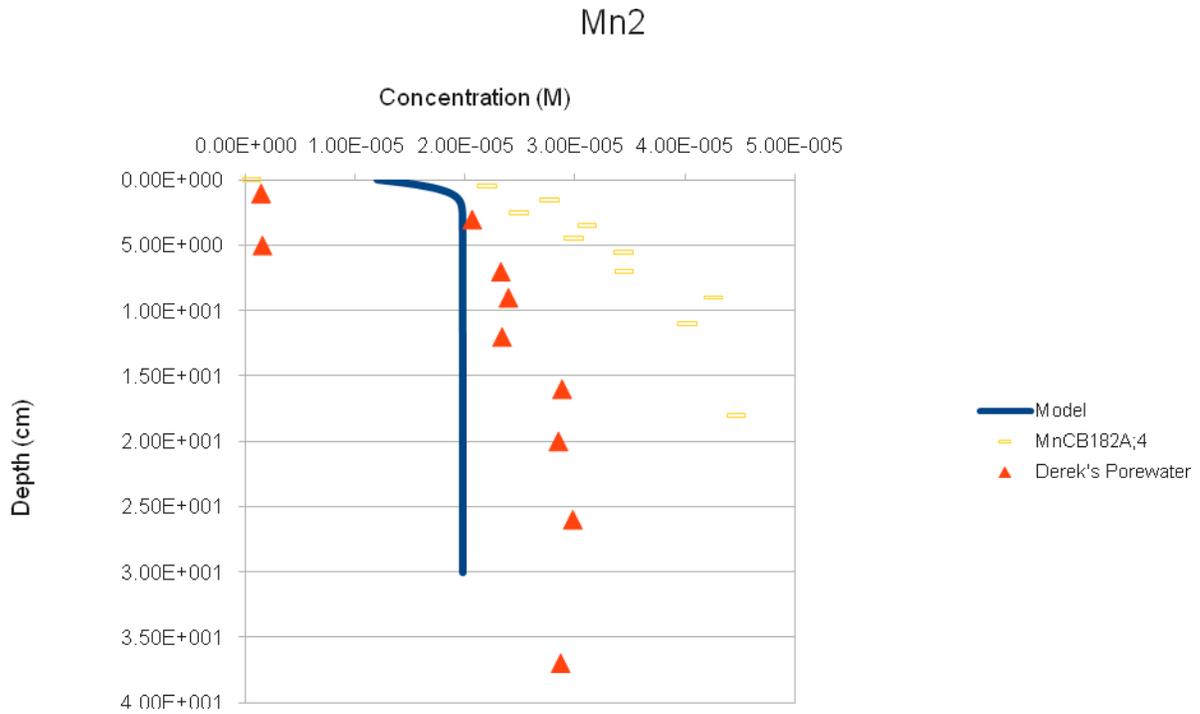


Figure 5. Model simulation of dissolved manganese concentrations along with pore water concentration profiles of manganese concentrations in cores collected in 1981 and 2002.

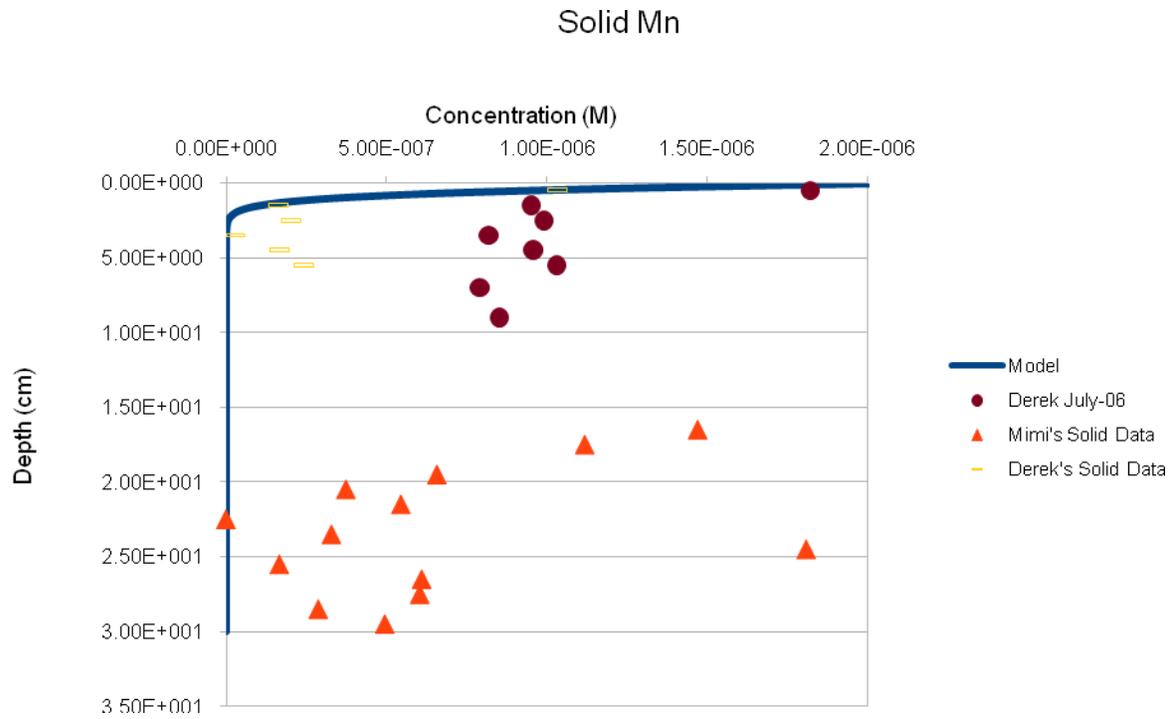


Figure 6. Model simulation of solid phase manganese concentrations along with extractable manganese concentration profiles in cores collected in 2002 and 2007.

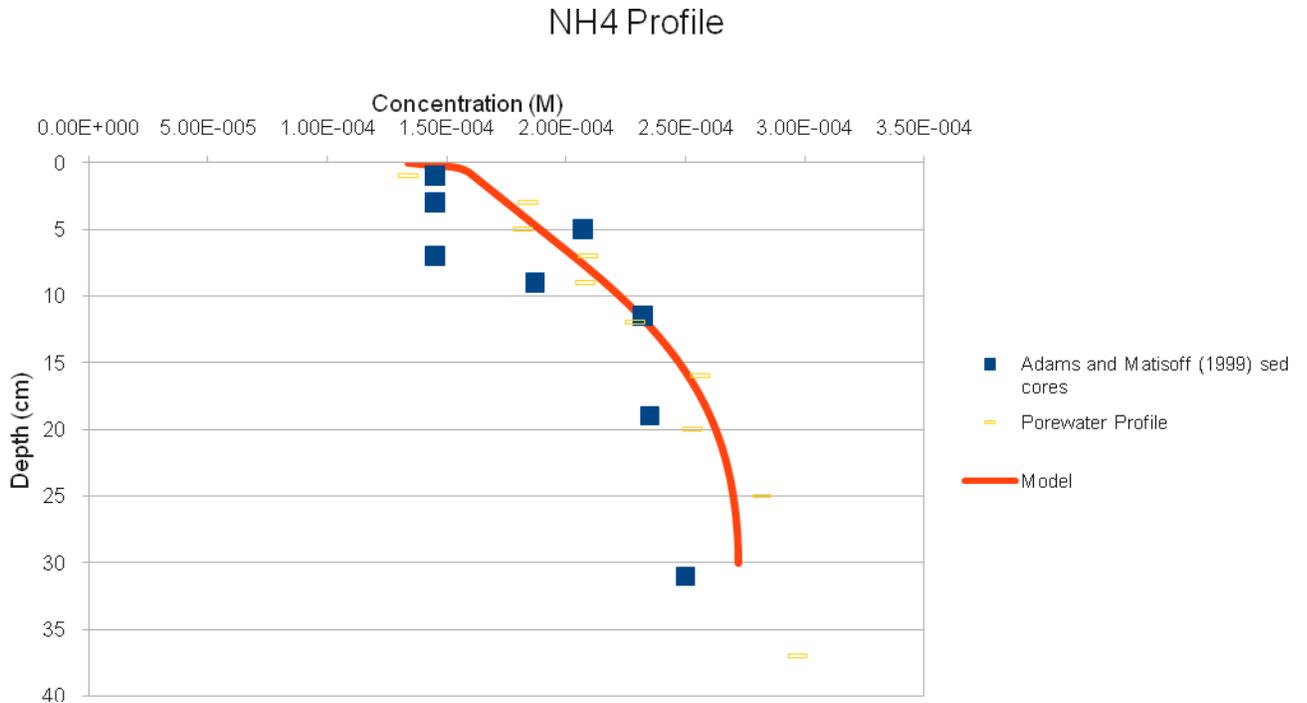


Figure 7. Model simulation of dissolved ammonium concentrations along with pore water concentration profiles of ammonium concentrations in cores collected in 1981 and 2002.

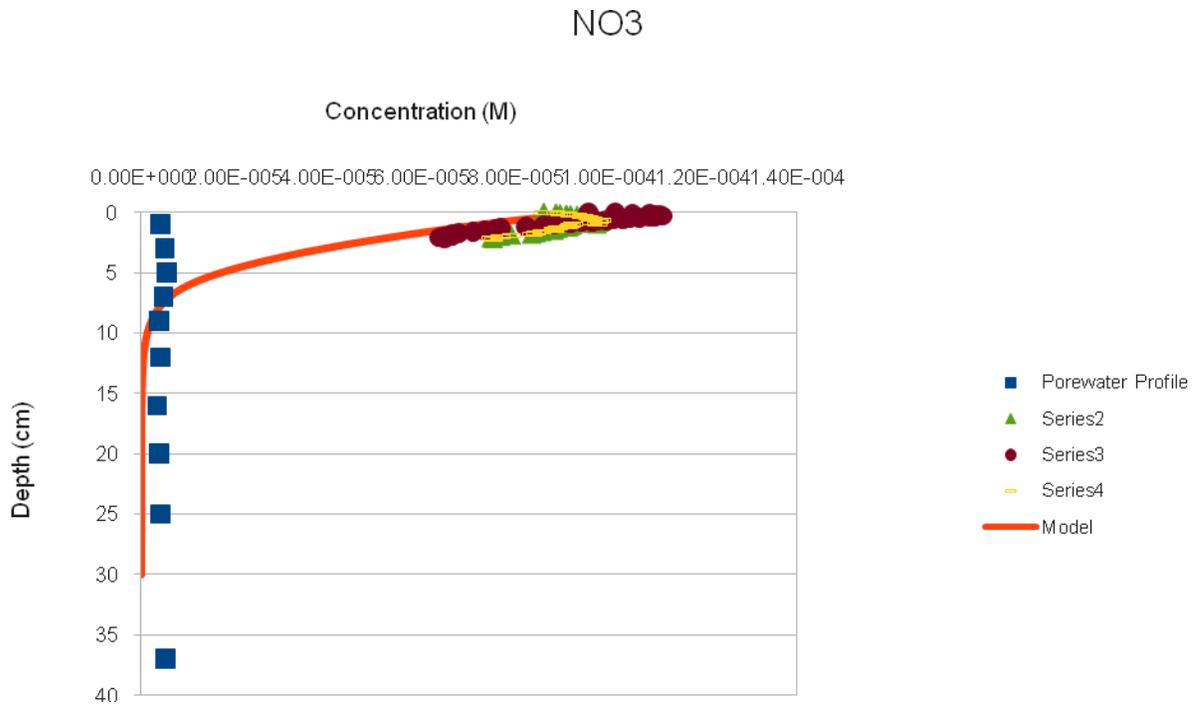


Figure 8. Model simulation of dissolved nitrate concentrations along with pore water concentration profiles of nitrate concentrations in cores collected in 2002.

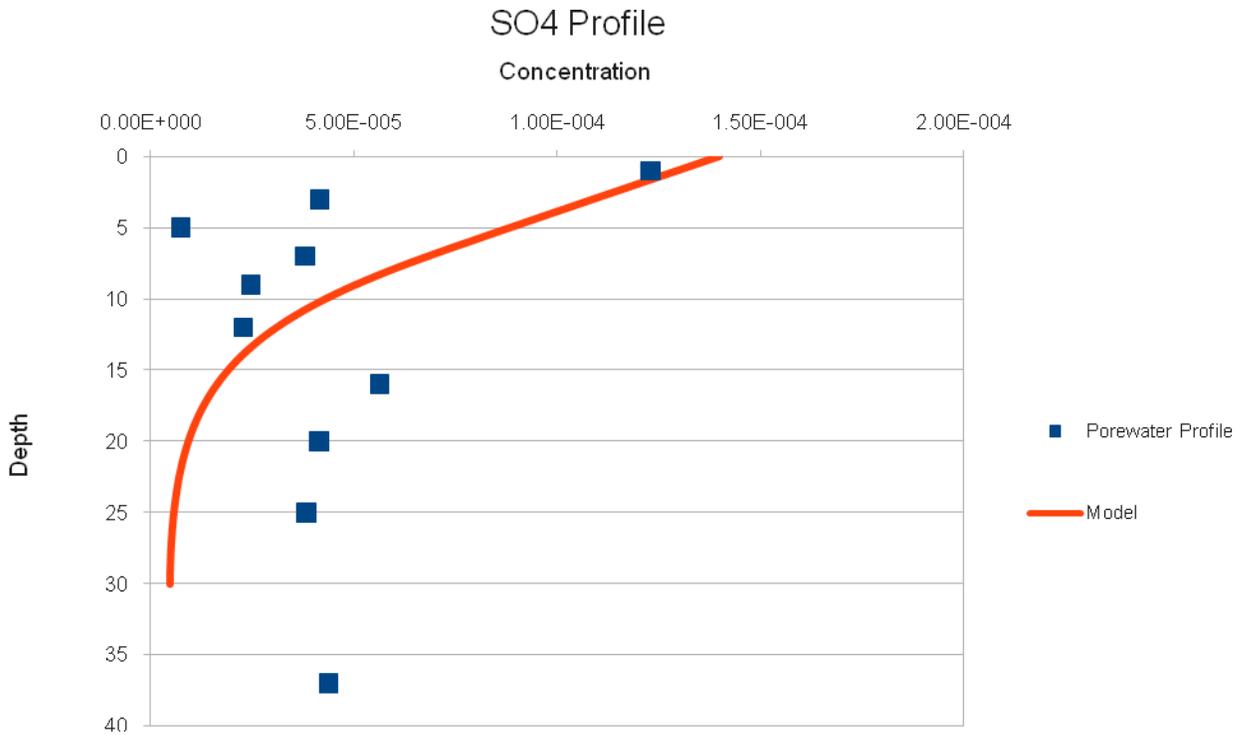


Figure 9. Model simulation of dissolved sulfate concentrations along with pore water concentration profiles of sulfate concentrations in cores collected in 2002.

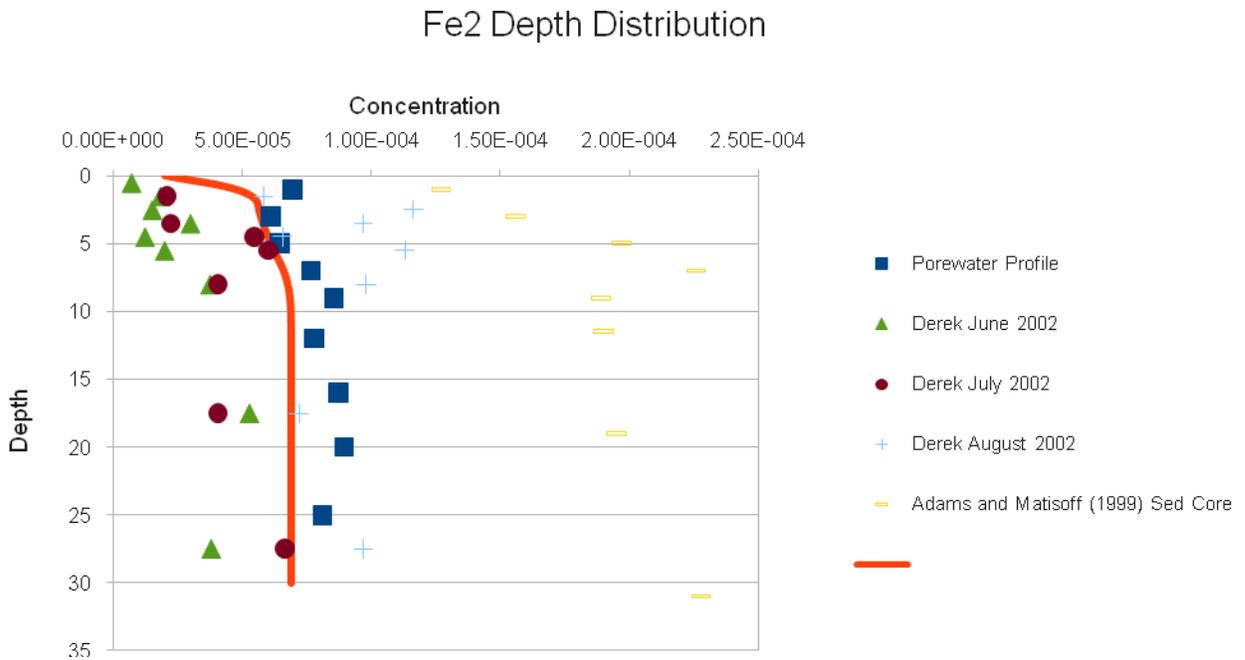


Figure 10. Model simulation of pore water ferrous iron concentrations along with pore water concentration profiles of iron concentrations in cores collected in 1981 and 2002.

improvements in water quality and it is possible that they may significantly increase SOD, and thus impact hypolimnetic dissolved oxygen concentrations. *Hexagenia* (mayfly) abundances in western Lake Erie declined catastrophically from dominance prior to the early 1950s to being rare by 1960 (Reynoldson et al., 1989). Recent improvements in the water quality of western Lake Erie have resulted in a recovery of the benthic community and the return of *Hexagenia* nymphs (Kreiger et al., 1996; Schloesser and Nalepa, 2001; Krieger et al., 2007). Densities of mayflies in western Lake Erie increased exponentially between 1991 and 1997 (Madenjian et al., 1998), and by 1997-98 were greater or similar to densities found in 1929-1930 (Schloesser et al., 2000). Because mayfly nymphs are burrow irrigators and can enhance the exchange of materials across the sediment-water interface (Matisoff and Wang, 1998) their return might be expected to increase SOD and affect water quality. Similarly, *Chironomus* spp. larvae are abundant and widely distributed across the central basin and can be found at densities up to 1000 m⁻² (Soster et al., 2001). The effects of burrowing mayfly nymphs and chironomid larvae on oxygen exchange between water and sediments in large lakes in general and Lake Erie in specific suggest the effects may be significant (Edwards et al., 2009).

Our simulations verify the significance of the effect of bioirrigation on SOD (Figure 11). Alpha (cm³/y) is a parameter that represents the rate of pore fluids exchanged by the macrobenthos. As is evident in Figure 11, SOD would be expected to increase by about a factor of 2 over the range of irrigation rates anticipated. This calculation supports previous findings that macrobenthos increase SOD and demonstrate that the BRNS model enables us to quantify those effects. Furthermore, the model permits the calculation of SOD as a function of macrobenthic populations, enabling the extrapolation of field benthic survey data to estimates of SOD.

These results are significant because it augments the coordinated current ECOFORE modeling project. Once completed the linked models may be used to evaluate the relative role of interannual variability of thermocline depth (i.e., hypolimnion volume) and P loading on the timing and extent of hypoxia. In addition, the models may be used to determine the relative contribution of each forcing function to hypoxia and whether that relationship has changed by conducting appropriate sensitivity analyses on selected model years. The ultimate goal is to use ensemble model predictions that capture both model uncertainties and the effects of variable climate, hydrology, dreissenid abundance, and P loading. Model simulations will enable estimates of variations in areal extent and timing (and thus habitat impact) of hypoxia under varying loads and climate, as input to ecological impact models. These analyses will allow us to determine the portion of the hypolimnion oxygen depletion rate that can be attributed to each factor. The model simulations are directly applicable to nutrient cycling and bioenergetic models, ecosystem models, and SOD monitoring. These data and eventual calculations of calibrated models of nutrient cycling and anoxia forecasting can help reduce uncertainty by increasing an understanding of the conditions that lead to hypoxia and in establishing target nutrient loadings. The results can be used by resource managers to assess management strategies and enable them to make informed decisions regarding hypoxia in Lake Erie. The project helps close the gaps between data generators, modelers, and resource managers. The data created from this project will be useful in the future evaluation of target chemical loads for Lake Erie. The project addresses the Great Lakes Water Quality Agreement, the Ecosystems and Habitats Thematic area

of Ohio Sea Grant's Strategic Plan, and the Ensure Sustainable Water Use objective of the Great Lakes Governor's Priorities.

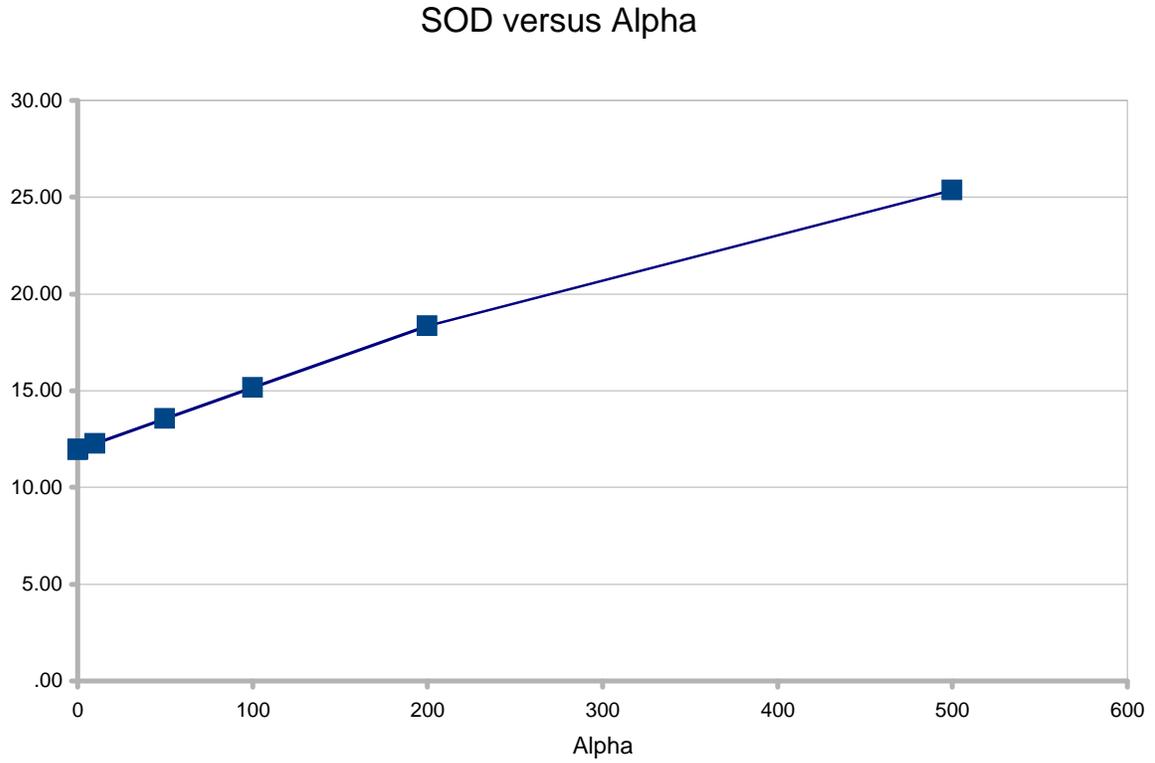


Figure 11. Effect of bioirrigation on SOD over the range of bioirrigation rates anticipated to be occurring in the central basin of Lake Erie.

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