Oxygen Concentration and Demand in Lake Erie Sediments

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ABSTRACT. *Regular ship-board monitoring of oxygen in the hypolimnion of Lake Erie 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). 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. One the most poorly known components of the Lake Erie oxygen budget is the sediment-oxygen demand (SOD). In this work, vertical oxygen concentration profiles in Lake Erie sediments are measured by incrementally inserting a micro-oxygen electrode. The SOD is the flux of oxygen across the sediment-water interface and is calculated from the oxygen profiles assuming Fickian diffusion at the sediment-water interface. Oxygen consumption was measured in sediments collected on four dates from 3, 13, and 5 stations in the western, central, and eastern basins, respectively. Oxygen concentration profiles in the sediment and the SOD are well described by a diffusion/reaction transport model where oxygen diffuses into the sediment and is consumed by reactions that follow Michaelis-Menten kinetics. The flux of oxygen into the sediment in the central basin in August 2002 was $1.03 \pm 0.271 \times 10^{-11}$ mol $O_2/cm^2/sec$, within about 30% of the hypolimnetic oxygen depletion rate derived from monitoring. These results suggest that modeling of oxygen profiles hold promise as an alternative technique to regular monitoring for determining hypolimnetic oxygen depletion rates.*

INDEX WORDS: *Oxygen, oxygen profiles, micro-electrode, sediment-oxygen demand, Lake Erie.*

INTRODUCTION

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 U.S./Canada Water Quality Agreement, IJC 1978). The basic approach was to synthesize process-oriented eutrophication research into complex mathematical models describing the relationship between nutrient loads and eutrophication symptoms. These 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 accurate in their predictions of the degree to which eutrophication symptions would be decreased (DePinto *et al.* 1986). Twenty years later this process was 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.

The United States Environmental Protection Agency (U.S. EPA) Great Lakes National Program Office monitors the water quality in Lake Erie as part of the Great Lakes Water Quality Agreement. 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

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have gone anoxic in the late summer months and the areal extent of the anoxia has increased during recent years (Rockwell *et al.* 2005). 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. This seasonal decrease in the oxygen concentration is termed the "hypolimnion oxygen depletion rate" and there is a difference of opinion on whether it 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.

Because water column oxygen concentrations are impacted by trophic dynamics, these findings indicate that there is a need to better understand how recent ecosystem changes affect oxygen concentrations in lake water. 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 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. 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 still suffered from a lack of comprehensive inclusion and from oxygen-nutrient coupling. Mechanisms for oxygen removal in sediments include diffusion and consumption by reaction. Oxygen in pore waters may be removed by microbial respiration (Rabouille and Gaillard 1991a), reaction with a counterdiffusing 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 ex-

tremely complex and most likely the consumption of oxygen is the result of many biologic and abiologic reactions. 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). These newer models 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 reoxidation of upwardly mobile reduced substances, and bioturbation and irrigation of bottom sediments. However, these models were developed for marine systems. Compared to Lake Erie, marine systems exhibit significantly lower sedimentation rates and organic matter, and significantly more sulfate and methane fermentation. Therefore, although the structure of these newer models can be used to describe sediment-water chemical exchange, they will need modification to be useful in freshwater environments. In addition, they will need appropriate calibration to the appropriate Lake Erie environment.

As a first step in the development of such a comprehensive model, this work focuses on the most poorly known component of the Lake Erie oxygen budget, the sediment-oxygen demand (SOD). SOD is the flux of oxygen from the water column into the bottom sediment and consists of microbial and macrobenthic respiration, oxidation of reduced solids and oxidation of reduced, counter-diffusing dissolved gases and solutes. Although microbial respiration is only one component of a comprehensive biogeochemical model, for the purposes of calculating SOD from modeled oxygen profiles, we assume it to be the majority of the cause of oxygen consumption (Murray and Grundmanis 1980). Technological advancements in the measurement of dissolved oxygen using microelectrodes have enabled the determination of detailed oxygen profiles in sediments (Revsbech *et al.* 1980, Revsbech *et al.* 1986, Reimers and Smith 1986, Glud *et al.* 2003) that have been used to calculate the flux of oxygen across the sediment-water interface. These measurements of the SOD have been used to constrain models representing oxic diagenetic processes (Reimers and Smith 1986). In this study, oxygen microelectrodes were used to obtain vertical oxygen concentration profiles in Lake Erie sediments, and these profiles were used to calculate the SOD. The flux of