140
034
THS

THESIS
2007

LIBRARY
Michigan State
University

This is to certify that the
thesis entitled

LAKE METABOLISM AND TROPHIC STATE IN LAKE ERIE: EVALUATION BASED ON R:P RATIOS DETERMINED BY THE CONCENTRATION AND STABLE ISOTOPIC COMPOSITION OF DISSOLVED O_2

presented by

LEAH K. PIWINSKI

has been accepted towards fulfillment
of the requirements for the

M.S. degree in GEOLOGICAL SCIENCES

Nathan E. Ostrom
Major Professor's Signature

April 12, 2007
Date

MSU is an affirmative-action, equal-opportunity employer

PLACE IN RETURN BOX to remove this checkout from your record.
TO AVOID FINES return on or before date due.
MAY BE RECALLED with earlier due date if requested.

DATE DUE	DATE DUE	DATE DUE

6/07 p:/CIRC/DateDue.indd-p.1

LAKE METABOLISM AND TROPHIC STATE IN LAKE ERIE: EVALUATION BASED ON R:P RATIOS DETERMINED BY THE CONCENTRATION AND STABLE ISOTOPIC COMPOSITION OF DISSOLVED O_2

By

Leah K. Piwinski

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Geological Sciences

2007

ABSTRACT

LAKE METABOLISM AND TROPHIC STATE IN LAKE ERIE: EVALUATION BASED ON R:P RATIOS DETERMINED BY THE CONCENTRATION AND STABLE ISOTOPIC COMPOSITION OF DISSOLVED O_2

By

Leah K. Piwinski

To characterize lake metabolism and trophic state in Lake Erie, the relative importance of photosynthesis and respiration (R:P) was evaluated during August of 2003 based on the concentration and stable isotopic composition of dissolved O_2. O_2 saturation in the epilimnion ranged from 0.8 to 1.1, indicating an influence of atmospheric gas exchange on O_2. O_2 saturation values consistently less than 1.0, with a minimum value of 0.04 in the hypoxic central basin, suggested respiration was the process controlling hypolimnetic O_2. $\delta^{18}O$-O_2 values lake-wide ranged from -4.0 to 12.9 ‰. This wide range in isotope values reflected a strong influence of biological activity on O_2 cycling relative to gas exchange. Slightly net heterotrophic conditions were evident in R:P values for the epilimnion suggesting that R:P may not provide a true measure of trophic state in eutrophic systems but reflect temporal and spatial decoupling of primary production and respiration. Assuming a closed system, a fractionation factor (ε) of 9.0 ‰ was calculated from hypolimnion samples using a Rayleigh Model. A comparison of the calculated ε value to that expected for water column (23.5 ‰) and sediment (3 ‰) respiration revealed that 71% of hypolimnion respiration in Lake Erie occurs in sediments. Consequently, the development of hypoxic conditions in Lake Erie is largely driven by respiration in sediments.

ACKNOWLEDGEMENTS

Support for this work was provided by the U.S. EPA Great Lakes National Program Office. I would like to thank the members of the Lake Erie Trophic Study team as well as the crew of the R/V *Lake Guardian* for their dedication and much needed assistance during sample collection. I am truly indebted to my advisor, Dr. Nathaniel Ostrom for his guidance and support from the very beginning and most of all for his unwavering patience. I thank my committee members, Dr. Peggy Ostrom, Dr. Lina Patino, and Dr. Grahame Larson for their guidance and commitment. I would like to express my gratitude to Dr. Hasand Gandhi, Dr. Mary Russ, and Amanda Field for showing me the ropes inside and outside of the lab. I would especially like to thank Malee Jinuntuya for depriving herself of sleep for a week in order to help me collect samples. I sincerely thank the principles and staff of Fitzgerald Henne & Associates, Inc. for their patience and understanding throughout this much longer than anticipated process. Finally, I would like to express my deepest gratitude to my parents, Al and Cindy Piwinski and my sister, Sarah, for their boundless support and encouragement.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

An understanding of the factors controlling lake metabolism and trophic state in Lake Erie has been sought after for over 30 years. Excess loading of phosphorus from anthropogenic inputs in the 1960's caused algal blooms and eutrophication of the lake (Rosa and Burns, 1987; Makarewicz and Bertram, 1991; Bertram, 1993; Sweeney, 1993). As a result, oxygen consumption by bacterial respiration increased, promoting hypoxic conditions in bottom waters and threatening fisheries (Bertram, 1993; Sweeney, 1993). Hypoxia is defined as oxygen concentration less than 2 mg/L (≈ 62 μmol/L) (www.epa.gov/glnpo/glindicators/water/oxygena.html). In response to the creation of legislative and restoration programs aimed towards reducing nutrient inputs from industrial, agricultural, and wastewater sources, conditions in the lake have significantly improved since the early 1970's (Makarewicz and Bertram, 1991; Sweeney, 1993). In recent years however increased phosphorus concentrations and increased frequency and extent of hypoxia in hypolimnetic waters have been observed (Charlton and Milne, 2005). In this paper we evaluate the cycling of O_2 through concentration and stable isotope determinations. In aquatic ecosystems O_2 is cycled via gas exchange with the atmosphere and the biological processes of photosynthesis and respiration. The balance between primary production and respiration is often termed lake metabolism, which has been shown to vary with the trophic state of aquatic environments (del Giorgio and Peters, 1993; 1994). External inputs of organic carbon tend to dominate lake metabolism in oligotrophic systems resulting in an excess of respiration (net heterotrophy)

whereas in eutrophic systems primary production predominates over respiration fueled by both internal and external carbon inputs (net autotrophy). Thus an evaluation of O_2 cycling by primary production and respiration is perhaps the most fundamental measure of ecosystem function and trophic state. The primary objective of this study was to evaluate lake metabolism and trophic state in Lake Erie utilizing the concentration and stable isotopic composition of dissolved O_2 ($[O_2]$ and $\delta^{18}O$-O_2) and the ratio of respiration to photosynthesis (R:P).

The processes that control oxygen flux in an aquatic ecosystem are photosynthesis, respiration and atmosphere exchange (Bender and Grande, 1987; Quay et al. 1995). A standard measure of the relative magnitude of respiration and photosynthesis is the fraction of O_2 saturation; the deviation of the measured O_2 concentration from that expected when the water column is in equilibrium with the atmosphere at a particular temperature (Weiss, 1970). O_2 saturation values equal to one indicate equilibrium with the atmosphere at a given temperature, values greater than one indicate oxygen supersaturation and values less than one are indicative of oxygen undersaturation. Therefore, undersaturation would be characteristic of net O_2 consumption (respiration) while supersaturation is indicative of net O_2 production (photosynthesis).

The relative importance of photosynthesis, respiration and atmospheric exchange cannot be determined from O_2 concentrations alone. Additional information, however, can be gained from stable isotope data (Bender and

Grande, 1987). Values of $\delta^{18}O\text{-}O_2$[1] are expressed with respect to O_2 in tropospheric air in which O_2 derived from the atmosphere has a value of 0.0 ‰. There is a slight isotopic fractionation effect during dissolution that favors the heavier isotope and shifts the value for dissolved O_2 to 0.7 ‰ (Knox et al. 1992). During photosynthesis O_2 is derived from the water molecule without fractionation (Stevens et al. 1975; Guy et al. 1993) and therefore the O_2 produced is similar in isotopic composition to the surrounding water. In Lake Erie, the $\delta^{18}O$ of water and O_2 produced by photosynthesis is approximately -29.7 ‰ (Ostrom et al. 2005a).

A substantial decline in the isotopic composition of O_2 occurs during periods with high rates of primary production (Stevens et al. 1975; Bender and Grande, 1987). During respiration, the consumption of oxygen leaves the residual O_2 pool enriched in ^{18}O due to preferential uptake of ^{16}O (Lane and Dole, 1956; Bender and Grande, 1987; Kiddon et al. 1993). Therefore, $\delta^{18}O\text{-}O_2$ values greater than those reflecting atmospheric equilibrium, 0.7 ‰, are indicative of respiration; while values less than 0.7 ‰ are the result of production from photosynthesis (Bender and Grande, 1987). If steady state is assumed, such that exchange with the atmosphere equals net production the R:P ratio can be determined from $\delta^{18}O\text{-}O_2$ and $[O_2]$ using the equations presented by Quay et al (1995).

---

[1] Oxygen stable isotope ratios are expressed in per mil (‰) notation: $\delta^{18}O = [(R_{sample}/R_{standard})-1] \times 1000$. $\delta^{18}O\text{-}O_2$ values are expressed with respect to tropospheric O_2. O_2 in air has a value of 23.5 ‰ with respect to VSMOW (Vienna Standard Mean Ocean Water).

Data on rates of primary production in Lake Erie are few which likely reflects the analytical limitations of traditional incubation approaches (Glooschenko, 1974; Ostrom et al. 2005a; b). The R:P ratio, however can be readily obtained independent of rate measurements using the concentration and isotopic composition of O_2 (Ostrom et al. 2005b). Thus insight into lake metabolism of an ecosystem can be obtained across broad spatial and temporal scales (Quay et al. 1995; Field, 2004; Russ et al. 2004; Ostrom et al. 2005b). Eutrophic lakes are generally considered net autotrophic whereby a predominance of *in situ* primary production causes photosynthesis to exceed respiration (R:P<1) (Jones, 1992; del Giorgio and Peters, 1993; 1994; Cole, 2000). In oligotrophic lakes the input of organic carbon from the watershed results in excess respiration relative to photosynthesis creating a net heterotrophic system (R:P>1) (Jones, 1992; del Giorgio and Peters, 1993; 1994; Cole, 2000). Use of R:P to assess trophic state has been validated for a variety of lake ecosystems where it correlates with traditional measures including chlorophyll-*a* and total phosphorus concentrations (Jones, 1992; del Giorgio and Peters, 1994).

Recently the use of R:P as a measure of trophic state has been called into question as periods of net autotrophy have been observed in net heterotrophic lakes (Hanson et al. 2003; Field, 2004; Russ et al. 2004; Ostrom et al. 2005b). The debate has been fueled by the role of DOC concentrations and sediment resuspension events in lake metabolism as well as methodological limitations (Carignan et al. 2000; Hanson et al. 2003). The observation that lake

ecosystems may fluctuate between periods of autotrophic and heterotrophic conditions was recently observed in Lake Superior (Russ et al. 2004) and Grand Traverse Bay in Lake Michigan (Field, 2004). For these predominately oligotrophic environments, periods of net autotrophy observed in the spring were the result of temporal decoupling of primary production and respiration and that the observation of net autotrophy within oligotrophic systems challenges earlier views of R:P as a trophic state indicator (Field, 2004; Russ et al. 2004; Ostrom et al. 2005b). This study was conducted in Lake Erie, a known eutrophic system, to further evaluate the use of oxygen isotopes and R:P to characterize trophic state and better understand the factors contributing to lake metabolism.

METHODS

Samples were collected in Lake Erie during August of 2003 aboard the EPA research vessel Lake Guardian. Four open water stations were selected along a west-east transect (91M, 43, 78M, 15M) that represent a gradient of trophic conditions from the eutrophic western basin to mesotrophic eastern basin (Figure 1). Water samples were collected using 8 L, lever-action Nisken bottles attached to a rosette, triggered at depths representative of the epilimnion, metalimnion, and hypolimnion throughout the thermally stratified water column. Temperature, chlorophyll-*a* fluorescence, and O_2 concentration measurements were obtained at half-meter intervals using a Seabird 25 CTD profiler deployed within the rossette. The concentration of O_2 was also determined from samples collected in 300 mL BOD bottles using a modified Winkler titration method (Carpenter, 1965; Emerson et al. 1999). To evaluate the precision, with which titrations were performed, replicate O_2 concentration samples were collected at station 43 from depths of 5 and 16 meters. The standard deviations of replicate O_2 concentration data were 3.05 and 1.10 μmol/L for the 5 and 16 m samples, respectively.

O_2 saturation (expressed as a fraction) in Lake Erie was calculated using O_2 concentration data obtained by Winkler titration and CTD temperature measurements (Weiss, 1970). At stations 91M (western basin) and 15M (eastern basin) saturation values from the CTD profile corresponded well with those determined by Winkler titration at the same depths (Figure 2). In the central basin O_2 saturation determined by Winkler titration was less than that

evident within the CTD profile at the oxycline. This lack of agreement between the CTD and titration profiles likely resulted from the tendency for the Niskin bottle to collect water from a depth range corresponding to the height of the bottle (≈1m) whereas electrode measurements are obtained over a much narrower interval. As the CTD reflects changes occurring over narrower depth intervals than bottle measurements, we use this data in discussion of variations in O_2 concentrations. O_2 saturation determined by Winkler titration, however, was used in the calculation of R:P given that both [O_2] and $\delta^{18}O$-O_2 samples were evaluated from the same water collected within a Niskin bottle.

Collection and preparation of samples for determination of the $\delta^{18}O$-O_2 followed the procedure of Emerson et al. (1991, 1999). Prior to sampling, 1 mL of saturated mercuric chloride solution ($HgCl_2$) was placed within 200 mL glass vessels equipped with high vacuum stopcocks and dried at 90°C to halt biological activity upon sample introduction (Emerson et al. 1999). The glass vessels were then evacuated and the necks filled with distilled H_2O to prevent contamination from air. Sample collection involved slowly purging the bottle neck with CO_2 and allowing a stream of water from the Niskin to overflow the neck while gradually opening the stopcock. The vacuum draws lake water into the vessel where upon O_2 degases into the headspace. Approximately 100 mL of lake water was collected in each vessel. Prior to analysis, samples were stored for 4 to 7 weeks with distilled H_2O in the necks of the glass vessels. In the laboratory, samples were equilibrated by submerging and rotating them in a water bath kept at a constant temperature of approximately 24°C for at least 6 h. Prior to $\delta^{18}O$

determination, all but 1 mL of lake water was removed from each vessel using a vacuum pump.

$\delta^{18}O\text{-}O_2$ was determined by gas chromatograph-isotope ratio mass spectrometry (GC-IRMS) as described in Roberts et al. (2000). The sample vessel was attached to the evacuated inlet of a gas chromatograph where ascarite and LiOH was used to remove CO_2 and water upon the release of sample gas into a pre-evacuated 3 mL gas sampling loop. Helium was used as a carrier to move the gas to a GC column. A molecular sieve 5A, 8 m long column was used to separate N_2 and O_2 gas in time. O_2 gas was allowed to enter the mass spectrometer where the isotope ratio was determined relative to a previously equilibrated reference gas. GC-IRMS provides an analysis of the isotopic composition of O_2 with a precision of ± 0.3 ‰ or better (Roberts et al. 2000).

R:P ratios were calculated from measured $[O_2]$ and $\delta^{18}O\text{-}O_2$ using the equations presented by Quay et al (1995).

(1) $$R{:}P = ({}^{18/16}O_w\alpha_p - {}^{18/16}O_g) / ({}^{18/16}O\alpha_r - {}^{18/16}O_g)$$

where

(2) $${}^{18/16}O_g = \alpha_g\{{}^{18/16}O_a\alpha_s - ([O_2]_{sol}/[O_2]_{sat})^{18/16}O\}/\{1 - ([O_2]_{sol}/[O_2]_{sat})\}$$

The isotopic composition of H_2O, atmospheric O_2, and dissolved O_2 are represented by the terms ${}^{18/16}O_w$, ${}^{18/16}O_a$ and ${}^{18/16}O$ respectively (Lane and Dole, 1956; Quay et al. 1995). ${}^{18/16}O$ is the measured $\delta^{18}O\text{-}O_2$ value determined for the

sample. $^{18/16}O_w$, measured by Mountain Mass Spectrometry, was determined to be -29.7 ‰ (with respect to air) for Lake Erie water (Ostrom et al. 2005a) the isotopic composition of the atmosphere ($^{18/16}O_a$) is 0 ‰. $^{18/16}O_g$ is the calculated gas transfer ratio of net O_2 flux between the water column and the atmosphere, which varies depending on the measured concentration of O_2 (Quay et al. 1995). $[O_2]_{sol}$ is the measured concentration of O_2 dissolved in solution and the $[O_2]_{sat}$ is the expected concentration of dissolved O_2 in equilibrium with the atmosphere at the observed temperature.

The ratio of the rates of reaction for the heavy and light isotopes defines the fractionation factor, α. Fractionation factors for photosynthesis ($H_2{}^{18}O/H_2{}^{16}O$ = 1.000 ± 0.003, Stevens et al. 1975, Guy et al. 1993), respiration (^{18}O-$^{16}O/^{16}O$-^{16}O = 0.9770, Luz et al. 2002), gas exchange (^{18}O-$^{16}O/^{16}O$-^{16}O = 0.9770, Knox et al. 1992) and gas dissolution (^{18}O-$^{16}O/^{16}O$-^{16}O = 1.0007, Kroopnick and Craig, 1972; Benson and Krause, 1984) are indicated by α_p, α_r, α_g, and α_s respectively. Respiration can occur via four pathways in aquatic ecosystems, Mehler reaction, photorespiration, cytochrome oxidase, and alternative oxidase (Kroopnick and Craig, 1972; Kroopnick ,1975; Guy et al. 1989; Kiddon, 1993). Therefore, α_r is a net respiratory fractionation factor representing the combined isotope effects of the respiration pathways on dissolved O_2. In the calculation for R:P, we used an estimated α_r value of 0.9770 determined by Luz et al. (2002) for epilimnetic waters in Lake Kinneret as representing a phytoplankton assemblage and trophic state similar to those of Lake Erie.

RESULTS

West to East Transect

Temperature profiles exhibited an overall cooling trend on a west to east transect across the lake (Table 1, Figure 3). Temperatures were near 25°C throughout the water column at station 91M indicative of mixing in the shallow western basin, while thermal stratification was present in the central and eastern basins. At station 43 in the central basin a marked thermocline was present at a depth of 15 m where the water temperature was near 17°C. Epilimnetic waters at this station were approximately 25°C while temperatures as low as 12°C were evident in the hypolimnion. The temperature profile at central basin station, 78M, followed a similar trend with depth to that present at station 43. A deeper and less defined thermocline was evident at a depth of 20 m in the eastern basin at station 15M. Temperature ranged from 18°C to 25°C above the thermocline while the hypolimnion in the eastern basin was considerably cooler relative to the other basins with bottom waters approaching 5°C.

A trend of decreasing chlorophyll-*a* fluorescence (expressed in relative fluorescence units (RFU)) was apparent from west to east across the lake (Table 1, Figure 3). RFU values were substantially higher in the western basin than in the other two basins with values as high as 2.7 consistent with relatively high productivity levels and nutrient loading (Charlton and Milne, 2005; Ostrom et al. 2005a; b). In the central basin fluorescence varied from 0.5 to 1.8. The lowest RFU values were observed in the eastern basin with values between 0.04 and 1.2. Fluorescence increased with depth in the mixed water column at station

91M, while at stations 43, 78M and 15M fluorescence decreased moderately with depth.

A decreasing trend in O_2 saturation with depth was apparent at all stations (Table 1, Figure 4). The variation in O_2 concentration with depth at station 91M was minimal (0.7 to 1.1), which likely reflected extensive water column mixing at this shallow station. At the central basin station 43 O_2 saturation (0.9 to 1.1) remained at or near equilibrium with the atmosphere throughout most of the epilimnion, however, intense undersaturation of O_2 in the hypolimnion was evident by values near 0.1. O_2 saturation in the epilimnion at 78M (0.8 to 1.0) was similar to that present at station 43, however, the degree of O_2 depletion in the hypolimnion was slightly less intense as indicated by values near 0.3. These saturation values equate to approximately 33 and 92 μmol/L at stations 43 and 78M respectively, indicating that hypoxia was present in the central basin at station 43, while only near hypoxic conditions were observed further east at station 78M. At station 15M in the eastern basin, O_2 saturation values ranging from 0.7 to 1.1 throughout the water column were more homogenous relative to the central basin stations. O_2 saturation values (>0.7) in the bottom waters at station 15M were indicative of O_2 consumption by respiration, however, the values were much greater than those observed within the central basin hypolimnion. The difference in volume of the hypolimnion and, therefore, total mass of O_2 within the hypolimnion, indicates that O_2 depletion is more readily accomplished within the central basin relative to the eastern basin (Charlton and Milne, 2005). Lake-wide values within the epilimnion ranged between

approximately 0.8 and 1.1, which indicates a strong influence of atmospheric exchange on O_2, while values in the hypolimnion were exclusively less then 1.0, showing a strong influence of respiration.

A framework for understanding isotopic variation in dissolved O_2 can be gained based on the premise that a value of 0.7 ‰ reflects atmospheric equilibrium and that biological processes cause deviation from this value (Bender and Grande, 1987). The isotopic composition of O_2 across the lake ranged from -4.0 to 12.9 ‰ and in general an increasing trend in the $\delta^{18}O$-O_2 was evident throughout the water column at all stations (Table 1, Figure 4). Little change in isotopic composition with depth was apparent at 91M (-1.5 and -2.7 ‰) which is likely the result of mixing given the shallow nature of the water column at this station. Values consistently less than 0.7 ‰ observed throughout the water column indicate primary production is predominate in the western basin. At station 43 isotope values were highly variable and ranged from -4.0 ‰ near the surface to 12.9 ‰ in deep water. A similar trend was found at station 78M with one noticeable difference; there was a slight decrease in $\delta^{18}O$ near the bottom of the lake following a steady increase in $\delta^{18}O$-O_2 values at shallower depths. This isotope shift may be an artifact of collecting samples from a thin hypolimnion as water from above the intended sampling depth is not thoroughly flushed from the Niskin bottle before it is triggered. At station 15M, $\delta^{18}O$-O_2 values ranged from -2.3 to 4.9 ‰. In the eastern basin the trend in $\delta^{18}O$ increased with depth, however, the range in isotope values below the thermocline was narrow relative to the central basin. In general, negative isotope values (<0.7 ‰) observed near

the lake surface suggest high levels of primary production whereas the increasing trend in $\delta^{18}O\text{-}O_2$ indicates respiration is the controlling O_2 cycling process at depth in Lake Erie. Overall trends in $\delta^{18}O\text{-}O_2$ exhibited considerable variation with depth at each station as well as across the lake.

In this paper we only report R:P values for epilimnion samples as hypolimnion values are not applicable to the evaluation of trophic state. R:P ratios observed in the epilimnion of Lake Erie were very near 1.0 with a narrow range from 1.0 to 1.2 (Table 2). This trend indicates that the rates of photosynthesis and respiration were approximately equal across the lake surface, with a slight predominance of net heterotrophy.

Diurnal Study

The concentration and isotopic composition of dissolved O_2 was measured at both central basin stations in Lake Erie over a diurnal cycle (Figure 5, 6). At station 43, O_2 saturation, $\delta^{18}O$-O_2, and R:P were determined 6 times over a 24 h period beginning at 9:15 pm. At station 78M, the same parameters were determined 5 times over a 24 h period beginning at 1:15 am. The diurnal study was conducted for the purpose of observing the influence of daytime and nighttime light conditions on the metabolic balance in the central basin.

Values of O_2 saturation at station 43 were as high as 1.18 in the epilimnion and as low as 0.06 in the hypolimnion over the diurnal cycle (Figure 5). A decrease in O_2 concentration was evident with depth for each sampling time indicating a strong consumption of O_2 by respiration. Slight O_2 undersaturation was evident at the surface for each sampling event (0.76 to 0.98). This was followed by a peak in the $[O_2]$ profile observed between 2 and 4 m, in which slight supersaturation was evident (1.03 to 1.18) with one exception; the maximum value observed for the 8:00 pm sampling event was 0.95. Average epilimnetic O_2 saturation below 3 m (3 to 11 m) decreased gradually between 9:15 pm and 9:05 am (1.03, 1.01, 0.96, and 0.91, respectively). This was likely due to respiration in the upper water column at night when light conditions do not support photosynthesis. Saturation values for the epilimnion were predominately near 0.95 for both the 5:00 pm and 8:00 pm sampling events. A predominance of values near 1 throughout the epilimnion over the diurnal period may be the result of mixing by high winds associated with

the passing of a storm. Hence, marked variation in [O_2] concentration (and $\delta^{18}O$) may be the result of mixing by the storm or due to storm induced internal waves. Hypolimnetic waters sampled at each time were characterized by values less than 0.09 indicating a predominance of respiration.

The $\delta^{18}O$-O_2 values determined for epilimnion samples collected over the diurnal cycle at station 43 were consistently less than 0.7 ‰, while values for the hypolimnion were highly enriched in ^{18}O (Figure 6). The lowest isotope value determined for the epilimnion (-4.0 ‰) was observed at 9:15 pm $\delta^{18}O$-O_2 generally increased between 9:15 pm and 5:00 pm from -4.0 to -1.5 ‰, followed by a decrease to a value of 3 ‰ observed at 8:00 pm. Observation of the lowest isotope values in the early evening likely indicated a temporal decoupling between elevated daytime primary production and the isotope signal. For each sampling event over the 24 h period, $\delta^{18}O$-O_2 increased to a depth of at least 16 m (near the thermocline) indicative of an increase in the predominance of respiration over production with depth. The increase, however, was greater over the nighttime sampling period between 9:15 pm and 9:05 am (16 m values increased 2.7 ‰) than after a period of daytime production (16 m values increased 0.8 ‰ from 5:00 and 8:00 pm). These values are reflective of greater O_2 consumption during the night when photosynthesis is absent. An anomalous decrease (except at 1:05 am) in the isotopic composition of O_2 occurred near the bottom of the lake where the value was expected to be the highest. This anomaly likely resulted from the tendency for the Niskin bottle to trap water from

multiple rather than discrete depths in the narrow and O_2 deficient hypolimnion of the central basin.

At station 78M O_2 saturation trends were similar to those observed at station 43 and in general little variation was evident between sampling events (Figure 5). In contrast to station 43, sampling at 78M occurred during a period of calm winds. Concentrations of O_2 near the surface were consistently undersaturated for each time sampled. The highest degree of undersaturation occurred at night with values of 0.78 and 0.67 observed at 1 m for the 1:15 am and midnight sampling events. This trend likely reflects nighttime respiration in the absence of photosynthesis. O_2 saturation values determined for the epilimnion (below 3 m) over the entire diurnal cycle were consistently near 1, indicating the importance of atmospheric exchange. Near hypoxic conditions were evident in the bottom waters as indicated by low saturation values between 0.2 and 0.3, however, the extent of O_2 depletion was less than that observed at station 43.

$\delta^{18}O$-O_2 values indicated photosynthesis was the primary process controlling O_2 in the epilimnion, while values for the hypolimnion suggested O_2 was consumed by respiration at depth throughout the diurnal cycle (Figure 6). Isotope values for the epilimnion over the 24 h period were -3.5 (1:15 am), -2.8 (6:05 am), -2.7 (12:05 pm), -3.8 (6:05 pm), and -2.9 ‰ (12:00 am). The low isotope value observed at 1:15 am indicates a lag in time for the isotope signal to respond to daytime primary production. An increasing shift was evident by morning as a result of nighttime respiration. The lowest isotope value was

observed at 6:05 pm likely following a period of high primary production throughout the day. Trends similar to that observed at station 43 occurred in the hypolimnion. Hypolimnion $\delta^{18}O\text{-}O_2$ values for nighttime and early morning sampling events (8.1 to 10.2 ‰) were higher than those observed during the day (5.6 to 7.5 ‰) indicating a greater degree of respiration over night. Furthermore, the same decreasing anomaly was evident near the bottom of the lake at station 78M.

DISCUSSION AND CONCLUSIONS

Hypoxia observed in the central basin of Lake Erie is largely driven by respiration of organic matter produced during photosynthesis rather than that derived from the watershed (Charlton et al. 1993; 1999; Charlton and Milne, 2005; Ostrom et al. 2005b). A study similar to this was conducted in Lake Erie in 2002, which characterized July as a period of net autotrophy whereas net heterotrophic conditions and the development of hypoxia were observed in August (Ostrom et al. 2005b). This study focussed on O_2 cycling and the metabolic balance between production and respiration in Lake Erie in August 2003.

The variation in abundance and isotopic composition of O_2 observed in Lake Erie suggests a strong influence of biological activity on lake-metabolism relative to gas exchange. The relationships between photosynthesis, respiration, and atmospheric gas exchange and their influence on dissolved O_2 in the lake can be understood by use of a quad plot (Quay et al. 1995; Field, 2004; Ostrom et al. 2005b) (Figure 7). Within this plot four quadrants are produced by the intersection (defined as the equilibrium locus) of lines representing O_2 saturation (1.0) and isotopic composition (0.7 ‰) associated with atmospheric equilibrium. These values likely represent conditions in the lake during winter and early spring when low light levels and cold temperatures limit biological activity and physical mixing favors equilibrium with the atmosphere (Russ et al. 2004, Ostrom et al. 2005b). The onset of primary production and respiration in the spring and summer months shift the concentration and isotopic composition of O_2 away from

the equilibrium locus. Predominance of photosynthesis over respiration will drive values into quadrant IV, which is characterized by O_2 saturation values greater than one and isotope values less than 0.7 ‰ indicative of O_2 production. When consumption by respiration is the predominant process controlling O_2 abundance, values will fall within quadrant II and be characterized by O_2 saturation values less than 1.0 and $\delta^{18}O$-O_2 values greater than 0.7 ‰. The magnitude of isotopic fractionation during respiration is large while little to no fractionation is associated with photosynthesis during which ^{18}O depleted O_2 is produced. Consequently, if photosynthesis and respiration occur at the same rate a net isotope shift will occur even though concentration remains constant.

Epilimnion samples obtained for this study lie within or near quadrant IV of the quad plot reflecting a predominance of photosynthesis at the surface while hypolimnion samples lie within quadrant II indicating a strong influence of respiration at depth. The epilimnion values are unique from those common in the oligotrophic Lake Superior and Grand Traverse Bay in which values reflective of atmospheric exchange were predominant (Field, 2004; Russ et al. 2004). Consequently, the wider range of $\delta^{18}O$ values and frequency of negative values in the epilimnion is consistent with a eutrophic ecosystem. Furthermore, the occurrence of values in quadrant II and III reflect the important influence respiration has on O_2 cycling in Lake Erie particularly within the hypoxic waters of the central basin.

Metalimnion samples transition between quadrant II and IV predominately occurring in quadrant III. If the equilibrium locus represents the concentration

and isotopic composition of dissolved O_2 prior to initiation of biological activity in the spring then values should not occur in quadrants I or III. While no values were observed in quadrant I, metalimnion values did in fact, lie within quadrant III. This trend suggests that the concentration and isotope values associated with atmospheric equilibrium do not define the equilibrium locus of the Lake Erie system much of the time. The locus in this system is instead shifted towards negative isotope values, which suggests an influence of photosynthesis on the "locus" values for Lake Erie. A shift in locus values may reflect the initiation of primary production in Lake Erie prior to thermal stratification in the spring (Ostrom et al. 2005b). The occurrence of values in quadrant III of the quad plot and thus a shift in the locus from atmospheric equilibrium was also observed in Lake Erie during the summer of 2002 (Ostrom et al. 2005b). Furthermore, a similar trend was evident in Lake Superior and Grand Traverse Bay with the exception that isotope values defining the locus reflected a predominance of respiration (Field, 2004; Russ et al. 2004). The distinction in locus values for Lake Erie relative to the more oligotrophic systems, Lake Superior and Grand Traverse Bay, is consistent with its eutrophic nature.

If the hypolimnion can be considered a closed system once stratification is established the Rayleigh model can be used to determine the fractionation factor for respiration (Ostrom et al. 2002; 2005b). The lack of O_2 production in the hypolimnion supports the assumption that Lake Erie is indeed a closed system (Ostrom et al. 2005a). Furthermore, diffusion of O_2 across the thermocline is a slow process and, therefore, is not likely a significant source of O_2 to

hypolimnetic waters (Emerson et al. 1999); particularly in a system characterized by high rates of photosynthesis and respiration (Carrick, 2004; Ostrom et al. 2005a). In a closed system in which only one process is controlling the isotopic signature of O_2, the fractionation factor, ε, can be calculated using a modified Rayleigh equation,

$$(3) \qquad \delta_s = \delta_{so} - \varepsilon \ln(C/C_o)$$

where ε is defined as $(1/\alpha-1)*1000$, α is the reaction rate for O_2 containing the light and heavy isotopes, respectively, δ_s and δ_{so} represent the isotopic composition of the residual and initial substrate of a reaction and C/C_o is the ratio of the observed to initial substrate concentration, respectively (Mariotti et al. 1981; Ostrom et al. 2002; 2005b). C/C_o can be replaced by the O_2 saturation value based on the assumption that the initial concentration reflects atmospheric equilibrium at the hypolimnetic temperature. Thus equation 3 becomes:

$$(4) \qquad \delta_s = \delta_{so} - \varepsilon \ln(O_2 \text{ Sat.})$$

If δ_s is plotted versus $-\ln(O_2 \text{ Sat.})$ then the slope of the line defines the fractionation factor, ε, associated with respiration (Ostrom et al. 2002; 2005b).

The slopes of hypolimnion data plotted for stations 78M and 15M yielded fractionation factors of 9.0 and 8.7 ‰, respectively. Owing to a poor correlation among values ($R^2 = 0.1$) ε from station 43 data was omitted. A poor correlation

for station 43 data may reflect the challenge of measuring $\delta^{18}O$ at low O_2 concentrations as well as the asymptotic nature of the Rayleigh model relationship at low O_2. The fractionation factors obtained are very similar to the preliminary values based on only a few data points reported by Ostrom et al. (2005b). The value of approximately 9.0 ‰ obtained for hypolimnion respiration is markedly different than the value of 23.5 ‰ reported by Luz et al. (2002). A fractionation factor for sediment respiration of 3.0 ‰ was reported by Brandes and Devol (1997). This low ε value is the result of diffusion limiting the supply of O_2 to the heterotrophic community in sediments. The low ε value of 9.0 ‰ in Lake Erie, therefore, indicates a strong influence of sediment respiration on hypolimnetic O_2. Based on ε values of 23.5 ‰ for water column respiration and 3.0 ‰ for sediment respiration we calculate that 71% of hypolimnetic respiration occurs in sediments. This indicates that the development of hypoxic conditions in the central basin of Lake Erie is largely driven by sediment respiration. The predominance of sediment respiration in controlling the development of hypoxia within the central basin may, in part explain why the deeper eastern basin is not susceptible to hypoxia.

The R:P ratio correlates with total phosphorus and chlorophyll-*a* concentrations in a variety of lakes and has therefore been proposed as a trophic state indicator (Jones, 1992; del Georgio and Peters, 1993;1994). Considering primary production in Lake Erie is largely restricted to the epilimnion we report R:P values for only the upper water column (Ostrom et al. 2005a). R:P for the epilimnion of Lake Erie in August 2003 ranged from 1.0 to 1.2 (Table 2). These

values indicate that in Lake Erie primary production and respiration are in balance with only a slight predominance of net heterotrophy. A period of net heterotrophy in August was also observed by Ostrom et al. (2005b) in 2002, following a period of net autotrophy in July. Furthermore, a similar oscillation between periods of net autotrophy and heterotropy was observed in the oligotrophic environments, Lake Superior and Grand Traverse Bay (Field, 2004; Russ et al. 2004, Ostrom et al. 2005b).

The seasonal variation in lake metabolism observed in Lake Erie, Lake Superior and Grand Traverse Bay indicates that R:P may not provide an accurate measure of trophic state. Respiration in oligotrophic systems is strongly affected by terrestrial inputs of organic carbon, and thus these environments tend to be net heterotrophic. Lake Erie is well recognized as a eutrophic system and is, therefore, expected to be net autotrophic. The R:P values we determined, however, are clearly not consistent with a net autotrophic system. The observation of net heterotrophy in a eutrophic system can be best explained due to temporal and spatial decoupling of photosynthesis and respiration. For example, organic matter produced in the spring may be respired at a later time or sediment resuspension events may further the respiration of material produced years to decades ago (Field, 2004; Russ et al. 2004, Ostrom et al. 2005b). The presence of high rates of production and algal blooms observed in the western basin of Lake Erie combined with the potential for transport of material during storm events in this relatively small and shallow lake may be a mechanism whereby material produced in one portion of the lake supports respiration in

another (Carrick et al. 2005; Ostrom et al. 2005a; b).

The wide range in $\delta^{18}O\text{-}O_2$ and $[O_2]$ observed in Lake Erie indicates a predominance of biological activity relative to inputs via atmospheric exchange. A much narrower range in $\delta^{18}O\text{-}O_2$ and $[O_2]$ values was evident in Lake Superior and Grand Traverse Bay (Figure 8). Within these systems O_2 cycling was controlled predominately by gas exchange (Field, 2004; Russ et al. 2004). A better indicator of trophic state may be the relative importance of gas exchange versus biological activity. Thus the wide range of $\delta^{18}O\text{-}O_2$ and $[O_2]$ values evident in Lake Erie relative to the oligotrophic lakes Lake Superior and Grand Traverse Bay define the lake as a eutrophic system.

Table 1: Data summary for samples collected in August, 2003.

Sample Date (2003)	Station Number	Depth (m)	Time (EST)	Temp (°C)	O_2 Saturation	O_2 Concen. (μmol/L)	$\delta^{18}O$ (‰, wrt air)
15-Aug	91M	1	0:15	25.6	0.98	260.2	-2.7
15-Aug	91M	8	0:10	24.2	0.81	219.5	-1.5
16-Aug	15M	1	5:00	24.6	1.01	272.8	-2.3
16-Aug	15M	10	5:00	21.2	0.89	250.8	0.1
16-Aug	15M	28	5:00	6.8	0.82	313.5	3.6
16-Aug	15M	40	5:00	5.2	0.76	304.1	4.2
16-Aug	15M	61	5:00	5.1	0.71	285.3	4.9
16-Aug	43	5	21:15	25.0	0.87	232.0	-4.0
16-Aug	43	12	21:15	22.1	0.31	87.8	4.3
16-Aug	43	16	21:15	12.2	0.05	15.7	9.6
16-Aug	43	20	21:15	11.8	0.07	25.1	4.2
17-Aug	43	5	1:05	24.7	1.00	268.7	-3.0
17-Aug	43	12	1:05	23.8	0.57	154.2	-0.9
17-Aug	43	16	1:05	12.3	0.10	34.5	10.3
17-Aug	43	20	1:05	11.9	0.07	22.6	12.9
17-Aug	43	5	5:05	24.4	0.83	223.5	-1.5
17-Aug	43	12	5:05	24.0	0.32	86.2	nd
17-Aug	43	16	5:05	11.9	0.04	14.4	12.3
17-Aug	43	20	5:05	11.9	0.05	17.9	6.8
17-Aug	43	5	9:05	23.7	0.82	224.5	-1.5
17-Aug	43	12	9:05	22.3	0.60	165.8	-0.9
17-Aug	43	16	9:05	11.6	0.08	26.0	11.4
17-Aug	43	20	9:05	11.6	0.07	22.6	4.5
17-Aug	43	5	13:05	24.3	0.78	211.9	-2.6
17-Aug	43	12	13:05	23.4	0.21	57.4	2.7
17-Aug	43	16	13:05	11.7	0.06	21.6	0.8
17-Aug	43	20	13:05	11.6	0.07	25.1	9.5
17-Aug	43	5	17:00	24.5	0.89	239.5	-1.5
17-Aug	43	12	17:00	23.0	0.46	126.3	0.0
17-Aug	43	16	17:00	11.7	0.11	36.4	7.2
17-Aug	43	20	17:00	11.6	0.10	32.9	3.8
17-Aug	43	5	20:00	24.4	0.88	237.0	-3.1
17-Aug	43	12	20:00	23.5	0.20	53.9	-3.2
17-Aug	43	16	20:00	11.9	0.06	20.4	8.0
17-Aug	43	20	20:00	11.7	0.11	38.9	3.4

Sample Date (2003)	Station Number	Depth (m)	Time (EST)	Temp (°C)	O_2 Saturation	O_2 Concen. (μmol/L)	$\delta^{18}O$ (‰, wrt air)
18-Aug	78M	5	1:15	23.9	1.03	280.3	-3.5
18-Aug	78M	15	1:15	16.0	0.28	85.6	9.0
18-Aug	78M	18	1:15	12.7	0.25	81.8	9.4
18-Aug	78M	21	1:15	12.7	0.25	83.7	8.1
18-Aug	78M	5	6:00	23.8	0.94	256.8	-2.8
18-Aug	78M	15	6:00	12.8	0.25	81.5	9.5
18-Aug	78M	18	6:00	12.7	0.25	82.1	8.5
18-Aug	78M	20	6:00	12.8	0.28	93.1	9.3
18-Aug	78M	5	12:05	23.8	0.95	259.3	-2.7
18-Aug	78M	15	12:05	20.0	0.33	96.3	6.4
18-Aug	78M	18	12:05	12.7	0.27	90.9	nd
18-Aug	78M	20	12:05	12.6	0.36	120.7	nd
18-Aug	78M	5	18:05	24.7	1.07	286.9	-3.8
18-Aug	78M	15	18:05	17.9	0.34	100.6	6.1
18-Aug	78M	18	18:05	12.8	0.29	94.7	7.5
18-Aug	78M	20	18:05	12.7	0.35	116.0	5.6
19-Aug	78M	5	0:05	23.8	0.97	264.0	-2.9
19-Aug	78M	15	0:05	16.6	0.32	97.2	nd
19-Aug	78M	18	0:05	12.7	0.23	74.6	10.2
19-Aug	78M	20	0:05	12.7	0.23	75.2	9.7

Table 2: R:P ratios calculated for the Lake Erie epilimnion.

Sample Date (2003)	Station Number	Depth (m)	Time (EST)	R:P
15-Aug	91M	1	0:15	1.0
15-Aug	91M	8	0:10	1.1
16-Aug	15M	1	5:00	1.0
16-Aug	15M	10	5:00	1.2
16-Aug	43M	5	21:15	1.0
17-Aug	43M	5	1:05	1.0
17-Aug	43M	5	5:05	1.1
17-Aug	43M	5	9:05	1.1
17-Aug	43M	5	13:05	1.1
17-Aug	43M	5	17:00	1.1
17-Aug	43M	5	20:00	1.1
18-Aug	78M	5	1:15	1.0
18-Aug	78M	5	6:00	1.0
18-Aug	78M	5	12:05	1.0
18-Aug	78M	5	18:05	1.0
19-Aug	78M	5	0:05	1.0

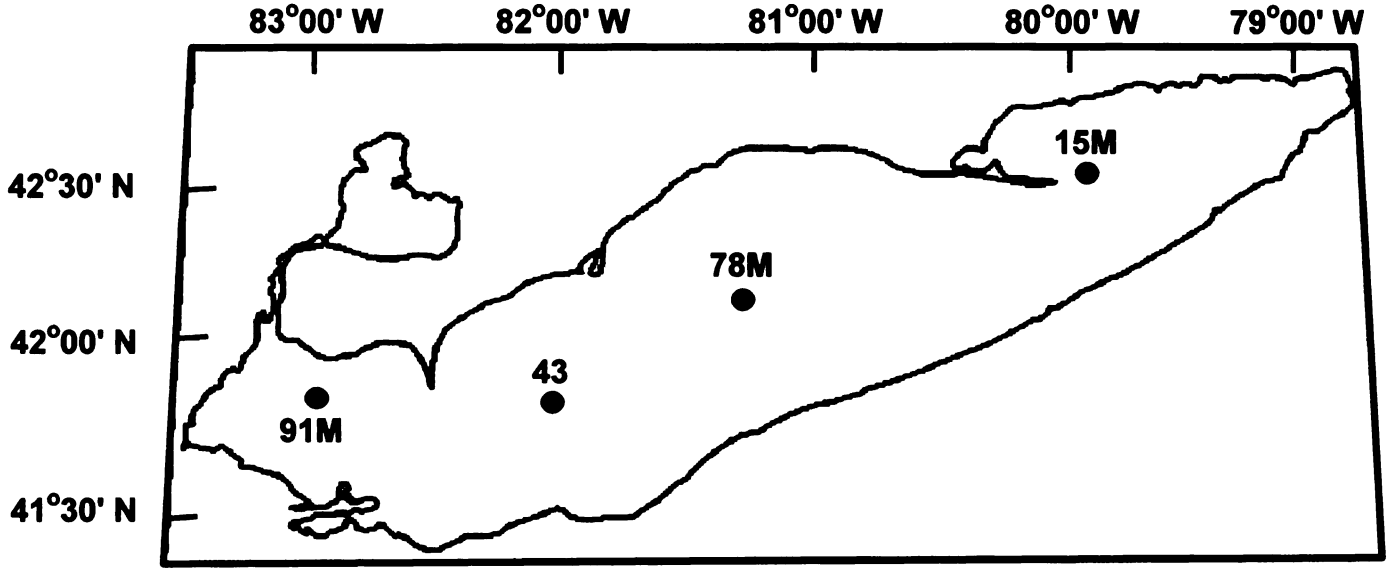


Figure 1: Locations of sampling stations forming a west-east transect in Lake Erie. The coordinates and maximum depth of each station are as follows: 91M (41 50.4°N, 82 55.0°W; 9 meters), 43 (41 47.3°N, 81 56.7°W; 21 meters), 78M (42 07.0°N, 81 15.0°W; 22 meters), and 15M (42 31.0°N, 79 53.5°W; 62 meters).

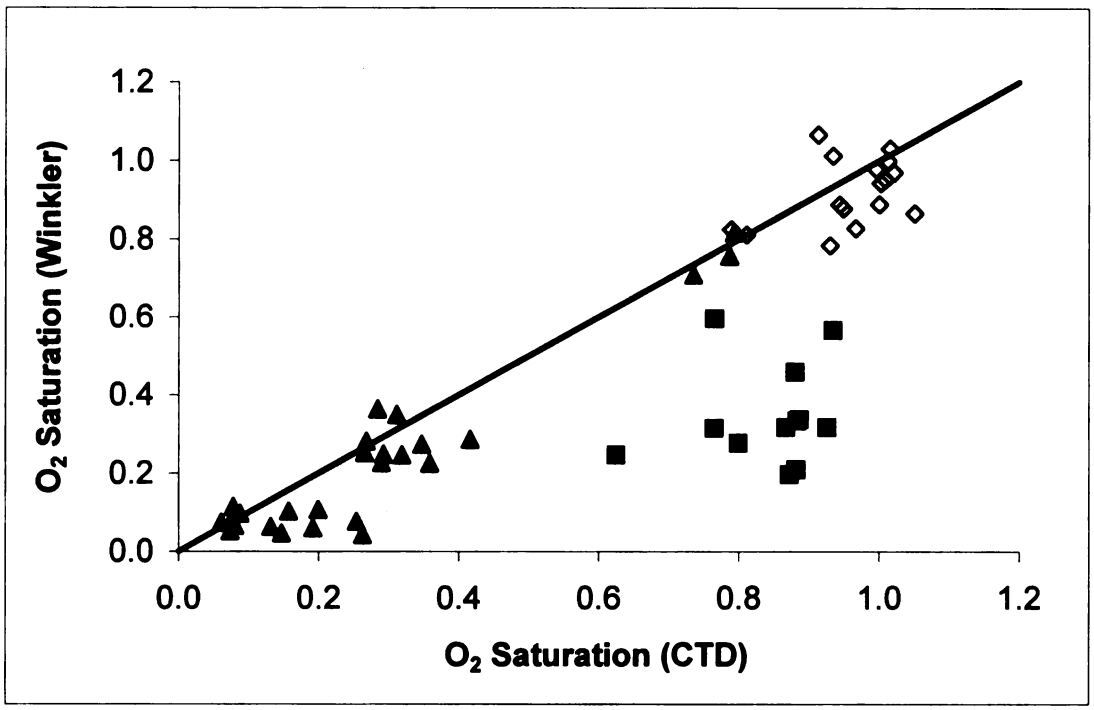


Figure 2: O_2 saturation determined from CTD measurements plotted versus O_2 saturation determined from Winkler titrations. The line represents a 1:1 relationship. Open diamonds are epilimnion samples for all stations, grey squares are metalimnion samples from stations 43 and 78M, solid triangels are hypolimnion samples from stations 43, 78M, and 15M.

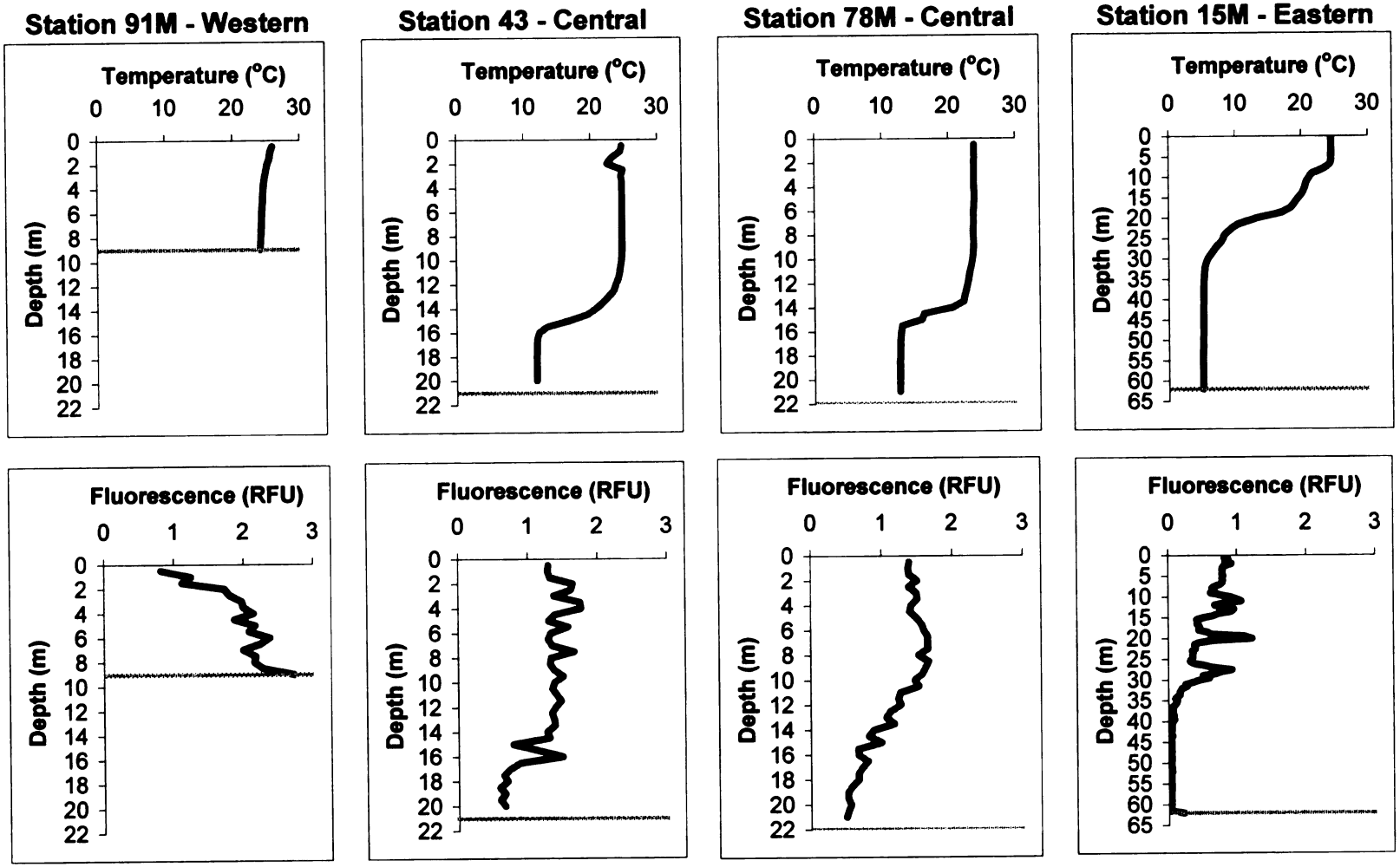


Figure 3: Temperature (°C) and chlorophyll-*a* fluorescence (RFU) as a function of depth along a west-east transect (91M-15M). The maximum depth at each station is represented by a hatched line.

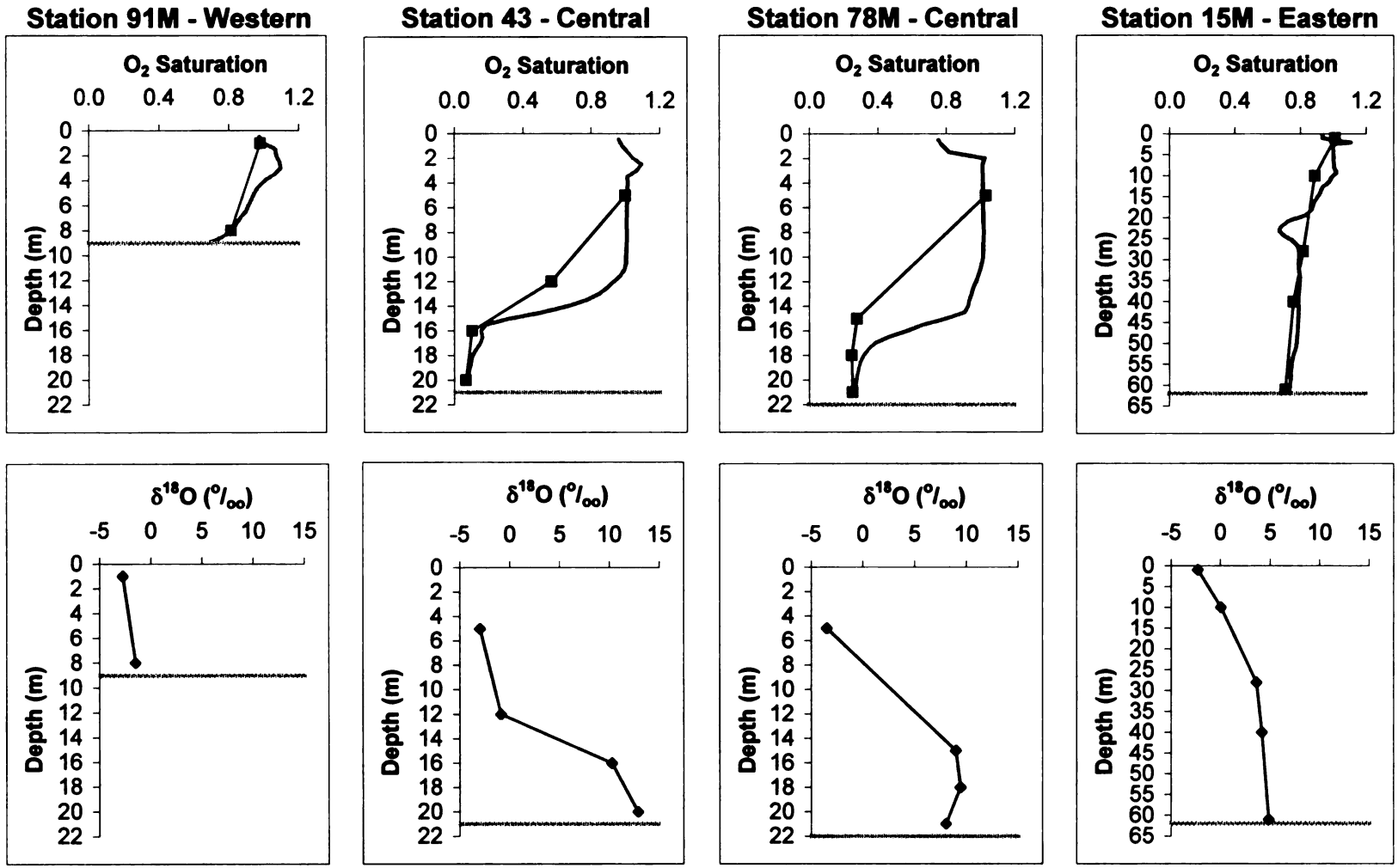
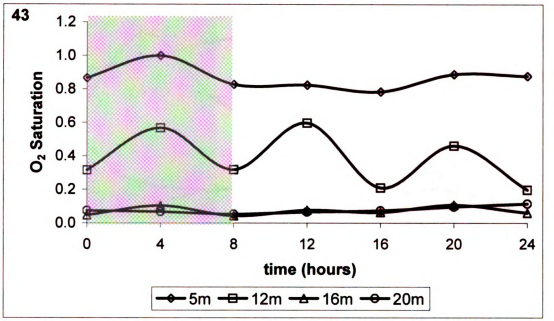


Figure 4: O_2 saturation (data obtained by Winkler titration (squares) and CTD (gray line)) and $\delta^{18}O$-O_2 as a function of depth along a west-east transect (91M-15M). The maximum depth at each station is represented by a hatched line.



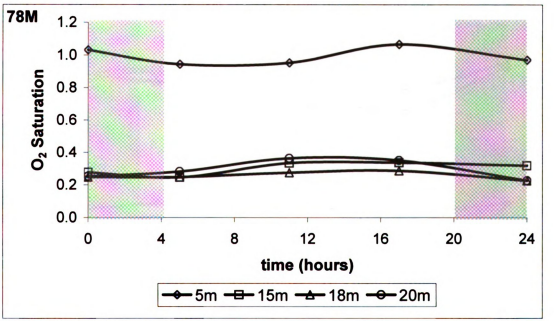
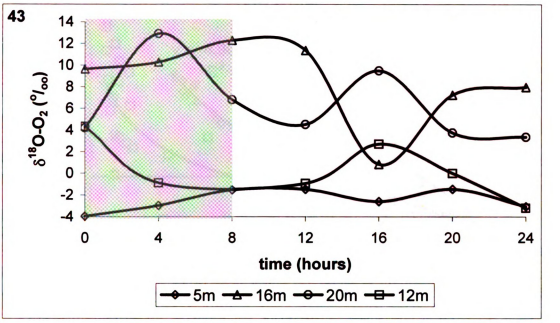


Figure 5: O_2 saturation plotted versus time for samples collected over a 24-hour diurnal cycle at central basin stations 43 and 78M. The shaded area represents nighttime conditions. Samples were collected at 5m(diamonds), 12m(squares), 16m(triangles), and 20m(circles) at station 43 and 5m(diamonds), 15m(squares), 18m(triangles), and 20m(circles) at station 78M.



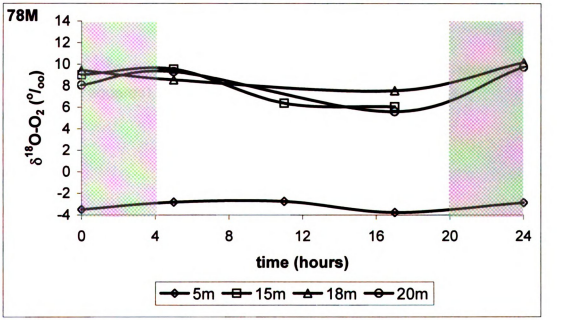


Figure 6: $\delta^{18}O\text{-}O_2$ plotted versus time for samples collected over a 24-hour diurnal cycle at central basin stations 43 and 78M. The shaded area represents nighttime conditions. Samples were collected at 5m(diamonds), 12m(squares), 16m(triangles), and 20m(circles) at station 43 and 5m(diamonds), 15m(squares), 18m(triangles), and 20m(circles) at station 78M.

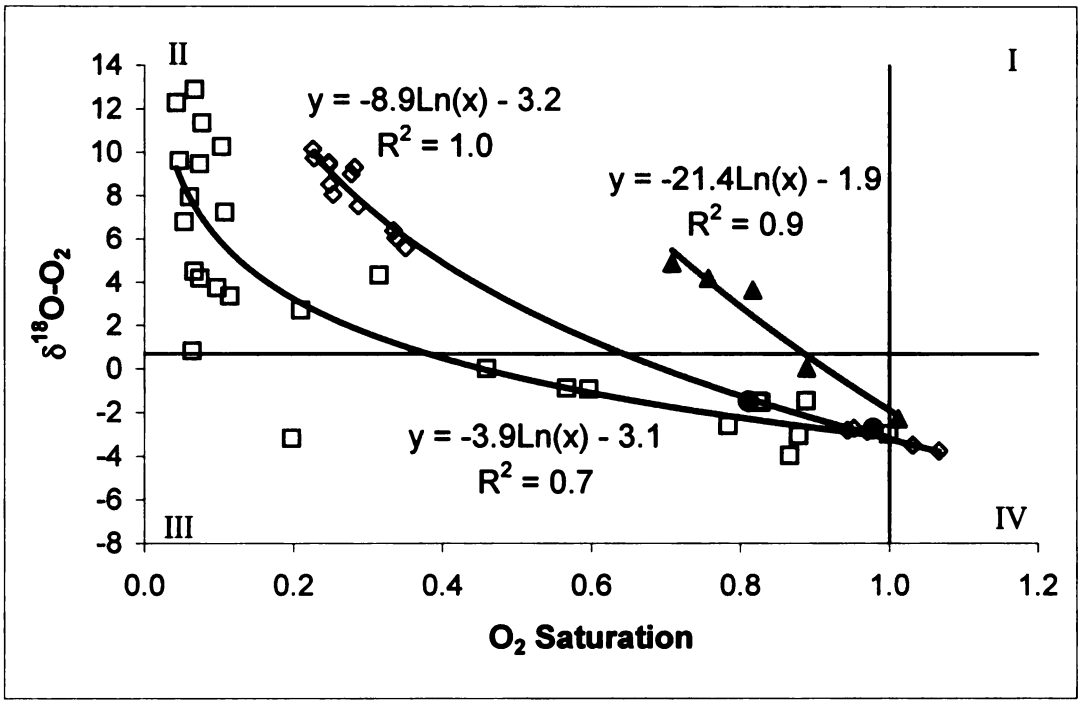


Figure 7: $\delta^{18}O\text{-}O_2$ plotted versus O_2 saturation for stations 91M(circles), 43(open squares), 78M(open diamonds), and 15M(triangles).

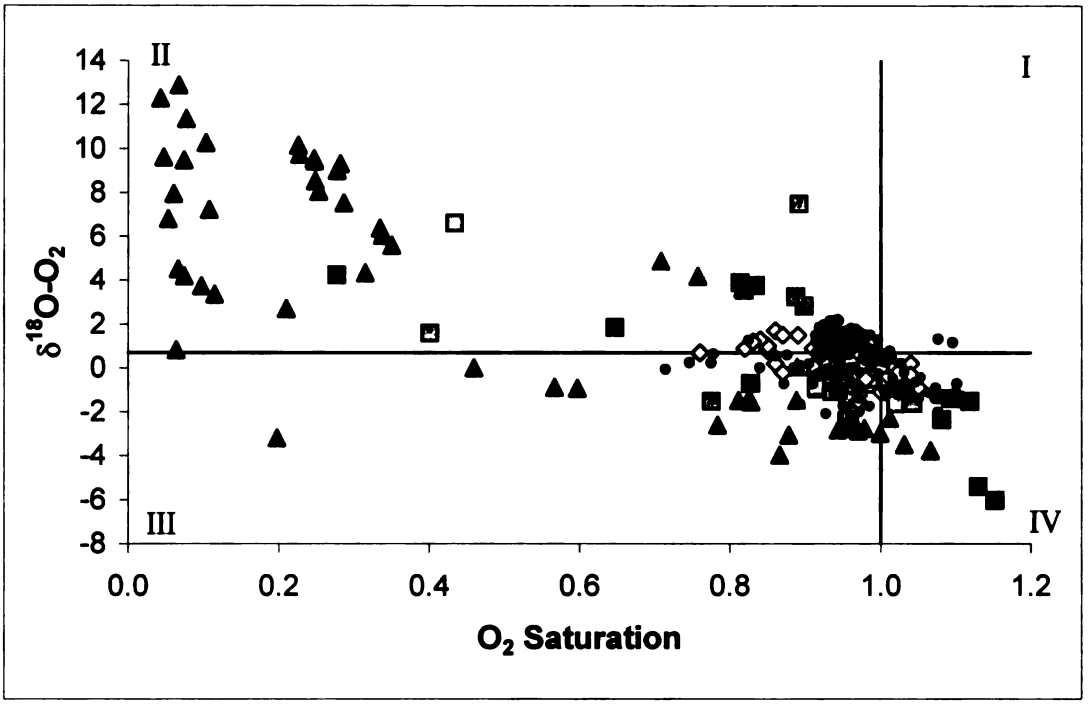


Figure 8: $\delta^{18}O\text{-}O_2$ plotted versus O_2 saturation reported for Lake Erie 2003 (triangles), Lake Eire 2002 (squares) (Ostrom et al., 2005), Grand Traverse Bay (open diamonds) (Field, 2004), and Lake Superior (circles) (Russ et al., 2004).

REFERENCES

Bender, M.L. and Grande, K.D. 1987. Production, respiration, and the isotope geochemistry of O_2 in the upper water column. *Global Biogeochem. Cycles* 1: 49-59.

Benson, B.B. and Krause, D. 1984. The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere. *Limnol. Oceanogr.* 29: 620-632.

Bertram, P.E. 1993. Total phosphorus and dissolved oxygen trends in the central basin of Lake Erie, 1970-1991. *J. Great Lakes Res.* 19: 224-236.

Biddanda, B.A. and Cotner, J.B. 2002. Love handles in aquatic ecosystems: The role of dissolved organic carbon drawdown, resuspended sediments, and terrigenous inputs in the carbon balance of Lake Michigan. *Ecosystems.* 5: 431-445.

Brandes, J.A. and Devol, A.H. 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. *Geochim. Cosmochim. Acta.* 61: 1793-1801.

Carignan, R., Planas, D. and Vis, C. 2000. Planktonic production and respiration in oligotrophic shield lakes. *Limnol. Oceanogr.* 45: 189-199.

Carpenter, J.H. 1965. The accuracy of the Winkler method for dissolved oxygen analysis. *Limnol. Oceanogr.* 10: 135-143.

Carrick, H.J. 2004. Algal distribution patterns in Lake Erie: Implications for oxygen balances in the eastern basin. *J. Great Lakes Res.* 30: 133-147.

Carrick, H.J., Moon,J.B. and Gaylord, B.F. 2005. Phytoplankton dynamics and hypoxia in Lake Erie: evidence for benthic-pelagic coupling in the central basin. *J. Great Lakes Res.* 31(Suppl. 2): 111-124.

Charlton, M.N. 1980a. Oxygen depletion in Lake Erie: Has there been any change? *Can. J. Fish. Aquatic Sci.* 37: 72-81.

Charlton, M.N. 1980b. Hypolimnion oxygen consumption in lakes: discussion of productivity and morphometry effects. *Can. J. Fish. Aquatic Sci.* 37: 1531-1539.

Charlton, M.N. and Lean, D.R.S. 1987. Sedimentation, resuspension, and oxygen depletion in Lake Erie (1979). *J. Great Lakes Res.* 13: 709-723.

Charlton, M.N. 1987. Lake Erie oxygen revisited. *J. Great Lakes Res.* 13: 697-708.

Charlton, M.N., Milne, J.E., Booth, W.G. and Chiocchio, F. 1993. Lake Erie offshore in 1990: Restoration and resilience in the central basin. *J. Great Lakes Res.* 19: 291-309.

Charlton, M.N. and Milne, J.E. 2005. Review of thirty years of change in Lake Erie water quality. NWRI contribution # 04-167. National Water Research Institute, Environment Canada.

Cole, J.J., Pace, M.L., Carpenter, S.R. and Kitchell, J.F. 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. *Limnol. Oceanogr.* 45: 1718-1730.

del Giorgio, P.A. and Peters, R.H. 1993. Balance between phytoplankton production and planktonic respiration in lakes. *Can. J. Fish. Aquatic Sci.* 50: 282-289.

del Giorgio, P.A. and Peters, R.H. 1994. Patterns in planktonic P:R ratios in lakes: influences of lake trophy and dissolved organic carbon. *Limnol. Oceanog.* 39: 772-787.

Emerson, S., Quay, P., Stump, C., Wilbur, D. and Knox, M. 1991. O_2, Ar, N_2, and ^{222}Rn in waters of the subarctic ocean: net biological O_2 production. *Global Biogeochem. Cycles.* 5: 49-69.

Emerson, S., Stump, C., Wilbur, D. and Quay, P. 1999. Accurate measurement of O_2, N_2, and Ar gases in water and the solubility of N_2. *Mar. Chem.* 64: 337-347.

Field, A.L. 2004. Seasonal variation in ratios of community respiration to gross photosynthesis determined by stable isotopes and concentrations of dissolved oxygen in Grand Traverse Bay, Lake Michigan. M. Sc. Thesis, Department of Geological Sciences, Michigan State University.

Garcia, H.E. and Gordon, L.I. 1992. Oxygen solubility in seawater: better fitting equations. *Limnol. Oceanogr.* 37: 1307-1312.

Glooschenko, W.A., Moore, J.E., Munawar, M. and Vollenweider, R.A. 1974. Primary production in Lakes Ontario and Erie: a comparative study. *J. Fish. Res. Board Can.* 31: 253-263.

Guy, R.D., Fogel, M.L. and Berry, J.A. 1993. Photosynthetic fractionation of the stable isotopes of oxygen and carbon. *Plant Physiol.* 101: 37-47.

Hanson, P.C., Bade, D.L. and Carpenter, S.R., Kratz, T.K. 2003. Lake metabolism: relationships with dissolved organic carbon and phosphorus. *Limnol. Oceanogr.* 48: 1112-1119.

Howarth, R.W. and Michaels, A.F. 2000. The measurement of primary production in aquatic ecosystems. In: Sala, O.E., Jackson, R.B., Mooney, H.A. and Howarth, R.W. (eds.) Methods in Ecosystem Science, Springer-Verlag, New York, New York, pp. 72-85.

Jones, R.I. 1992. The influence of humic substances on lacustrine planktonic food chains. *Hydrobiologia.* 229: 73-91.

Kiddon J., Bender M.L., Orchardo J., Caron D.A., Goldman J.C., Dennett M. 1993. Isotopic fractionation of oxygen by respiring marine organisms. *Global Biogeochem. Cycles.* 7: 679-694.

Knox, M., Quay, P.D. and Wilbur, D. 1992. Kinetic isotopic fractionation during air-water gas transfer of O_2, N_2, CH_4, and H_2. *J. Geophys. Res.* 97: 20335-20343.

Kroopnick, P.M. 1975. Respiration, photosynthesis, and oxygen isotope fractionation in oceanic surface water. *Limnol. Oceanogr.* 20: 988-992.

Kroopnick, P. and Craig, H. 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science.* 175: 54-55.

Lane, G.A. and Dole, M. 1956. Fractionation of oxygen isotopes during respiration. *Science.* 123: 574-576.

Laws, E.A., Landry, M.R., Barber, R.T., Campbell, L., Dickson, M.L. and Marra, J. 2000. Carbon cycling in primary production bottle incubations: inferences from grazing experiments and photosynthetic studies using ^{14}C and ^{18}O in the Arabian Sea. *Deep-Sea Res. II.* 47: 1339-1352.

Luz, B., Barkan, E., Yftach, S. and Yacobi, Y.Z. 2002. Evaluation of community respiratory mechanisms with oxygen isotopes: a case study in Lake Kinneret. *Limnol. Oceanogr.* 47: 33-42.

Makarewicz, J.C. and Bertram, P. 1991. Evidence for the restoration of the Lake Erie ecosystem. *Bioscience.* 41: 216-223.

Mariotti, A., Germon, J.C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A. and Tardieux, P. 1981. Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. Plant and Soil. 62: 413-430.

Odum, H. 1956. Primary production in flowing waters. *Limnol. Oceanog.* 1: 102-117.

Ostrom, N.E., Hedin, L.O., von Fisher, J.C. and Robertson, G.P. 2002. Nitrogen transformations and nitrate removal at a soil-stream interface: a stable isotope approach. Ecol. Appl. 12: 1027-1043.

Ostrom, N.E., Carrick, H.J., Twiss, M.R. and Piwinski, L. 2005a. Evaluation of primary production in Lake Erie by multiple proxies. *Oceaologia.* 144: 115-124.

Ostrom, N.E., Russ, M.E., Field, A.L., Piwinski, L., Twiss, M.R. and Carrick, H.J. 2005b. Primary production and respiration in Lake Erie based on oxygen isotope techniques. *J. Great Lakes Res.* 31(Suppl. 2): 138-153.

Prairie, Y.T., Bird, D.F. and Cole, J.J. 2002. The summer metabolic balance in the epilimnion of southeastern Quebec lakes. *Limnol. Oceanogr.* 47: 316-321.

Quay, P.D., Emerson, S., Wilbur, D.O. and Stump, C. 1993. The $\delta^{18}O$ of dissolved O_2 in the surface waters of the subarctic Pacific: a tracer of biological productivity. *J. Geophys. Res.* 98: 8447-8458.

Quay, P.D., Wilbur, D.O., Richey, J.E., Devol, A.H., Benner, R. and Forsber, B.R. 1995. The ^{18}O:^{16}O of dissolved oxygen in rivers and lakes in the Amazon Basin: determining the ratio of respiration to photosynthesis rates in freshwater. *Limnol. Oceanogr.* 40: 718-729.

Roberts, B.J., Russ, M.E. and Ostrom, N.E. 2000. Rapid and precise determination of the $\delta^{18}O$ of dissolved and gaseous dioxygen via gas chromatography-isotope rate mass spectrometry. *Environ. Sci. Technol.* 34: 2337-2341.

Rosa, F. and Burns, N.M. 1987. Lake Erie central basin oxygen depletion changes from 1929-1980. *J. Great Lakes Res.* 13: 684-696.

Russ, M.E., Ostrom, N.E., Gandhi, H. Ostrom, P.H. and Urban, N.R. 2004. Temporal and spatial variations in R:P ratios in Lake Superior an oligotrophic freshwater environment. *J. Geophysical Research-Oceans.* 109, doi: 10.1029/2003JC001890.

Stevens, C.L.R., Schultz, D., Van Baalen, C. and Parker, P.L. 1975. Oxygen isotope fractionation during photosynthesis in a blue-green and green alga. *Plant Physiology.* 56: 126-129.

Sweeney, R.A. 1993. "Dead" Sea of North America? - Lake Erie in the 1960s and '70s. *J. Great Lakes Res.* 19: 198-199.

Verduin, J. 1956. Primary production in lakes. *Limnol. Oceanog.* 1: 85-91.

Wang, X. and Veizer, J. 2000. Respiration-photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada. *Geochim. Cosmochim. Acta.* 64: 3775-3786.

Weiss, R.F. 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.* 17: 721-735.


MICHIGAN STATE UNIVERSITY LIBRARIES
3 1293 02845 7566