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Ratios of Community Respiration to Photosynthesis and Rates of Primary Production in Lake Erie Via Oxygen Isotope Techniques

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ABSTRACT. *To evaluate levels of primary production and community metabolism in Lake Erie, we conducted incubations with ^{18}O-labelled water and determined the ratio of respiration to primary production (R:P) during the summer and early fall of 2002. The epilimnion of Lake Erie was characterized by $\delta^{18}O$ values less than 0.7‰ at all times that reflects a strong contribution of O_2 from primary production. High $\delta^{18}O$ values (maximum of 6.6‰) were common in the O_2 depleted waters of the hypolimnion as a consequence of isotope fractionation during respiration. Hypoxic conditions were evident in the central basin in August when the fractional abundance of O_2 reached a minimum value of 0.04. Rates of primary production varied from 0.23 to 1.76 mmol-$O_2 \cdot m^{-3} \cdot h^{-1}$, decreased from west to east in August, and were at a minimum in the central basin in September. Ratios of respiration to photosynthesis (R:P) (determined from the abundance and isotopic composition of dissolved O_2) in the epilimnion as low as 0.45 in July were strong evidence of net autotrophy and preceded the development of hypoxia in August. Net heterotrophy prevailed in August and September. The absolute values of R:P ratios were not indicative of trophic state, however, the wide range of R:P ratios (0.45 to 20.40), fraction of O_2 saturation (0.04 to 1.36), and $\delta^{18}O$-O_2 (–6.0 to 7.5‰) values were all indicative of a eutrophic system. An average isotope fractionation factor for respiration of 7.9‰ was determined from samples in the hypolimnion in July and August. Based on unique fractionation factors for respiration in the water column (23.5‰) and in sediments (3‰) we calculate that 61% of hypolimnion O_2 respiration occurs within sediments and 39% occurs within the water column.*

INDEX WORDS: *Hypoxia, oxygen isotopes, primary production, R:P ratios, Lake Erie, trophic state.*

INTRODUCTION

Deterioration of the water quality of the Laurentian Great Lakes has been a consequence of human settlement and urban and population growth over the last 200 years. Declines in sport and commercial fisheries, windrows of dead alewives accumulating on shorelines, accumulation of algae mats, and odors emitted from decaying fish and algae peaked in the 1960s and early 1970s and were tangible indicators of undesirable water conditions

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(Sweeney 1993). Extensive legislation enacted in the mid 1970s to restore water quality focused on measures to reduce eutrophication. These included limiting phosphorus loadings, a key nutrient responsible for eutrophication, and placing an emphasis on long term monitoring of water column characteristics, particularly concentrations of phosphorus, dissolved oxygen (O_2), and chlorophyll-*a* (Charlton 1980a,b; Charlton and Lean 1987; Rosa and Burns 1987). While improvements to Lake Erie's overall water quality are apparent, evaluation of the restoration of the Lake Erie based on traditional water column parameters (i.e., [P] and [O_2]) continues to be challenging and is exemplified by the observation that while concentrations of P in Lake Erie have shown recent increases there does not appear to be a response by the phytoplankton community (Charlton and Milne 2005). Direct measurement of rates of primary production in Lake Erie are limited (Glooschenko *et al.* 1973, Ostrom *et al.* 2005) most likely owing to the methodological difficulty of obtaining such measurements over broad spatial and temporal scales. In this paper we address the evaluation of trophic state in Lake Erie using two oxygen isotope techniques: (1) direct measurement of rates of primary productivity by incubations with ^{18}O-enriched water and (2) determination of the ratio of respiration to primary production (R:P ratio) based on the concentration and isotopic composition of dissolved O_2.

The use of ^{18}O-enriched water to evaluate rates of primary production (^{18}O-PP) is based on the transfer of elemental oxygen from water to O_2 during photosynthesis. The primary advantage of this approach is that the rate obtained is a direct measure of the production of O_2 by photosystem II and, therefore, an value for gross primary production is obtained (Laws *et al.* 2000). In this manner, some of the inherent problems in the use of [^{14}C]-$NaHCO_3$, such as loss of label to dissolved organic carbon or respired CO_2, are avoided (Laws *et al.* 2000; Bender *et al.* 1987; 1999). Rates of primary production based on $H_2{}^{18}O$ incubations are commonly greater than those obtained using ^{14}C by a factor of 2 to as much as a factor of 8 (Bender *et al.* 1987; 1999; Kiddon *et al.* 1995; Laws *et al.* 2000; Luz *et al.* 2002). Within Lake Erie, rates based on incubations with $H_2{}^{18}O$, ^{14}C and the light-dark bottle were found to be of comparable magnitude, however, ^{18}O-PP underestimated rates based on ^{14}C by an average of 36% (Ostrom *et al.* 2005). Such differences between productivity estimates in other systems and Lake Erie is likely a consequence of variation in the photosynthetic quotient (ratio of O_2 production to CO_2 uptake), phytoplankton community composition, and experimental conditions (Ostrom *et al.* 2005).

The R:P ratio provides a fundamental measure of lake metabolism and has provided insight into the trophic state of a variety of lake ecosystems. In contrast to most studies that obtain rates of respiration and primary production by incubation, the evaluation of R:P ratios used in this study is based on the ambient concentration and isotopic composition of dissolved O_2 ($\delta^{18}O$-O_2)[1]. Consequently, an important advantage of the oxygen isotope approach to determine R:P ratios relative to traditional measures is that samples can be collected across a broad range of temporal and spatial scales without the artificial conditions imposed by incubation. Use of the R:P ratio as a measure of trophic state is based on the observation of a correlation of R:P with chlorophyll-*a* and total phosphorus in a variety of lakes (Jones 1992; del Giorgio and Peters 1993; 1994). Net heterotrophy in lake ecosystems results when allochthonous inputs of organic carbon drive respiration in excess of photosynthesis. Within eutrophic lakes, *in situ* production is sufficient to exceed the respiration of autochthonous and allochthonous organic carbon and the environment becomes net autotrophic (R:P < 1). In contrast, oligotrophic environments tend to be net heterotrophic (R:P > 1) (Jones 1992; del Giorgio and Peters 1993, 1994). The relationship between trophic state and the R:P ratio has not, however, been found to be robust across all ecosystems and differences between systems may reflect variation in the abundance of dissolved organic carbon and/or methodology used to obtain rates (Carrignan *et al.* 2000, Hanson *et al.* 2003). Within Lake Superior (Russ *et al.* 2004) and Grand Traverse Bay, Lake Michigan (Field 2004) the predominance of R:P values greater than 1.0 reflected oligotrophic conditions, however; brief periods of net autotrophy were evident that are in conflict with the use of R:P ratios to define trophic state. Seasonal oscillation in R:P ratios between net heterotrophic and autotrophic conditions was evident in both systems. The observation of net autotrophy in Lake Superior was likely the result of the summer onset of a shal-

[1]Stable isotope ratios for O are expressed in per mil (‰) notation:

$$\delta^{18}O = [(R_{sample}/R_{standard}) - 1] \times 1000$$

where R = abundance ratio of ^{18}O to ^{16}O. All $\delta^{18}O$-O_2 values are expressed with respect to O_2 in atmospheric air. O_2 in air has a value of 23.5‰ with respect to VSMOW (Vienna Standard Mean Ocean Water).

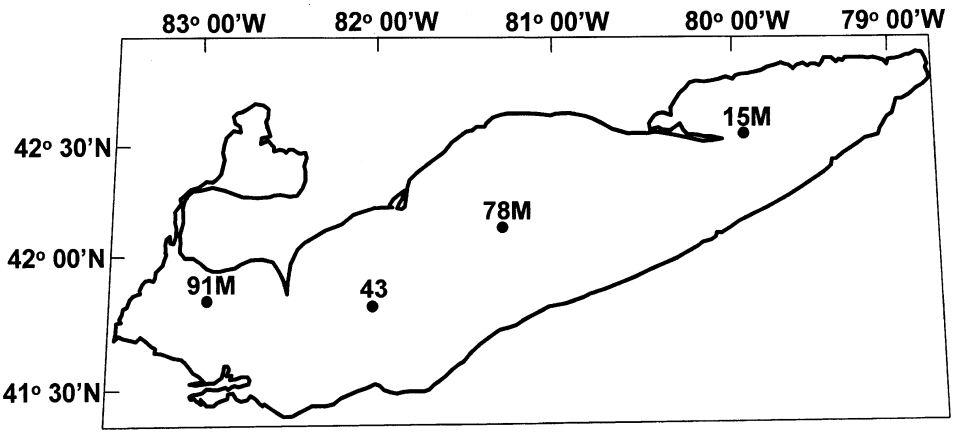

FIG. 1. Locations of sampling stations 91M (41 50.4°N, 82 55.0°W), 43 (41 47.3°N, 81 56.7°W) , 78M (42 07.0°N, 81 15.0°W) and 15M (42 31.0°N, 79 53.5°W) in Lake Erie.

low thermocline creating a stratified water column and a temporal decoupling of primary production and respiration (Russ *et al.* 2004, Field 2004). This study contrasts with the prior research in Lake Superior and Grand Traverse Bay in applying the oxygen isotope approach for evaluating R:P ratios within a much more eutrophic system, Lake Erie.

METHODS

All samples were collected during three research cruises of the US EPA's research vessel *Lake Guardian* in 2002 (17–21 July, 17–21 August, and 14–18 September) at four stations forming a west-east transect across the center of the lake (Fig. 1). Station codings follow those used by the U.S. EPA for these locations. Lake Erie is functionally divided into three unique basins: the western, central, and eastern. The western basin (mean depth = 7 m) is polymictic since thermal stratification is readily destroyed by wind-driven mixing. In contrast, the central and eastern basins develop stable thermoclines and have maximum depths of 24 and 63 m, respectively. Station locations were chosen to coordinate with ongoing studies by the U.S. EPA and afforded an opportunity to study environments representing a range of P levels and rates of primary production (Charlton and Milne 2005, Ostrom *et al.* 2005). Temperature, chlorophyll fluorescence, and $[O_2]$ were obtained at each station by deployment of the *Lake Guardian*'s SeaBird 25 CTD equipped with a Seatech fluorometer and YSI electrode. All CTD data were bin averaged at 1 m intervals. Water column samples were collected in 8-L Niskin bottles. Concentrations of O_2 in water column samples were determined shortly after collection using a modified Winkler method (Carpenter 1965, Emerson *et al.* 1999). A subset of $[O_2]$ samples (approximately 10%) were analyzed in triplicate and yielded a precision (coefficient of variation) less than 2%. Concentrations of O_2 are expressed in terms of fractional saturation which divides the observed concentration by that predicted to occur at the ambient temperature if equilibrium with the atmosphere is obtained (Weiss 1970). A value of 1.0 indicates equilibrium with the atmosphere whereas values greater or less than one represents supersaturated or undersaturated conditions, respectively.

Samples for the isotopic analysis of dissolved O_2 were initially collected with evacuated 200-mL glass bottles fitted with a high vacuum stopcock (Chemglass, Inc.) following the protocol of Emerson *et al.* (1991, 1999). Sampling involved purging the neck of the bottle with pure CO_2 gas to displace air, introducing a flow of water from the Niskin bottle, and gradually allowing vacuum to draw water in. As water enters the vessel it immediately degases to create a headspace of sample gases. Vessels were filled with approximately 100 mL of water. All biological activity within the vessels and during storage was arrested by the prior addition of 1 mL of saturated mercuric chloride followed by drying (90°C) and evacuation. Samples were stored with CO_2 in the neck of the vessel to avoid contamination from air during storage and analyzed within 2 months of collection. Prior to analysis, samples

were allowed to equilibrate at constant temperature (28°C) with agitation for 8 hours followed by removal of all but 1 mL of sample water by vacuum. The headspace gases were then analyzed for the isotopic composition of O_2 on a GV Instruments Prism stable isotope ratio mass spectrometer using a gas chromatograph interface (Roberts *et al.* 2000). Analysis of replicates samples (approximately 10% of samples collected) yielded a precision better than 0.3‰.

Incubations performed to evaluate rates of primary production using ^{18}O-enriched water closely followed the procedures of Bender and Grande (1987), Kiddon *et al.* (1995), and Luz *et al.* (2002). Water from the various depths sampled was collected at night and promptly placed within 60-mL pyrex serum bottles to which was added 50 to 150 µL of 95% $H_2{}^{18}O$ (Medical Isotopes, Inc.). This resulted in a final isotopic composition of the water of between 400 and 1,200‰ that was substantially enriched relative to the initial Lake Erie water (–29.7‰ with respect to O_2 in Air) (Ostrom *et al.* 2005). Samples were incubated *in vivo* using Percival Scientific, Inc. (Perry, Iowa; model I-30BLL) growth chambers at conditions reflecting the depth from which they were collected for a duration of 12 h. Light levels within the incubators ranged from 340–400 $\mu E \cdot m^{-2} \cdot s^{-1}$ for samples collected at depths of 4 m or less. Samples incubated from depths between 8 and 20 m were exposed to light levels of 80-130 $\mu E \cdot m^{-2} \cdot s^{-1}$; similar to that observed in the water column at depths of 10–15 m. A 12 hr incubation period reflected that used in previous studies and assured accumulation of sufficient levels of ^{18}O in O_2 (Bender and Grande 1987, Kiddon *et al.* 1995, Luz *et al.* 2002). Rate measurements obtained at all stations in August and at Sta. 91M in September are the result of individual samples; measurements performed at the remaining stations in September were conducted in triplicate. An additional incubation was conducted, *in situ* and in triplicate, at Sta. 78M in September by deployment on an anchored mooring line. At the end of the incubation period all biological activity was ceased by addition of 100 µL of saturated mercuric chloride. Incubation samples were transferred to the same evacuated glass vessels for isotopic analysis as described previously. Calculation of gross primary production is based on the initial O_2 concentration ($[O_2]_i$), the change in the isotopic composition of O_2 from initial ($\delta^{18}O_i$) to final values ($\delta^{18}O_f$), and the $\delta^{18}O$ of water ($\delta^{18}O_{water}$) in the serum bottle following addition of label by the following equation (Kiddon *et al.* 1995):

$$^{18}O\text{-PP} = [O_2]_i(\delta^{18}O_f - \delta^{18}O_i)/(\delta^{18}O_{water} - \delta^{18}O_i) \quad (1)$$

All incubations were performed in parallel with experimental controls under identical conditions with the exception of the addition of distilled water instead of isotopically enriched water. Any shift in $\delta^{18}O$ during the course of the incubation in the control experiments was subtracted from the $\delta^{18}O_f$ value prior to calculation of ^{18}O-PP. The precision of triplicate incubations yielded coefficient of variations from 4.1 to 42.7%.

Ratios of R:P were calculated from the measured values of $[O_2]$ and $\delta^{18}O$-O_2 by the model presented in Quay *et al.* (1995):

$$R/P = (^{18/16}O_w\ \alpha_p - {}^{18/16}O_g) / (^{18/16}O\ \alpha_r - {}^{18/16}O_g) \quad (2)$$

and

$$^{18/16}O_g = \alpha_g\{{}^{18/16}O_a\ \alpha_s - ([O_2]_{sol}/[O_2]_{sat})\ {}^{18/16}O\}/\{1 - ([O_2]_{sol}/[O_2]_{sat})\} \quad (3)$$

where $^{18/16}O_w$ is the measured natural isotopic composition of Lake Erie water, α_p is the photosynthetic fractionation factor (1.0000) (Guy *et al.* 1993), $^{18/16}O$ is the $\delta^{18}O$-O_2 of a sample, α_r is the fractionation factor associated with community respiration (0.9770) (Luz *et al.* 2002), α_g is the gas transfer fractionation factor (0.9972) (Knox *et al.* 1992), $^{18/16}O_a$ is the $\delta^{18}O$ of atmospheric O_2 (Lane and Dole 1956), and α_s is the fractionation factor corresponding to gas dissolution (1.0073) (Benson and Krause 1984). Fractionation factors (α) are defined as the ratio of the reaction rates of the heavy to light isotopically substituted molecules. The precision of replicate samples (calculated for two depths at two stations) yielded a standard deviation in the R:P ratio of 0.13 or better. Because the Winkler $[O_2]$ measurements were based on water collected from the same Niskin bottle as the $\delta^{18}O$-O_2 samples we use Winkler values rather than the CTD electrode data in the calculation of fractional saturation and R:P ratios.

RESULTS

Thermal Structure of the Water Column

Warm waters near or greater than 20°C were present in the epilimnion at all stations during July, August and September of 2002 (Fig. 2). The shal-

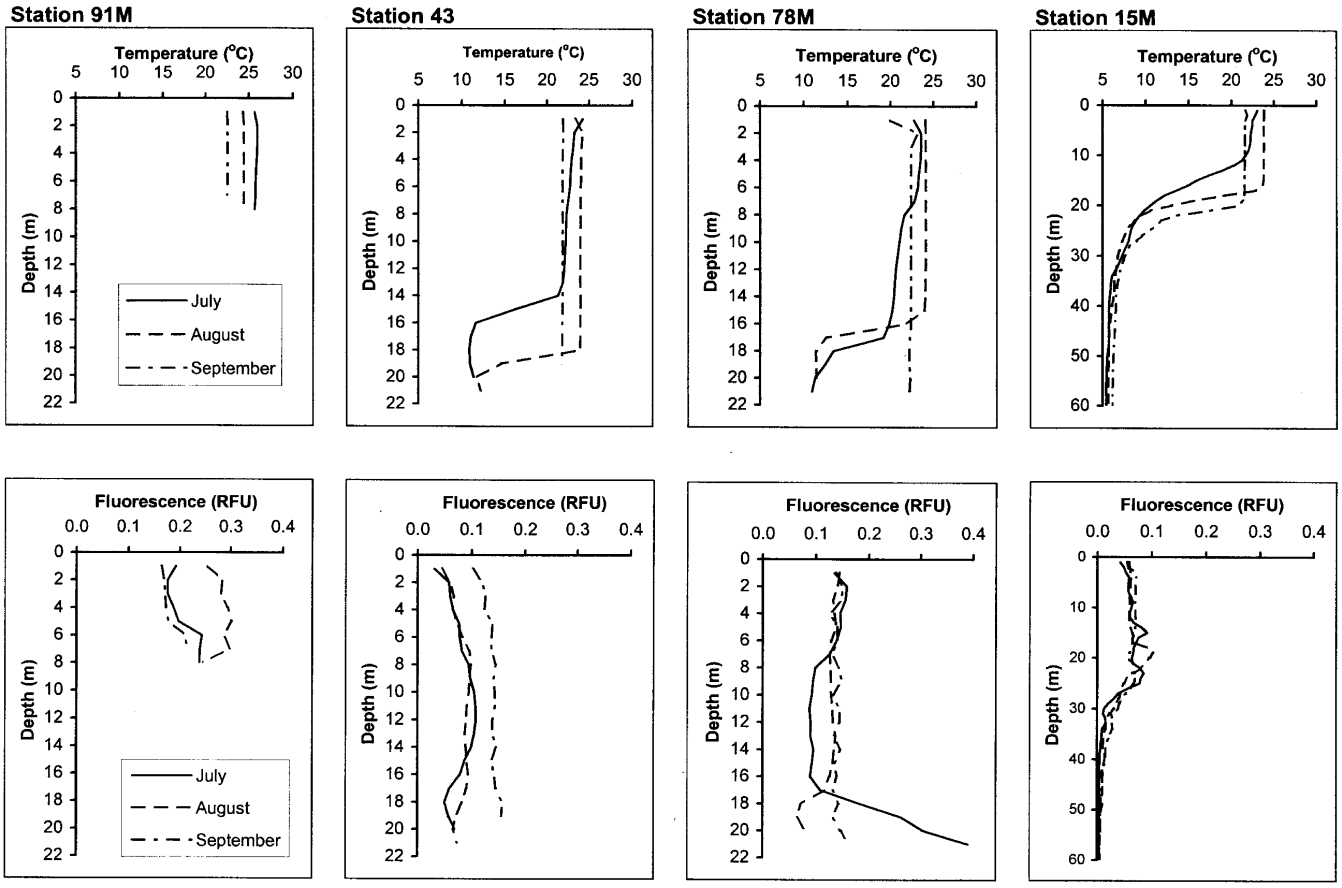

FIG. 2. Depth profiles of temperature and chlorophyll fluorescence (RFU) for July, August, and September at each of the sampling stations.

low western Sta. 91M was isothermal at all times and a cooling trend was evident from July through September. A strong thermocline was present at Stations 43, 78M, and 15M in July and August. The thermocline was absent from the stations in the central basin in September even though temperatures remained warm. The lack of stratification in September was most likely a consequence of water column mixing by wind. The thermocline occurred at a shallower depth in July at Sta. 43 than in August. The reverse trend was observed at Sta. 78M, however, the difference in the depth of the thermocline was only a meter. The thermocline at Sta. 15M in the eastern basin showed a gradual deepening from July through September although the deepening of the thermocline and cooler surface temperatures in September likely reflect the water column mixing that was evident at stations in the central basin.

Chlorophyll Fluorescence

Values of chlorophyll-*a* fluorescence (expressed as relative fluorescence units (RFU)) exhibited a general trend of increasing from east to west during each sampling period (Fig. 2). RFU values were lowest at Sta. 15M and showed little variation between sampling periods. Higher values near the surface waters (upper 30 m) at Sta. 15M likely reflect recent productivity. Within the central basin September was the month with highest fluorescence at Sta. 43. High values of fluorescence in the near bottom waters of Sta. 78M in July may be a consequence of the recent settling of phytoplankton material. August was the time of highest fluorescence at Sta. 91M.

Abundance and Isotopic Composition of O_2

Concentrations of O_2 from Winkler titrations and from CTD profiles are expressed in terms of frac-

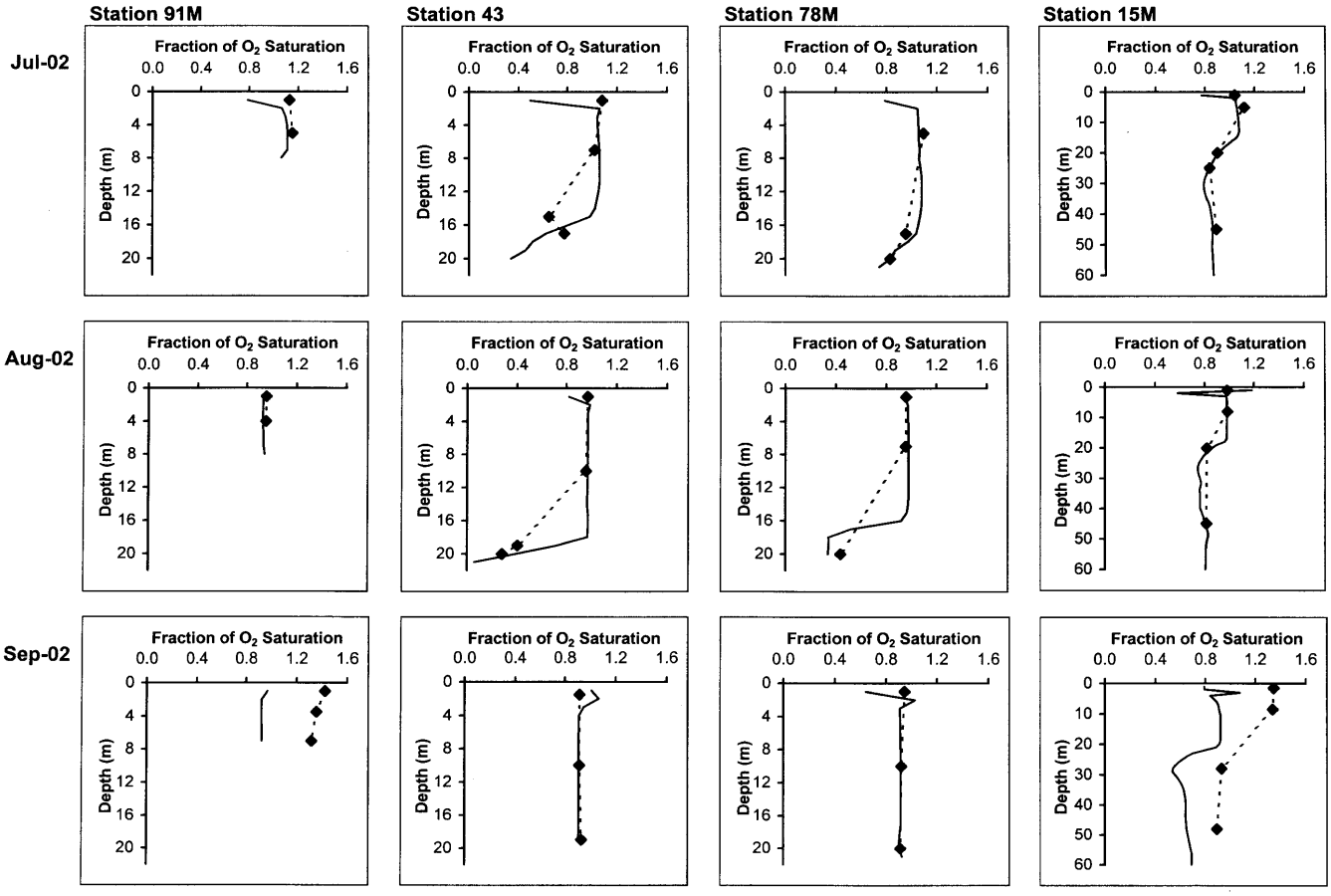

FIG. 3. The fraction of O_2 saturation as measured by the CTD electrode (solid line) and by Winkler titration (diamonds) in July, August, and September for each of the sampling stations.

tional saturation where a value of 1 represents equilibrium with the atmosphere at the *in situ* temperature (Fig. 3). There is good agreement overall between the values of concentration provided from titrations and from the CTD with a few exceptions. Surface water values (< 2 m) provided by the CTD were often less than those obtained by titration and this likely reflects depletion of O_2 within the electrode during the equilibration period of a few minutes prior to deployment. Only at stations 91M and 15M in September were substantial differences in O_2 concentrations between CTD and titration profiles evident, however, the trends with depth were quite similar. Concentrations in excess of saturation were evident in the epilimnetic waters of all stations in July reflecting a time of high primary production. All stations had slightly undersaturated concentrations of O_2 in August suggesting a period when respiration exceeded primary production. In September, the epilimnion of the eastern and western stations was strongly supersaturated (> 1.2); however, the central basin was undersaturated (< 0.9). Concentrations of O_2 at all stations, with the exception of isothermal Sta. 91M, tended to decrease with depth consistent with consumption by respiration. Depth profiles of O_2 saturation were nearly constant with time at Sta. 15M; however, profiles in the central basin were quite variable between sampling periods. The development of hypoxic conditions in the central basin in July was evident and the lowest concentrations at this time (< 0.4) were recorded by the CTD at Sta. 43 at 20 m (Fig. 3). Strong hypoxic conditions were evident at the central basin stations with the lowest recorded fraction of O_2 saturation of less than 0.1 at the bottom waters of Sta. 43 in August. Values for the fraction of O_2 saturation in hypolimnion were lower at Sta. 43 in July and August than at Sta. 78M. Hypoxic conditions were not evident in the bottom waters of the central basin in September and O_2

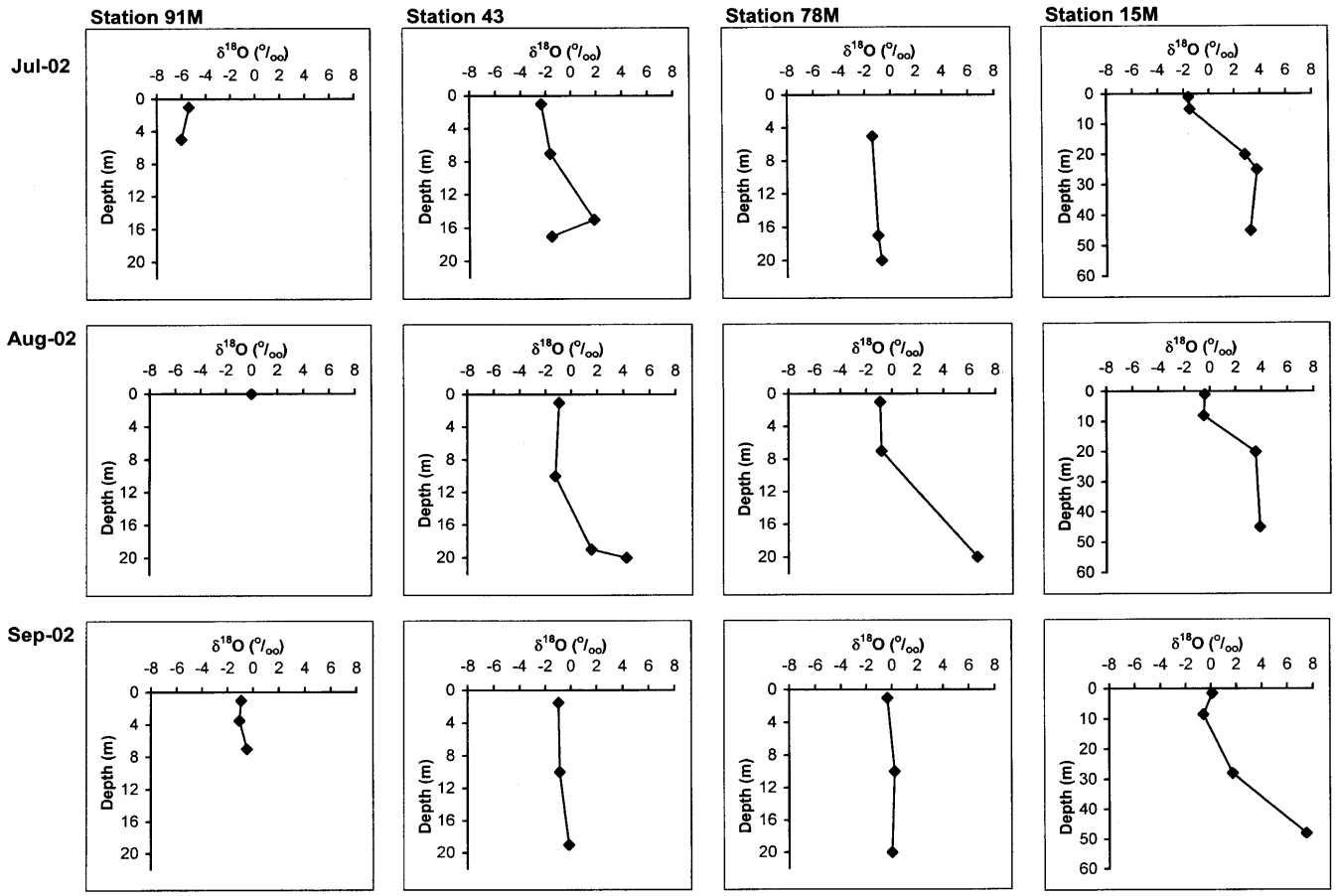

FIG. 4. The $\delta^{18}O$ of O_2 for each of the sampling stations in July, August, and September.

saturation values tended to be constant with depth. This consistency in O_2 concentration with depth is similar to that observed at this time in temperature (Fig. 2) and is a reflection of water column mixing most likely in response to wind activity.

The stable isotopic composition of O_2 within Lake Erie was highly variable and ranged between –6.0 and 7.5‰. Values less than 0.7‰, the value reflecting equilibration with the atmosphere, were observed in the surface waters of all stations at all times (Fig. 4). In general, such values reflect primary production in excess of respiration (Bender and Grande 1987). The lowest $\delta^{18}O$ values in surface waters were present in July and the lowest value observed, –6.0‰, was observed at this time at Sta. 91M. Isotope values at nearly all stations and sampling periods (with the exception of Sta. 91M in July and August and Sta. 78M in September increased with depth and coincided with declines in O_2 concentrations (Figs. 3 and 4). This trend is the result of isotope fractionation during respiration in which the heavy isotope is concentrated in the residual O_2 (Kiddon *et al.* 1993, Russ *et al.* 2004). The nearly constant values with depth for the $\delta^{18}O$ of O_2 at stations 43 and 78M in September is likely a consequence of water column mixing that resulted in homogeneous profiles of temperature and $[O_2]$ (Figs. 2 and 3).

Ratios of Respiration to Primary Production

Ratios of community respiration to photosynthesis in Lake Erie varied from as low as 0.45 to as high as 3.49 (Fig. 5). This high R:P ratio indicates that the rate of respiration was approximately 3.5 times greater than the rate of photosynthesis. The epilimnion of all stations in July was characterized by R:P ratios less than 1 indicative of net autotrophy. Values very close to 1 prevailed in August within the epilimnion of all stations and values approaching 1.5 were evident at stations 91M and 15M in September. R:P ratios generally increased

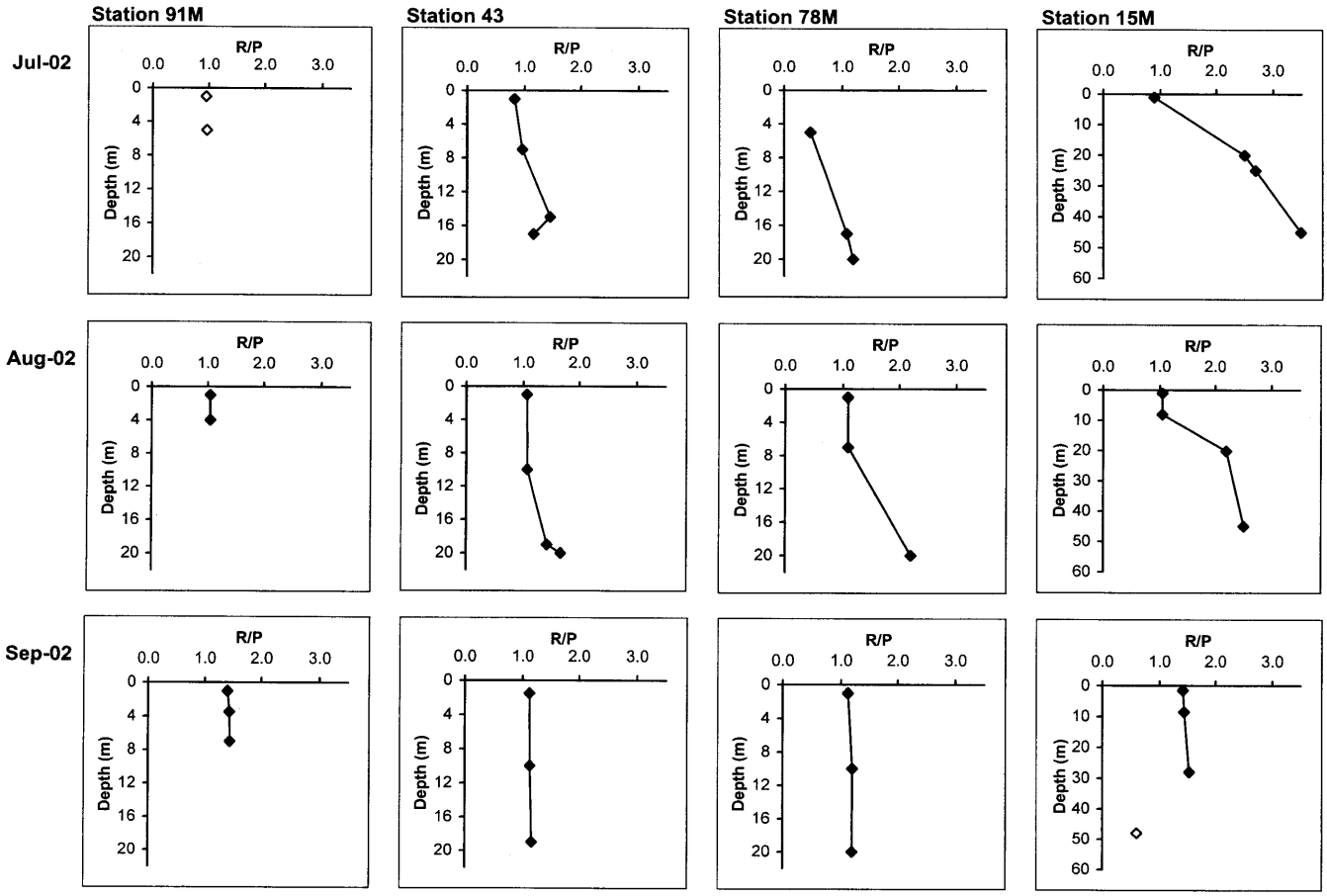

FIG. 5. Ratios of respiration to photosynthesis (R/P) for each of the sampling stations in July, August, and September. Open symbols indicate suspect data.

with depth at all stations reflecting reduced photosynthetic O_2 input to deeper waters. Homogeneous profiles of R:P ratios with depth at all stations in September were likely a consequence of water column mixing.

Rates of primary production based on the $H_2{}^{18}O$ incubation method varied from 0.20 mmol-$O_2 \cdot m^{-3} \cdot h^{-1}$ at Sta. 78M in September to as high as 1.77 mmol-$O_2 \cdot m^{-3} \cdot h^{-1}$ at Sta. 91M in September (Fig. 6). In August, rates of primary productivity decreased from west to east across the lake. Rates of primary production in September were at a minimum at Sta. 78M in the central basin. Although all incubations were conducted for the same time period (12 h), productivity measured *in situ* at Sta. 78M was approximately half of that measured *in vivo*. The results of *in situ* incubations are likely more indicative of actual rates of primary production than those conducted *in vivo* owing to differ-

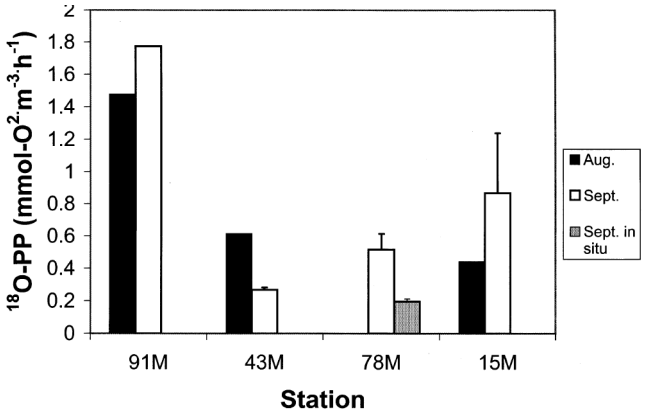

FIG. 6. Rates of primary productivity in Lake Erie based on incubations with ^{18}O-labelled water. Error bars reflect one standard deviation, however, replicates were not performed in August and at Sta. 91M in September. Rates were measured both **in vivo** *and* **in situ** *at Sta. 78M in September.*

ences in light regimes between the water column and incubator.

DISCUSSION

Lake Erie has experienced a long history of anthropogenic impacts that have altered nutrient levels, trophic status and contributed to the development and persistence of hypoxia within its central basin (Charlton *et al.* 1993, 1999; Charlton and Milne 2005). While the exact conditions that result in hypoxia are complex, O_2 depletion is a direct consequence of the respiration of allochthonous and autochthonous organic matter. Our study, therefore, concentrated on understanding rates of primary production and R:P ratios during the warmest part of the year when hypoxia is most prevalent. The development of thermal stratification precedes development of hypoxia in the central basin of Lake Erie (Charlton *et al.* 1993, Charlton and Milne 2005) and was evident in all months sampled in the eastern basin (Sta. 15M) and in July and August in the central basin stations (43 and 78M) (Fig. 2). Station 91M remained unstratified, which is likely a function of its shallow depth and susceptibility to mixing. The development of hypoxia was clearly evident in the central basin in July and particularly strong in August (Fig. 3). Hypoxia was no longer evident in the hypolimnion of the central basin in September and was most likely a response to extensive water column mixing that was indicated by the deepening of the thermocline at Sta. 15M and disappearance of stratification in the central basin.

Our observations of a trend of an increase in chlorophyll fluorescence (Fig. 2) and rates of primary production in August (Fig. 6) from east to west across the lake is similar to that reported 30 years ago (Glooschenko *et al.* 1973) and consistent with a greater degree of nutrient loading in the western basin (Charlton and Milne 2005). Vertical mixing of the water column is common in September and likely contributed to higher primary production in the eastern and western basins but not in the central basin. Comparison of ^{18}O-PP rates to those obtained previously in Lake Erie is dependent on conversion of measurements in units of O_2 to those of C. Based on simultaneous incubations using [^{14}C]-$NaHCO_3$ and $H_2{}^{18}O$ in Lake Erie in 2003 an average photosynthetic quotient (ratio of O_2 production to CO_2 consumption) of 0.64 was determined (Ostrom *et al.* 2005). Based on a photosynthetic quotient of 0.64 our rates of primary production are within the range of those reported by Glooschenko *et al.* (1973) 30 years ago, however, our maximum value is approximately a factor of 2 lower. Without more detailed measurements in time and space it is difficult to determine if rates of primary production in Lake Erie have changed. Consequently, the evaluation of changes in the trophic state based on rate measurements is currently limited.

O_2 Abundance and Isotopic Variation

Variation in the abundance and isotopic composition of dissolved O_2 in aquatic environments is a consequence of three predominant processes; primary production, respiration and atmospheric gas exchange. A reasonably accurate framework for a qualitative interpretation of isotope variation in O_2 is to consider values of approximately 0.7‰ to reflect atmospheric input, values less than 0.7‰ to be indicative of O_2 from primary production, and values greater than 0.7‰ to be the result of O_2 consumption by respiration (Bender and Grande 1987). Isotope values close to 0.7‰ are common in surface waters (Ostrom *et al.* 2000, Russ *et al.* 2004); however, the epilimnion of Lake Erie is dominated by values consistently less than 0.7‰ (Fig. 4). This trend indicates that the relative importance of biological activity with respect to atmospheric exchange is particularly important in Lake Erie relative to more oligotrophic systems (e.g., Russ *et al.* 2004). Furthermore, the occurrence of $\delta^{18}O$ values less than 0.7‰ indicates a strong input of O_2 from primary production during the summer in Lake Erie and this is consistent with a net autotrophic or eutrophic community. The common occurrence of values of O_2 saturation greater than 1 in the epilimnion of Lake Erie (Fig. 3) is further indicative of an ecosystem marked by high rates of primary production. In July, $\delta^{18}O$ values in the epilimnion were lower than other sampling periods and the lowest values of the entire study occurred at Sta. 91M at this time (Fig. 4). This suggests that July was a highly productive time period, particularly for the western basin; however, we lack primary production rate data to verify this. High values of the fraction of O_2 saturation are evident in the epilimnion of the western and eastern basins of Lake Erie in September indicative of high rates of primary production; however, $\delta^{18}O$ values reflect an atmospheric influence at this time perhaps as a consequence of the introduction of O_2 from recent wind activity. The observation of increasing $\delta^{18}O$-O_2 and decreasing O_2 abundance with increasing

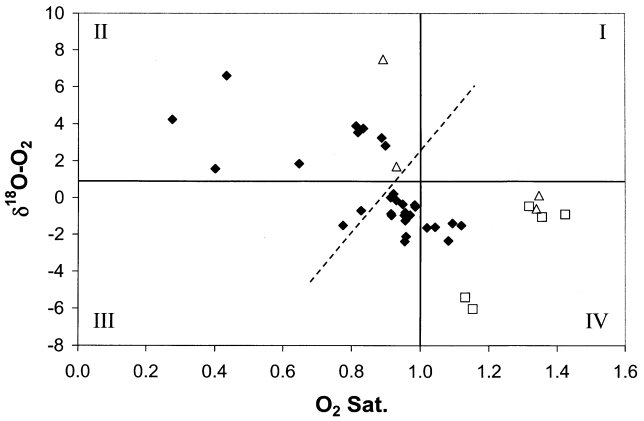

FIG. 7. Quad plot of the isotopic and fractional saturation (O_2 Sat.) of dissolved O_2 at all stations in Lake Erie. Open triangles indicate samples from Sta. 15M in September. Open squares indicate samples from Sta. 91M in July and September. All other data are indicated by solid diamond symbols. Samples to the left of the dashed line are all from hypolimnetic or near bottom waters.

depth in the water column is consistent with the consumption of O_2 by respiration (Kiddon *et al.* 1993, Ostrom *et al.* 2000, Russ *et al.* 2004). This trend was common in Lake Erie (Figs. 3 and 4) and particularly noteworthy in the central basin in August and at the western basin in September. Isotope shifts as a function of depth are similar between the central basin stations and Sta. 15M despite the fact that there is a much stronger decline in O_2 abundance in the central basin. Such differences in the relationship between O_2 abundance and isotope values may reflect variation in the fractionation factor associated with respiration between stations. In summary, the stable isotope and abundance data on O_2 establish July as a period of high primary production, August as a time of strong respiration in the central basin, and September as a period of strong atmospheric O_2 introduction.

A convenient means of understanding O_2 stable isotope and abundance data is by use of a "quad" plot (Quay *et al.* 1995, Field 2004) (Fig. 7). The intersection of the solid lines in Fig. 7 (equilibrium locus) indicates the isotope and fractional saturation values (0.7‰ and 1.0, respectively) obtained if exchange with the atmosphere is the only process affecting O_2. Temperate lake environments likely return to these values in winter and early spring once low light levels and cold temperatures limit biological activity. The distance between the intersection and data points is a qualitative reflection of the degree of O_2 cycling and trophic state which is exemplified by the fact that 2 years of data within ultra-oligotrophic Lake Superior lie between ±2‰ in $\delta^{18}O$ and fractional saturations of 0.8 to 1.2 (Russ *et al.* 2004); a small range relative to what we observed in Lake Erie. Quadrant 4 contains fractional saturation values greater than 1 (supersaturation) and $\delta^{18}O$ values less than 0.7‰ that are both indicative of O_2 production by photosynthesis. The values within quadrant II result from respiration in which the abundance of O_2 is reduced to values less than 1 and $\delta^{18}O$ values increase owing to fractionation during consumption. Primary production and respiration shift the abundance and $\delta^{18}O\text{-}O_2$ in opposite directions away from the central values reflecting equilibrium with the atmosphere.

Within Lake Erie a large number of samples lie within quadrant III for which O_2 saturation values indicate net heterotrophy; however, isotope values indicate a predominance of photosynthesis over respiration. There are two possible mechanisms to explain this result: either (1) the equilibrium locus values do not represent the isotope and fractional saturation values once photosynthesis and respiration initiate in early spring, and/or (2) the isotope effects associated with respiration and photosynthesis are not equal and opposite. The former is supported by the observation in Lake Superior that even during the cold unstratified spring O_2 fractional saturations were less than 1; i.e. the equilibrium locus did not describe values for the system prior to initiation of the spring bloom (Russ *et al.* 2004). The latter is exemplified by the fact that if rates of photosynthesis and respiration are equal the concentration of O_2 will be unaffected, however, a net isotope shift will occur. This result is a consequence of the fact that primary production introduces O_2 without fractionation (and therefore $\delta^{18}O$ is linear with respect to $1/[O_2]$), however, respiration is a strongly fractionating process ($\delta^{18}O$ linear with respect to $\ln[O_2]$) (see Ostrom *et al.* 2002 for review). The isotope shifts resulting from primary production and respiration are, therefore, not equal and opposite. Consequently, as the O_2 fluxes by photosynthesis and respiration begin to predominate over that from gas exchange the location of data points within the Quad plot will deviate progressively from the equilibrium locus. The tendency for values to be concentrated within quadrant III reflects the strong predominance of respiration on O_2 within the Lake Erie ecosystem. Environments dominated by net autotrophy would very

likely be characterized by a common occurrence of values in quadrant II. Overall, the wide range of O_2 concentration and isotope values and tendency for values to deviate from the equilibrium locus is a function of the strong predominance of biological activity relative to gas exchange.

Ratios of R:P

As an indicator of the relative importance of rates of community respiration and primary production, the R:P ratio provides a measure of lake metabolism. Ratios of R:P in the epilimnion of Lake Erie (10 m or less) progressed with season from values indicative of net autotrophy in July (0.45 to 1.03), slight net heterotrophy in August (1.04–1.11), and strongly net heterotrophy in September (1.12 to 1.44). The net heterotrophy and hypoxia within the hypolimnion of the central basin of Lake Erie in August was likely driven by metabolism of autotrophic materials given that primary productivity prevailed over respiration in July. This trend is consistent with the accumulation of chlorophyll in central basin sediments in mid-summer and its subsequent decline (Carrick *et al.* 2004). Rates of primary production did not show consistent changes from August to September (Fig. 6), therefore, the seasonal trends in R:P ratios must be affected by variation in rates of respiration in addition to changes in autochthonous production. The range of values for the epilimnion of Lake Erie (0.45 to 1.44) are not markedly distinct from the epilimnion of the oligotrophic systems of Lake Superior (0.5 to 2.1) and Grand Traverse Bay, Lake Michigan (0.6 to 1.4) (Field 2004, Russ *et al.* 2004). Only upon inclusion of values within the hypolimnion of Lake Erie does the maximum R:P value of 3.5 distinguish the eutrophic Lake Erie from the other Great Lakes.

Small but important differences in the ratio of R:P reported can be a consequence of the methodology used. Recently, observations of net heterotrophy in oligotrophic ocean regions far from shore have been explained as a tendency for incubation approaches to underestimate primary production (Karl *et al.* 2003). The use of [^{14}C]-$NaHCO_3$ in incubation, for example, may yield a rate intermediate between net and gross production (Howarth and Michaels 2000). Furthermore, incubation approaches to primary production reflect the short-term activity of the pelagic community within bottles and may not reflect production on longer time scales (Howarth and Michaels 2000, Hanson *et al.* 2003). Production estimates based on continuously deployed *in situ* electrodes have a greater ability to capture episodic production events that may be missed by short term bottle incubations (Emerson *et al.* 2002, Hanson *et al.* 2003, Karl *et al.* 2003). Continuous *in situ* measurements of O_2 may, therefore, provide lower values for R:P ratios than ^{14}C-based estimates of primary productivity and reflect longer time scales approaching the residence time of O_2 (Hanson *et al.* 2003). The R:P ratios presented in this study are based on the concentration and isotopic composition of dissolved O_2 (equations 2 and 3). Because this measure of R:P is based on analysis of ambient O_2 and does not involve incubation it provides a measure on a time scale approaching that of the residence time of O_2 and, therefore, the values obtained are comparable to *in situ* measurements. Furthermore, an important advantage of oxygen isotope R:P ratios relative to electrode measurements are that they can readily be obtained across broad spatial and temporal scales.

During time periods in which the contrast in the $\delta^{18}O$ of O_2 between the epilimnion and hypolimnion is great, the epilimnetic R:P ratio can be influenced by the mixing of ^{18}O enriched O_2 from deep waters. The change in $\delta^{18}O$ that results ($^{18}\Delta_m$) is a function of the contrast in isotope values between the epilimnion ($\delta^{18}O_e$) and hypolimnion ($\delta^{18}O_h$), variation in the mixed layer depth (ΔZ) and depth of the mixed layer (Z_m) (Sarma *et al.* 2005):

$$^{18}\Delta_m = (\delta^{18}O_h - \delta^{18}O_e) \times \Delta Z/Z_m \qquad (4)$$

Deepening of the mixed layer over the time frame of the residence time of O_2 would result in an increase in $\delta^{18}O_e$ and R:P that can be corrected for if $^{18}\Delta_m$ is calculated. Determination of ΔZ requires repeated observation of the mixed layer depth on a time frame approaching the residence time of O_2 (9–40 days). Between July and August of 2002, the mixed layer depth increased from approximately 15 m to 19 m at station 43 (a decrease was observed at 78M). Given that August was the time of greatest contrast in $\delta^{18}O$ between surface (–0.8‰) and deep waters (4.2‰) at 43, we estimate a value for $^{18}\Delta_m$ of 0.41‰. This worst-case-scenario results in a change in R:P ratio from our reported value of 1.06 to 1.04. We consider this is a relatively minor influence and have, therefore, made no further attempt to correct R:P values for mixing.

Fundamental to the application of equations 2 and 3 to determine R:P ratios based on oxygen isotope values is an underlying assumption of steady

state with respect to O_2 fluxes. At steady state, the control of gas exchange on the isotopic composition of and abundance of O_2 is offset by photosynthesis and respiration. Based on the rates of primary production we measured (Fig. 6) and observed concentrations of O_2, we calculate that the turnover time for O_2 in Lake Erie (corrected for the hydraulic residence time of 986 days) varies between 9 and 40 days. These values indicate a strong biological control on O_2 and suggest that deviation from the steady state assumptions is possible during periods of high primary production. We believe there are several data points in which equations 2 and 3 fail to predict R:P ratios accurately. At Sta. 91M in July, strong supersaturation is evident (Fig. 3) and very negative $\delta^{18}O$ values are indicative of O_2 derived predominantly from photosynthesis; nonetheless predicted R:P ratios are close to 1. At Sta. 15M in September, a strong predominance of respiration over photosynthesis is indicated by a moderate degree of undersaturation and a very positive $\delta^{18}O$ value of 7.5‰ for the deepest sample. The R:P model, however, predicts a value of 0.6 indicative of net autotrophy. We believe that these R:P ratios for Sta. 91M in July and the hypolimnion for station 15M in September are erroneous. These samples are extremes in the isotope data set and suggest that, likely as a consequence of the violation of the steady state assumption, the oxygen isotope R:P model is not successful for extremely high (> 7‰) or low (< –5‰) isotope values.

The application of R:P ratios to indicate trophic state is based on the premise that external inputs of organic carbon from rivers and groundwater drive oligotrophic systems toward net heterotrophy (R > P). In eutrophic systems, in contrast, *in situ* primary production is sufficient to exceed the respiration of both allochthonous and autochthonous material and results in the prevalence of net autotrophy (P > R) (Jones 1992; del Giorgio and Peters 1993, 1994). The observation of periods or regions of net autotrophy within many oligotrophic environments, however, has recently brought into question the use of the R:P ratio as an indicator of trophic state (Carignan *et al.* 2000, Hanson *et al.* 2003, Russ *et al.* 2004). R:P ratios for surface waters in Lake Erie varied between 1 and 1.4 in August and September and are indicative of a predominance of net heterotrophy at this time, even though rates of primary production are high in September (Fig. 6). Net autotrophy, however, was clearly evident in July in Lake Erie by R:P ratios that are less than 1 for the surface waters of all stations (Fig. 5). Lake Erie, therefore, oscillates between a period of strong net autotrophy in July to a period of net heterotrophy in August and September. A very similar pattern of seasonal oscillation in R:P ratios, with net autotrophy prevailing following stratification in Lake Superior and net heterotrophy at other times was evident in the oligotrophic Lake Superior and Grand Traverse Bay, Lake Michigan (Field 2004, Russ *et al.* 2004). Consequently, Lake Erie oscillates between periods of net autotrophy and net heterotrophy in a manner and range of R:P ratios that is similar to that observed in the oligotrophic systems of Lake Superior and Grand Traverse Bay. Given this, the absolute values of R:P ratios are not a satisfactory measure of the trophic state of Lake Erie.

The vast areal extent and volume of the Great Lakes indicates that they are inherently distinct systems relative to the smaller lakes in which most R:P ratios have previously been reported (e.g., del Giorgio and Peters 1994, Carignan *et al.* 2000). The input and metabolism of terrestrial organic matter within the Great Lakes must comparatively be less important than in smaller lakes with larger watershed to lake ratios. The minor influence of terrestrial organic matter is substantiated by C and N isotope data and C:N molar ratios that indicate a predominance of autochthonous organic matter in the water column and sediments of the Great Lakes (Schelske and Hodell 1995; Ostrom *et al.* 1998a, 1998b; McCusker *et al.* 1999). Within such systems, variation in the degree of net autotrophy or heterotrophy must be driven primarily by temporal decoupling of primary productivity and respiration (Biddanda and Cotner 2002, Field 2004, Russ *et al.* 2004). Rapid settling of spring bloom production, for example, may result in a period of net autotrophy followed later in time by net heterotrophy when fall water column mixing returns settled material to the upper water column.

The comparatively small size (on an areal basis), volume, and depth of Lake Erie dictate that lake metabolism will function in a fundamentally distinct manner from the other Great Lakes. The shallow depth of Lake Erie results in a tendency for extensive water column mixing and associated resuspension of sedimentary organic matter that may contribute to net heterotrophy in late summer and fall when high rates of primary production suggest that autotrophy is expected. There exists a realistic possibility that at least part of the predominance of net heterotrophy in Lake Erie is driven by metabolism of organic matter deposited decades ago when

the lake was heavily impacted by excessive anthropogenic phosphorus loadings. Net heterotrophy in Lake Erie may, furthermore, be enhanced by highly enriched coastal waters. Rates of primary production within Sandusky Bay, a coastal embayment near the western end of Lake Ere, were approximately 20 times greater than that occurring in the central and eastern basins of Lake Erie (Ostrom *et al.* 2005). The introduction of this material into Lake Erie and subsequent eastward transport would result in a misbalance of respiration and production. Consequently, Lake Erie may not only be a system characterized by temporal decoupling of respiration and production but by spatial decoupling as well. Rain events or turbidity plumes may introduce organic matter that is metabolized as it is transported across the lake shifting the metabolic balance in favor of respiration (Carrick *et al.* 2005).

The Relative Importance of Sediment Vs. Water Column Respiration

An important component of the R:P model (equations 2 and 3) is the value used for the fractionation factor for respiration. Respiration can proceed by a number of different pathways that have unique magnitudes of fractionation (Kiddon *et al.* 1993, Luz *et al.* 2002). The net fractionation factor for an ecosystem cannot be predicted without knowing the relative importance of each respiration pathway and it is best to measure this value experimentally within the system of interest. We did not obtain a sufficient isotope shift in dark bottle incubations to calculate the respiration isotopic enrichment fractionation factor for Lake Erie and have assumed a value that was determined in Lake Kinneret of 23.5‰ (Luz *et al.* 2002). The isotopic enrichment factor, ε, is defined here as $(1/\alpha\text{-}1)*1{,}000$. Small variations in the value of the respiration fractionation factor do not impart large changes in R:P ratios (Russ *et al.* 2004) but variations in excess of several ‰ will. Because of the limitation of diffusion to the sites of respiration, consumption of O_2 in sediments has been shown to occur with little fractionation (3‰) (Brandes and Devol 1997). The $\delta^{18}O\text{-}O_2$ values for the hypolimnion of central basin stations in August and the eastern basin Sta. 15M in September are all greater than 5‰ and approximately equal; however, the values of fractional O_2 saturation are much lower in the central basin than at Sta. 15M (Figs. 3 and 4). This distinction suggests that the net ε value for hypolimnetic respiration in the central basin in August was substantially less than it was for the eastern basin in September.

If a system can be considered closed and only one process affects the concentration and isotopic abundance of a material, the isotopic enrichment factor, ε, can be determined by the following modification of the Rayleigh equation (Mariotti *et al.* 1981; Ostrom *et al.* 2002):

$$\delta_s = \delta_{so} - \varepsilon \ln(C/C_o) \quad (5)$$

where the isotopic composition of the residual substrate of a reaction (δ_s) is related to that of the initial substrate (δ_{so}), ε, and the ratio of the observed to initial substrate concentration (C/C_o). We can apply this equation to evaluate respiration of O_2 in the hypolimnion of Lake Erie based on the assumptions that the initial concentration of O_2 reflects that which resulted from equilibrium with the atmosphere at the observed temperature and that hypolimnetic warming was negligible. With this assumption C/C_o can be replaced with the O_2 fractional saturation (O_2 Sat.) and equation 5 becomes:

$$\delta_s = \delta_{so} - \varepsilon \ln(O_2 \text{ Sat.}) \quad (6)$$

If equation 6 is plotted in the coordinates of δ_s vs. $-\ln(O_2 \text{ Sat.})$ then the slope of the line is equivalent to ε and the intercept is the $\delta^{18}O\text{-}O_2$ prior to development of the hypolimnion. Data from hypolimnetic waters in July and August for stations 43, 78M, and 15M to yield a slope equal to ε in Figure 8. While the relationships shown in Figure 8 are based on sparse data the r^2 values (when more than two data points are available) are excellent. To our knowledge, this is the first time that isotopic enrichment factors for respiration in hypolimnetic waters based on *in situ* data have been calculated. Owing to sampling constraints and the narrow depth of the hypolimnion in the central basin we did not obtain sufficient samples to more thoroughly test the relationship in equation 6, however, a more exhaustive data set from 2003 in Lake Erie shows similar trends (Piwinski and Ostrom, unpublished data). Nonetheless, the strong relationships obtained are compelling and the low values of ε obtained have important implications for calculations of R:P ratios in the hypolimnion (as discussed below).

The average of estimates for the respiration ε value in the hypolimnion of Lake Erie is 7.9‰; a value that is substantially less than the fractionation factor of 23.5‰ that we assumed from the water

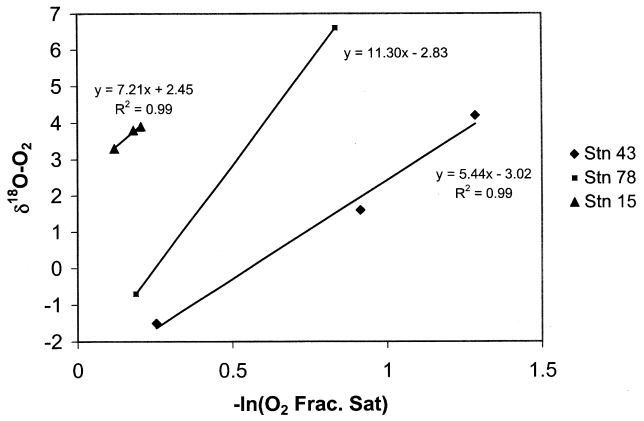

FIG. 8. Relationship between the $\delta^{18}O$ of O_2 and the natural log of the O_2 fractional saturation for hypolimnetic waters. The slope of the line indicates the isotopic enrichment factor (ε) (units in ‰) for respiration.

column of Lake Kinneret (Luz *et al.* 2002). While the Lake Kinneret value of the isotopic enrichment factor for use in the R:P model is reasonable for the epilimnion and metalimnion of Lake Erie its use for hypolimnion samples will provide underestimates of R:P ratios. Revised estimates of R:P ratios for hypolimnion samples based on an ε value of 7.9 ‰ increase. The most dramatic increase in R:P ratios is for samples at Sta. 43 that increased from 1.5 to 7.1 in July (15 m) and from 1.7 to 20.4 in August (20 m). This extremely high ratio of R:P clearly distinguishes Lake Erie from the oligotrophic environments of Lake Superior and Grand Traverse Bay, Lake Michigan where values did not exceed 2.6 (Field 2004, Russ *et al.* 2004).

The low value for ε that we report indicates that much of the respiration of O_2 in the hypolimnion of Lake Erie occurs within sediments where expression of isotope fractionation is reduced. Based on values for fractionation during respiration in the water column (23.5‰) (Luz *et al.* 2002) and those in sediments (3‰) (Brandes and Devol 1997) we predict that 61% of total O_2 respiration occurs within sediments and 39% occurs within the water column of the hypolimnion. This determination is susceptible to diffusion of O_2 across the hypolimnion. However, if this process had occurred then the tendency would have been for the relationship shown in Figure 8 to become non-linear, which is not what we observe with the limited data available.

SUMMARY AND CONCLUSIONS

While improvements to Lake Erie's overall water quality over the past 30 years are apparent (i.e., reductions in algal blooms and decreases in turbidity), evaluation of the restoration of Lake Erie based on traditional water column parameters ([P], [chl-*a*] and [O_2]) continues to be elusive and is exemplified by the observation that while concentrations of P in Lake Erie have shown recent increases there does not appear to be a response by the phytoplankton community (Charlton and Milne 2005). Given that many of the undesirable conditions characteristic of poor water quality are a direct or indirect consequence of algal growth perhaps the best measure of the health of an ecosystem or trophic state would be direct measures of primary production rates. Currently there are not sufficient data to evaluate long-term trends in primary production in Lake Erie and our results based on incubation with ^{18}O enriched water (Ostrom *et al.* 2005) should serve as a basis to evaluate future changes whether rates are based on this technique or more traditional approaches.

We determined the R:P ratio for the mid- to late summer in Lake Erie, a time when the development of hypoxia in the central basin is typically problematic and related to the eutrophic nature of the lake. We observed in July strong evidence of net autotrophy, indicative of eutrophic conditions, preceding the development of hypoxia in August. Thus it is quite likely that the net production of organic matter in July fostered the development of hypoxia, although physical factors, such as depth of the hypolimnion, are most certainly contributing factors (Charlton and Milne 2005). In August and September we observed net heterotrophy in the epilimnion that, based on the relationship between R:P ratios and trophic state proposed by del Giorgio and Peters (1993, 1994), would previously have been considered to reflect oligotrophic conditions. While net heterotrophy is consistent with oligotrophic conditions, we contend that the predominance of R:P ratios less than 1 in July, the tendency for R:P ratios to exhibit a wide range relative to the oligotrophic systems of Lake Superior (R:P between 0.5 and 2.5) and Grand Traverse Bay (R:P between 0.6–1.4), and wide range of fractional O_2 abundance (0.04 to 1.36) and $\delta^{18}O$ values (–6.0 to 7.5‰) all identify Lake Erie as a eutrophic system

The observation of strong net heterotrophy in this eutrophic system is likely a reflection of the metabolism of resuspended sedimentary organic matter in

addition to terrestrial inputs. As sediments may have been deposited months to decades ago the metabolism of this material decouples primary production and respiration in time and contributes to the observation of net heterotrophy. Furthermore, nutrient loading to coastal embayments in Lake Erie may stimulate autochthonous production and the respiration of this material as it is introduced to Lake Erie and progresses across the lake strongly alters lake metabolism in favor of respiration. Consequently, while absolute ratios of R:P may not be direct indicators of trophic state they are quite valuable in monitoring the response of phytoplankton and bacterial communities to seasonal and episodic events.

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