

# Are the Great Lakes a significant net source or sink of CO<sub>2</sub>?

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## Introduction

It is widely recognized that many lakes are net sources of CO<sub>2</sub> to the atmosphere (COLE et al. 1994, KLING et al. 1991, SOBEK et al. 2005). Recent estimates suggest this flux is significant in the global carbon cycle (COLE et al. 2007); however, our ability to predict CO<sub>2</sub> fluxes from any particular lake remains limited. SOBEK et al. (2005) suggested that dissolved organic carbon (DOC) supply to lakes was the major determinant of the dissolved CO<sub>2</sub> content of the lakes. Inputs of DOC to lakes are affected by the amount of wetlands in the catchment and the relative size of lake and catchment (ENGSTROM 1987, GERGEL et al. 1999, HOULE et al. 1995); however, the respired fraction of DOC inputs to a lake will depend on many site-specific factors such as water retention time, lake temperature, amount of solar radiation received, and nutrient supply. For example, the turnover time of DOC in Lake Superior was estimated to be about 8 years (URBAN et al. 2005); only a fraction of DOC inputs could be respired in lakes with shorter water residence times. This study demonstrates that even lakes with small catchments and correspondingly small areal loadings of DOC may be net sources of CO<sub>2</sub> to the atmosphere.

The processing of DOC inputs is only one term to consider in predicting whether a lake will be a net source of CO<sub>2</sub>. All lakes fix CO<sub>2</sub> and bury some amount of the autochthonously produced organic matter in their sediments. The net emissions of CO<sub>2</sub> reflect the difference between burial (and outflow) of autochthonous organic matter and respiration of allochthonous organic matter inputs. Rates of autochthonous organic carbon burial in lakes are a function of a variety of factors including nutrient availability, lake depth, lake mixing regime, and sedimentation rate.

Despite their large size, little effort has been made to assess whether the Laurentian Great Lakes are net sources or sinks of CO<sub>2</sub> to the atmosphere. One goal of the North American Carbon Program is to establish regional carbon budgets for North America. To date, such efforts have neglected the role of lakes in storing or emitting carbon (e.g., DAVIS et al. 2003). A simple assessment of the 3 factors listed above (allochthonous DOC supply, water residence time relative to DOC turnover, and organic carbon burial rates within the sediments) would suggest that all the Great Lakes should be

net sources of CO<sub>2</sub> to the atmosphere. We evaluate that hypothesis with the historical record of *p*CO<sub>2</sub> in the Great Lakes as measured by the U.S. Environmental Protection Agency (EPA) in their Great Lakes monitoring program. Some detailed measurements on Lake Superior are also presented to illustrate the factors regulating gas emissions and to elucidate the work that would be required to obtain better estimates of annual emissions from the Great Lakes.

**Key words:** carbon dioxide, emission, Great Lakes

## Study site

The 5 Laurentian Great Lakes, the focus of this work, span a range in lake size, depth, water residence time, and concentrations of chlorophyll, DOC, and inorganic nutrients that may predispose them to have different emissions of CO<sub>2</sub> (Table 1). Data from the EPA's biannual Great Lakes surveillance program are presented. A synoptic survey of all 5 Great Lakes is conducted in spring (April–May) and August of each year. Monitoring of Lake Superior began in 1992; 19 stations are visited in spring and 23 sites in summer. Monitoring for the other 4 lakes began in 1983; the number of stations varies (e.g., Lake Michigan: 13 stations in spring and 21 stations in summer; Lake Ontario: 8 sites in spring and 12 in summer). The stations cover open lake areas well, but coverage of shallow areas and embayments is limited.

Data are also presented for recent sampling of Lake Superior for above-lake CO<sub>2</sub> concentrations and for seasonal changes in dissolved CO<sub>2</sub> (*p*CO<sub>2</sub>). Air above the lake was sampled on a short cruise in the vicinity of Ontonagon, Michigan. The cruise track (approximately 18 km) went from a station 9 km from shore (46°57.469'N, 89°20.206'W) to a station 0.5 km from shore (46°50.151'N, 89°34.460'W). Water samples for determination of *p*CO<sub>2</sub> were collected in 2 areas near the towns of Ontonagon and Marquette, Michigan. The Ontonagon area samples were collected at a station 9 km from shore (57-m water depth) and at a second station 0.5 km from shore (6-m water depth). Near Marquette, samples were collected at a single location 0.5 km from shore (water depth of 18 m). Additional water samples were collected from the

**Table 1.** Characteristics of the Great Lakes.

Parameter	Superior	Huron	Michigan	Erie	Ontario
Surface area (m <sup>2</sup> ) <sup>a</sup>	8.21×10 <sup>10</sup>	5.78×10 <sup>10</sup>	5.96×10 <sup>10</sup>	2.57×10 <sup>10</sup>	1.90×10 <sup>10</sup>
Catchment: Lake area ratio <sup>a</sup>	1.6	2.2	2.0	3.0	3.4
Max. depth (mean depth, m) <sup>a</sup>	406 (147)	282 (85)	229 (59)	64 (19)	244 (86)
Hydrologic Residence Time (yr) <sup>a</sup>	191	22	99	2.6	6
Summer chlorophyll (mg m <sup>-3</sup> ) <sup>b</sup>	0.4	0.5	0.6	1.3	1.5
Spring total phosphorus (mg m <sup>-3</sup> ) <sup>c</sup>	2.4	3.5	4.2	18.2 <sup>e</sup>	4.4
DOC (mg m <sup>-3</sup> )	1.40 <sup>f</sup>	2.43 <sup>d</sup>	1.68 <sup>g</sup>	3.49 <sup>d</sup>	2.60 <sup>d</sup>

a) From the Great Lakes Atlas (U.S. EPA 1995)

b) Data for 1998 from BARBIERO & TUCHMAN (2001)

c) Data from U.S.EPA spring 2002 (<http://www.epa.gov/glnpo/monitoring/limnology/>)

d) Data from SMITH et al. (2004).

e) Central basin

f) URBAN et al. (2005)

g) BIDDANDA & COTNER (2001)

municipal water intakes of these 2 towns; the intakes draw water from the near-shore stations described above.

## Methods

Water samples from the 2 municipal water intakes were obtained monthly from January through June of 2007. Raw lake water was collected from a tap in the treatment plants; a 20-L carboy was filled completely such that no headspace was present. The pH was measured at both plants using benchtop pH meters. In May and June (2007), additional water samples were obtained at the stations described above from aboard the *R/V Agassiz* using a 30-L Niskin bottle; sampling depths were 5 m below the surface and 1 m above the bottom. Water from the Niskin bottle was used to completely fill a 20-L carboy such that no headspace remained. The pH was measured in the field in a closed container that allowed no gas exchange with the atmosphere; readings were obtained immediately after sample retrieval such that no temperature change occurred. Precision of replicate field pH measurements was generally 0.1 pH unit. We analyzed 18 water samples over a 6-month period.

In the laboratory, samples were analyzed for alkalinity and total inorganic carbon (C<sub>T</sub>). For alkalinity measurements, three 50-mL aliquots of water were transferred to beakers and allowed to reach room temperature. Samples were then titrated with pre-standardized acid (0.024 N HCl) using an autotitrator (ManTech Associates PC-Titrate). Titration endpoints were determined using Gran's analysis. Acid strength was calibrated with reagent-grade NaHCO<sub>3</sub>. Precision on replicate titrations was generally <2%. Total inorganic carbon was measured with a Sievers 800 Total Carbon Analyzer; samples were transferred to glass vials sealed with neoprene septa and analyzed in triplicate. Precision on triplicate analyses was better than 1%, and recovery of certified standards was between 95.5 and 100%.

Data obtained from the EPA Great Lakes National Program Office included values for temperature, pH, and alkalinity measured in depth profiles at all monitoring stations for 1983–2006. Dissolved CO<sub>2</sub> (pCO<sub>2</sub>) concentrations for both the EPA data as well as the 2007 Lake Superior samples were calculated (Table 2).

On one occasion, CO<sub>2</sub> concentrations were also measured in the air above Lake Superior. A LICOR 7500 open-path CO<sub>2</sub> sensor was used to monitor CO<sub>2</sub> concentrations at a sampling frequency of 1 Hz during a sampling cruise in June 2007. The sensor head was mounted vertically on the roof of the boat cabin, approximately 2.5 m above water level. The LICOR unit was calibrated in the laboratory using certified standards (zero gas and 501 ppm + 2%) obtained from Air-Gas Inc. Calibration was performed immediately before the cruise; the standards were measured again upon return to the laboratory to verify that no drift occurred during sampling. Wind speed (5.9 m/s at 5 m height) and direction (249° or WSW) were relatively constant throughout the sampling time as indicated by measurements from NDCB buoy 45006 in that region of the lake.

## Results

Measured values for alkalinity and pH in the Lake Superior samples were within the range previously reported for the lake. Values of pH ranged from 7.6 to 8.2; this range coincides exactly with the seasonal range reported by WEILER (1978) for the first intensive study of the lake in 1973. The 18 measured alkalinity values were between 0.695 and 0.966 meq/L, with an average of 0.888 meq/L; the single low value occurred on a day when the Ontonagon River plume impacted the water from the municipal water intake at Ontonagon, as evidenced by high turbidity and low conductivity of the

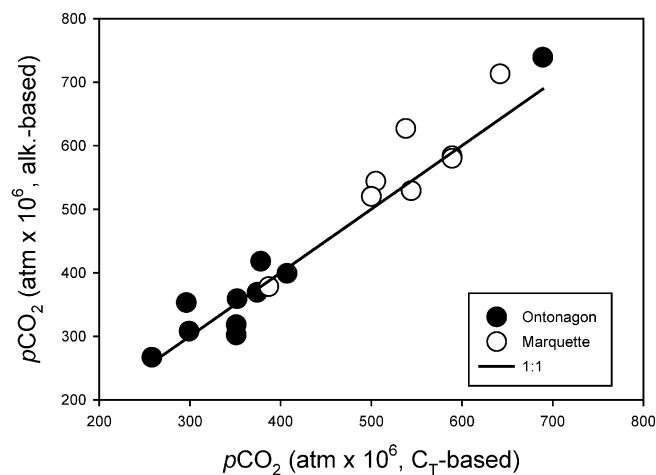
Equation	Symbol	Definition
$Alk = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$	[ ]	denote concentrations
$[H^+] = \frac{1}{\gamma_{(1)}} \cdot 10^{-pH}$	pH $\gamma_{(1)}$	measured pH activity coefficient for monovalent ion
$[OH^-] = \frac{K_{w(T)}}{\gamma_{(1)} \cdot 10^{-pH}}$	$K_{w(T)}$	Temperature-corrected equilibrium constant for water dissociation
$pCO_2 = \frac{\{H_2CO_3^*\}}{K_{H(T)}}$	$K_{H(T)}$	Temperature-corrected Henry's law constant
$\{H_2CO_3^*\} = \frac{C_T \{H^+\}^2}{\{H^+\}^2 + \frac{\{H^+\}K_1}{\gamma_{(1)}} + \frac{K_1K_2}{\gamma_{(2)}}}$	$C_T$ $K_1, K_2$  $\gamma_{(2)}$	Dissolved inorganic C Temperature-corrected acid dissociation constants for carbonic acid and bicarbonate Activity coefficient for divalent ion
$C_T = \frac{Alk + [H^+] - [OH^-]}{\alpha_1 + 2\alpha_2}$		
$\alpha_1 = \left[ \frac{\gamma_{(1)}^2 [H^+]}{K_1} + 1 + \frac{K_2}{\gamma_{(2)} [H^+]} \right]^{-1}$		
$\alpha_2 = \left[ \frac{\gamma_{(2)} \gamma_{(1)}^2 [H^+]^2}{K_1 K_2} + \frac{\gamma_{(2)} [H^+]}{K_2} + 1 \right]^{-1}$		

**Table 2.** Relationships used to compute  $pCO_2$  from measured values of pH, temperature and alkalinity.

water. The next lowest value was 0.835 meq/L. The average alkalinity reported by WEILER (1978) was 0.84 meq/L, and the average observed in the KITES study (1998–2001) was 0.89 meq/L (URBAN et al. 2004). There was excellent agreement between  $pCO_2$  calculated from alkalinity and from  $C_T$  measurements (Fig. 1). The 2% uncertainty in alkalinity translates into an uncertainty of 12  $\mu atm$  in  $pCO_2$ , while the <1% uncertainty in DIC results in a lower uncertainty of 6  $\mu atm$ . In contrast, the estimated uncertainty in pH (0.1 units) results in an uncertainty of 100–150  $\mu atm$  in  $pCO_2$ . The total uncertainty is dominated by the uncertainty in pH and is on the order of 150  $\mu atm$ . Values of  $pCO_2$  calculated for these samples ranged from 260 to 800  $\mu atm$  with a median of 408.

Closer examination of the  $pCO_2$  data reveals that values for the Ontonagon site were systematically lower than values at the Marquette site (Fig. 1), for reasons not yet known. The Marquette station is within an embayment; longer water residence times, higher water temperatures, or higher nutrient concentrations may contribute to the higher values at this site. The Ontonagon site may be more representative of “open lake waters” because it is not in an embayment and more likely to mix with open lake waters. For both sites, the agreement between  $pCO_2$

estimated from alkalinity and dissolved inorganic carbon (Fig. 1) indicates that both measurements yielded comparable results; because the 2 analyses are independent, this comparison suggests both methods are accurate. Hence

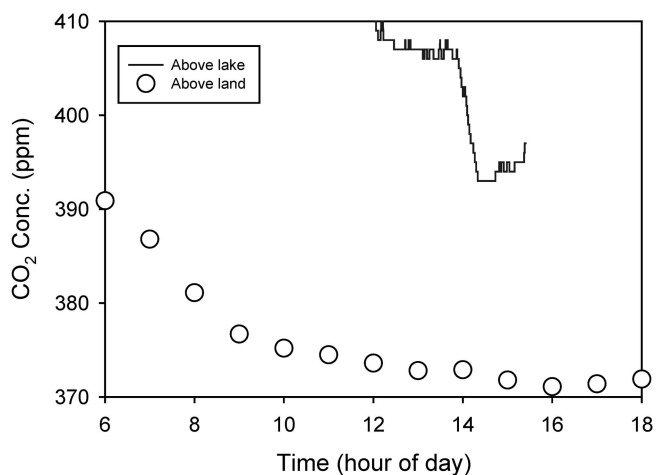


**Fig. 1.** Comparison of  $pCO_2$  estimated from measurements of alkalinity and pH and  $C_T$  and pH. Both methods yield identical results. The  $pCO_2$  values in the Ontonagon samples are, with one exception, all lower than those measured at the Marquette location.

the error in the estimation of  $p\text{CO}_2$  is primarily dependent on the accuracy and precision of the pH measurement.

Within the EPA data set there were 2175 samples for Lake Superior, 4540 for Huron, 4951 for Michigan, 5570 for Erie, and 2398 samples for Ontario that had all 3 parameters (temperature, alkalinity, pH) reported. The ranges and median values for pH and alkalinity for lakes Michigan (pH 7.27–8.93 [average 8.21], alkalinity 1.54–2.32 [average 2.18] meq/L) and Ontario (pH 7.35–8.95 [average 8.05], alkalinity 1.46–2.04 [average 1.84] meq/L) were comparable to those previously reported for Lake Michigan (pH 8.2, alkalinity 2.2 meq/L; BROOKS & EDGINGTON 1994) and Ontario (pH 7.95–8.65, alkalinity 1.78–2.02 meq/L; EADIE & ROBERTSON 1976). The values for Lake Superior (pH 6.72–8.51, alkalinity 0.09–1.00 meq/L) were similar to those cited above.

The  $\text{CO}_2$  concentrations measured above Lake Superior were elevated above those expected on land, and they showed a gradient of increasing concentrations with increasing wind travel distance from shore. From the 1-Hz data, 3-min running averages were calculated (Fig. 2) and ranged from 393 to 410  $\mu\text{atm}$ . While data are not yet available for the same date from nearby land-based stations (Ameriflux towers in Wisconsin), values can be predicted from the record of the preceding 10 years. When those data (72-m height) are detrended, hourly averages calculated for the corresponding week in June of each year, and then projected to 2007, the range of concentrations expected over land is found to be 372–374  $\mu\text{atm}$  in the window of time (12:00 a.m.–15:30) in



**Fig. 2.** Mixing ratios of  $\text{CO}_2$  above Lake Superior and those predicted to exist in the air before it reached the lake shore.

which concentrations were recorded over the lake (Fig. 2). Concentrations over the lake are 20–35  $\mu\text{atm}$  higher than concentrations predicted to exist over the forests of Wisconsin at that time.

The abrupt decline in concentrations over the lake (from 407 to 393  $\mu\text{atm}$ ; Fig. 2) was recorded while the boat was in transit between 2 sampling stations, one 9 km from shore and the other only 0.5 km from shore. Based on the wind direction, the over-water fetch is estimated to have decreased from about 30 to 3 km. The higher concentrations observed offshore are probably the result of the longer over-water fetch and the greater time for the air mass to accumulate  $\text{CO}_2$  from the lake. The magnitude of the  $\text{CO}_2$  efflux can be roughly estimated from the lake using these data. If we assume that the flux out of the lake is uniform spatially and that the  $\text{CO}_2$  emitted from the lake is mixed rapidly into a column of air of a fixed height, the flux is equal to the change in concentration (i.e., concentration above lake less the concentration above land) times the mixing height divided by the travel time of the wind over the lake. Given the stable atmospheric conditions over the lake, the mixing height was probably small, 20–50 m. For this range of mixing heights, the concentrations observed at the 2 stations indicate that  $\text{CO}_2$  fluxes out of the lake were 4–14  $\text{gC/m}^2\text{d}$ .

A more conventional way to estimate gas fluxes ( $F$ ) from the lake is to apply the Whitman 2-film model:

$$(1) \quad F \left( \frac{\text{gC}}{\text{m}^2\text{d}} \right) = k_{aw} (C_{water} - C_{air}) K_H$$

where  $k_{aw}$  is the mass transfer coefficient (corrected for temperature using the Schmidt number);  $K_H$  is the Henry's law constant (also temperature corrected); and  $C_w$  and  $C_a$  are the  $\text{CO}_2$  concentrations in the water and the air. There are several empirical formulations for the mass transfer coefficient (COLE & CARACO 1998, CRUSIUS & WANNINKHOF 2003, WANNINKHOF 1992); using these, the mass transfer coefficient for this day is calculated to be 1.8–4.4 m/d. The estimated flux using the Marquette  $p\text{CO}_2$  values is 0.12–0.34  $\text{gC/m}^2\text{d}$ , more than an order of magnitude smaller than that estimated above.

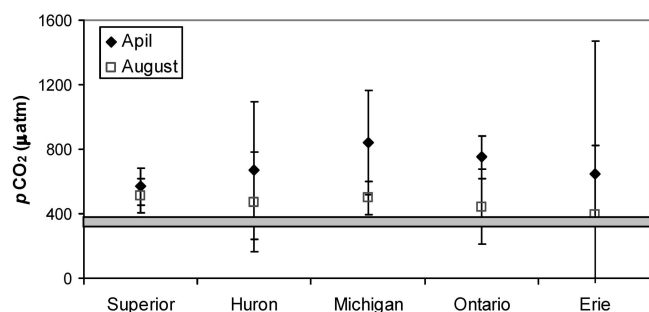
## Discussion

The EPA data clearly demonstrate that the upper waters of the Great Lakes are highly supersaturated with respect to atmospheric  $\text{CO}_2$  in April (Fig. 3). The median  $p\text{CO}_2$  values for the upper 10 m of water in April over the monitoring period ranged from 570 ppm in Lake Superior to

840 ppm in Lake Michigan. Unless the pH measurements are systematically too low by 0.2–0.3 units, the lakes are definitely supersaturated in spring. Intriguingly, the degree of supersaturation among the 5 lakes does not correspond with variations in concentrations of chlorophyll, phosphorus, or DOC (Table 1). Rather, it varies with the alkalinity and pH of the lakes. Lake Superior has the lowest alkalinity and pH, and it also has the lowest  $p\text{CO}_2$  in April. Lake Michigan has the highest values for all 3 parameters.

This data set also demonstrates that all 5 lakes have lower  $p\text{CO}_2$  in summer than in spring (Fig. 3). The median  $p\text{CO}_2$  values for the top 10 m in all 5 lakes remain above the atmospheric concentrations over land, but many of the individual measurements are below this threshold. The seasonal oscillation presumably results from the drawdown of  $p\text{CO}_2$  by algae in summer. The data suggest that some of the lakes may act as sinks for  $\text{CO}_2$  for brief periods in some summers.

To determine whether the lakes are a net source or sink of  $\text{CO}_2$  on an annual basis will require measurements in months other than April and August. Because of the large effect of pH on the calculated  $p\text{CO}_2$ , either more accurate pH measurements or direct measurement of  $p\text{CO}_2$  would be preferable. Nevertheless, given that supersaturation is much greater in spring than in summer, that most of the lakes appear to be slightly supersaturated with  $\text{CO}_2$  even in summer, and that summer stratification persists for less than half of the year in all of the lakes, we can conclude from these data that all 5 of the Laurentian Great Lakes act as net sources of  $\text{CO}_2$  to the atmosphere.



**Fig. 3.** Monthly mean  $p\text{CO}_2$  in surface waters (upper 10 m) of the Laurentian Great Lakes. Values represent the median values over the entire period of record (1983–2006) for the two sampling periods; error bars represent the standard deviations. The gray bar represents equilibrium with atmospheric  $\text{CO}_2$ .

The question of whether the lakes are significant sources of  $\text{CO}_2$  is more difficult to answer. The lakes occupy approximately one-third of their cumulative watershed. If rates of  $\text{CO}_2$  emissions from the lakes were twice the rate of carbon storage in the terrestrial portion of the watersheds, then they would completely cancel the continental sink for this region. However, while annual rates of  $\text{CO}_2$  uptake (120–280  $\text{gC}/\text{m}^2\text{yr}$ ) for the terrestrial ecosystems have been measured (CURTIS et al. 2002, LEE et al. 1999), we have very little basis for estimating annual fluxes for any of the Great Lakes. The emission estimates that have been made for Lake Erie (120  $\text{gC}/\text{m}^2\text{yr}$ ; EADIE & ROBERTSON 1976) and Superior (35–140  $\text{gC}/\text{m}^2\text{yr}$ ; URBAN 2006, URBAN et al. 2005) are of the same order of magnitude as but opposite in direction to the fluxes on land. Existing evidence suggests, therefore, that the Great Lakes are significant players in the regional  $\text{CO}_2$  budget.

The  $\text{CO}_2$  concentrations measured over the lake and the  $p\text{CO}_2$  measured within the lake point to the complexities of air flow over the lake and the difficulty in determining the true flux. During summer the lake is colder than the air, and this temperature difference creates a stable layer of air above the lake surface. Much of the air blowing offshore from the land is lofted above the stable boundary layer and does not contact the lake surface. As a result, the  $\text{CO}_2$  emitted from the lake mixes into a relatively small volume of air (low mixing height above the lake) in which  $\text{CO}_2$  concentrations may increase substantially. The high  $\text{CO}_2$  concentrations in the air act to slow the flux out of the lake. The elevated  $\text{CO}_2$  concentrations reported for the one date in this study would reduce the flux 20–30% relative to fluxes in the absence of the stable boundary layer. This implies that fluxes are likely higher during those times when the stable boundary layer does not exist in fall and winter, and even in spring and summer during the passage of synoptic weather fronts.

It is useful to compare the magnitude of the estimated  $\text{CO}_2$  fluxes with the inventory of dissolved  $\text{CO}_2$ . At a  $p\text{CO}_2$  of 520 ppm (the  $p\text{CO}_2$  measured at the Marquette location in June), the upper 10 m of the water column contains only about 1  $\text{mg C}/\text{m}^2$  of excess  $\text{CO}_2$  (i.e., amount in excess of equilibrium with the atmosphere), an amount inadequate to sustain the estimated effluxes across the lake surface. The fluxes estimated with the Whitman 2-film model were on the order of 100–300  $\text{mg C}/\text{m}^2\text{d}$ , amounts that would exhaust the excess  $\text{CO}_2$  (i.e., the amount in excess of saturation with the atmosphere) in the upper 10 m of water in 5–15 minutes. Respiration rates in the upper 10 m of water were 160  $\text{mg C}/\text{m}^2\text{d}$  in 1999 and 720  $\text{mg C}/\text{m}^2\text{d}$  in 1998 (URBAN et al. 2004), rates high enough to sustain the  $\text{CO}_2$  effluxes estimated



with the Whitman 2-film model and point to the dynamic balance between respiration rates and air-water exchange that regulates the  $p\text{CO}_2$  in the lake. The respiration rates cited above are not high enough to sustain the fluxes estimated from the  $\text{CO}_2$  concentrations over the lake (4–14  $\text{gC/m}^2\text{d}$ ). This discrepancy likely points to the inaccuracy of the simple model applied to the  $\text{CO}_2$  concentrations to estimate a flux. Clearly, either direct flux measurements by eddy covariance techniques or parallel measurements of  $\text{CO}_2$  above the lake and  $p\text{CO}_2$  within the lake made on a seasonal basis under different conditions of atmospheric stability above the lake will be needed to improve our annual estimate of  $\text{CO}_2$  emissions from the Great Lakes.

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