Observed variability of Lake Superior pCO₂

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Abstract

We present and compare direct and indirect pCO₂ observations taken in Lake Superior in the last decade and use them to understand temporal and spatial variability in lake carbon cycle processes. In situ observations from 2001 and biannual survey data for 1996–2006 indicate that Lake Superior was, on average, supersaturated (annual mean = 46.7 ± 17.3 Pa [461 ± 171 μatm]) with respect to atmospheric pCO₂ (mean = 38.3 ± 0.6 Pa) in April and close to equilibrium (mean = 37.5 ± 6.7 Pa) with respect to atmospheric pCO₂ (mean = 36.4 ± 0.7 Pa) in August. Both data sets indicate that temporal variability in surface lake pCO₂ from weekly to interannual timescales was predominantly controlled by changing dissolved inorganic carbon and associated changes in pH. An unstratified water column appears to have limited pCO₂ fluctuations in spring. Through summer and into early fall, pCO₂ variability on a daily timescale at 12 m increased with time to a maximum amplitude of 19 Pa, likely as a result of internal waves on the thermocline. Year-to-year changes in mean surface lake pCO₂ and temperature were of the same sign and approximate magnitude at all observed points, consistent with the lake’s small size relative to the synoptic-scale meteorological systems that force it. Variability in pCO₂ was not correlated with major climate indices. While these data provide a first large-scale overview of Lake Superior’s pCO₂ and its temporal variability, their time–space resolution and accuracy are not sufficient to further refine previously imbalanced lake-wide carbon budgets.

Of the total export of organic carbon (C) from terrestrial ecosystems in North America, only 50% reaches the coastal oceans, while 20% is respired in lakes and 30% is respired in rivers (Cole and Caraco 2001). Cole et al. (2007) and Tranvik et al. (2009) synthesized global observations and determined that inland waters receive approximately 1.9–2.9 Pg yr⁻¹ of carbon from the landscape, of which 0.2–0.6 Pg C yr⁻¹ is buried in the systems, at least 0.8–0.6 Pg C yr⁻¹ is respired in lakes and 30%–40% reaches the coastal oceans, at least 0.8–1.4 Pg C yr⁻¹ is outgassed, and the remaining 0.9 Pg C yr⁻¹ is delivered to the oceans. Landscapes such as Northern Wisconsin may have particularly strong aquatic–terrestrial carbon budget links because lakes and rivers cover a significant portion of the landscape (Buffam et al. 2011). The literature indicates that the net primary productivity in Lake Superior is between 18 and 93.7 g C m⁻² yr⁻¹ (Urban et al. 2005; Sterner 2010), significant in comparison to that of the surrounding terrestrial biosphere (400 g C m⁻² yr⁻¹; Aih et al. 2005). In order to determine the North American carbon budget (Science Implementation Strategy for the North American Carbon Program, http://www.narbon.org/nacp/documents/NACP-SIS-final-july05.pdf), the Great Lakes must be considered. Recent studies illustrate that independently estimated terms in the carbon budget of the lake do not balance with respect to each other (Cotner et al. 2004; Urban et al. 2005). This, as well as the fact that the Upper Midwestern United States is a region of intense study with regard to the terrestrial carbon cycle and budget (Chen et al. 2008; Desai et al. 2008), motivates our current focus on Lake Superior.

As the headwaters of the Laurentian Great Lakes, Lake Superior has the largest surface area of all of the lakes in the world (81,200 km²). With maximum depths of over 400 m, it holds 10% of the world’s freshwater, and water residence times are over 170 yr (Quinn 1992). The ecosystem and biogeochemistry of Lake Superior are understudied, in part because of the lake’s size and harsh climate, which make observations difficult. In 1973, a Canadian intensive field campaign offered the most comprehensive study to date. This study revealed that seasonal fluctuations of phytoplankton, biomass, chlorophyll, particulate organic carbon, and primary production were similar across most of the lake (Munawar and Munawar 1978; Munawar et al. 1978; Thompson 1978).

The ratio of the watershed to the Lake Superior surface area is small (approximately 1.55) compared to that of the other Great Lakes, such as Lake Michigan (ca. 2), Lake Huron (ca. 2.25), and Lakes Erie and Ontario (ca. 3) (Great Lakes Atlas, http://www.epa.gov/gltno/atlas/index.html). Smaller impoundments generally have watershed area–to–lake surface area ratios of 100–200 (Weizel 2001). Since the carbon budgets of lakes with large watershed area–to–lake surface area ratios are generally thought to be dominated by terrestrial inputs (Hanson et al. 2004; Cole et al. 2007),
the small ratio of Lake Superior indicates that most of its carbon cycling may occur internally (i.e., with relatively less influence from the surrounding watershed) (Thompson 1978). Because of this large volume, it is likely that the physical properties of Lake Superior have a dominant influence on its carbon cycle, as is the case in the global oceans (Sarmiento and Gruber 2006).

Lake Superior is oligotrophic, with low phosphorus concentrations. A ratio of photosynthesis to respiration (P : R) of less than 1 indicates heterotrophy and is common in mesotrophic and oligotrophic lakes (del Giorgio and Gasol 1995; del Giorgio et al. 1997; Cole and Caraco 2001). Urban et al. (2005) suggest that Lake Superior has a P : R ratio of 0.2–0.4. If the lake is dominantly heterotrophic, it indicates that there must be a substantial terrestrial carbon subsidy. However, independent estimates of that subsidy are small (0.5–0.9 Tg C yr\(^{-1}\)) in comparison to estimates of respiration (13–81 Tg C yr\(^{-1}\)), gross primary production (3–8 Tg C yr\(^{-1}\)), and net annual lake-to-air flux rates (3 Tg C yr\(^{-1}\)). Other terms in the budget are not large enough to close the budget; inputs from precipitation are only 0.1–0.9 Tg C yr\(^{-1}\), and outputs from rivers and burial are 0.1 and 0.5 Tg C yr\(^{-1}\), respectively (Cotner et al. 2004; Urban et al. 2005). The small number of studies, focused either in the lake’s western arm or in the nearshore zone and lacking wintertime observations, certainly contribute to the current inability to balance Lake Superior’s carbon budget.

There have been a few previous studies of the surface lake pCO\(_2\). Urban et al. (2004) estimated pCO\(_2\) values from measured pH and alkalinity and found that the lake was supersaturated with respect to atmospheric CO\(_2\) for most months between April and November, but with a large amount of uncertainty. Alin and Johnson (2007) estimated pCO\(_2\) from observations in May through November of 1968 and 1969 (Bell 1980a,b) and found the lake to be predominantly supersaturated. Based on a few observations in Thunder Bay, Ontario, Canada, Kelly et al. (2001) reported summertime pCO\(_2\) to be below the annual atmospheric mean. These findings, if each is assumed to be representative of the entire lake, appear to disagree as to the magnitude and direction of air–lake carbon fluxes, but it is possible that their poor resolution in space and time contributes substantially to the apparent disagreement.

In the oceans, the magnitude of primary productivity and carbon fluxes in coastal areas are orders of magnitude larger than in the open ocean (Knauer 1993; Frankignoulle and Borges 2001). Satellite images of the Great Lakes generally indicate the highest productivity in the nearshore (C. Mouw and G. McKinley unpubl.). Previous estimates of terms in the carbon budget have been based primarily on measurements taken within 10–30 km from the shoreline (Kelly et al. 2001; Urban et al. 2004, 2005) and may be more representative of nearshore conditions than the lake-wide system.

In this article, we investigate temporal and spatial variability of pCO\(_2\) in Lake Superior by analyzing historical, in situ, direct pCO\(_2\) observations from one western arm location taken during summer 2001 as well as indirect estimates from biannual surveys for 1996–2006. These data were collected in the context of independent investigations, and we endeavor to apply them to our present question of the lake’s CO\(_2\) exchange with the atmosphere. We ask if these data can shed new light on the lake’s carbon cycle and help us to understand the processes controlling diurnal, seasonal, and interannual variability in the surface lake pCO\(_2\) and lake-to-air CO\(_2\) flux. It is our intent that this work will inform ongoing efforts by these authors and others to close the lake’s carbon budget.

Methods

Study area—Lake Superior currents and stratification are controlled by surface wind forcing and heat fluxes (Chen et al. 2004; Bennington et al. 2010). Water temperatures are cold, with an average April surface temperature of 1.97°C. The lake mixes completely twice each year, bringing remineralized dissolved inorganic carbon (DIC) and nutrients from depth to the surface. There can be weak stratification in winter, when the coldest water at the surface is colder than 4°C. As the ice cover diminishes under the influence of climate warming (Austin and Colman 2007), the lake could move toward a warm monomictic state. Currently, the stratified season starts in July and lasts through early December, and during this time the thermocline is typically located at 25–35 m and the euphotic zone is approximately 28 m deep.

Lake Superior receives nearly half of its annual water supply via discharges of numerous but relatively small tributaries. When its large volume is considered, the inputs from these tributaries are small and are not considered to influence biogeochemical properties of the lake (Thompson 1978). During the Keweenaw Interdisciplinary Transport Experiment from 1998 to 2000, total phosphorus concentrations ranged from 1.5 to 3.5 mg m\(^{-3}\) (Siew 2003), and chlorophyll concentrations ranged between 0.2 and 1.5 mg m\(^{-3}\) (Bub 2001), indicating that the lake is oligotrophic. The 1973 Canadian intensive field campaign results also show that the coastal lake characteristics can be different than those of the open lake but that when the lake is considered in its entirety, it is largely homogeneous (Munawar et al. 1978).

Environmental Protection Agency (EPA) data for indirect pCO\(_2\) estimates—The U.S. EPA has been monitoring Lake Superior water quality since the early 1990s in twice-yearly surveys (spring and summer). During surveys, water quality measurements are taken at 19 stations across the lake (Fig. 1). EPA stations have been selected to primarily represent open-lake conditions (17 out of 19 stations). pH (electrode measurement, National Bureau of Standards [NBS] Scale), alkalinity, and temperature in the water column were sampled at four depths in April (surface, middepth, bottom minus 10 m, and bottom) and at six depths in August (surface, lower epilimnion, thermocline, deep chlorophyll maximum, bottom minus 10 m, and bottom) between 1996 and 2006. We used the surface observations with CO2SYS (Lewis and Wallace 1998) with freshwater constants to calculate pCO\(_2\) from pH (NBS scale), alkalinity, and temperature. EPA measurements of pH and alkalinity were made at 25°C and were corrected for
the calculation of \( pCO_2 \) at in situ temperatures. We consider data from 1996-2006 because prior to 1996 EPA sampling efforts were not consistent for stations sampled and variables measured. We refer to these sampling times as “April” and “August” because this is most representative of the cruise timings, but in fact the sampling times started as early as 14 April and as late as 05 May in the spring and as early as 13 August and as late as 30 August in summer, with the exception of 2005, when the summer sampling did not start until 23 September. These data are available for download at www.epa.gov/glnpo/monitoring/data_proj/glenda/glenda_query_index.html.

Bias in the EPA pH data due to electrode pH measurements could substantially modify our conclusions. French et al. (2002) found that pH measured with electrodes in freshwater had a systematic negative bias, with a mean value of \(-0.137\) pH units. We do not apply any correction to the EPA data used in this analysis. However, concern about this potential bias is part of our motivation to incorporate existing direct \( pCO_2 \) observations into this study.

The EPA data were processed as follows. We removed one data point with \( pCO_2 \) greater than 405 Pa (4000 m\text{atm}), as the pH value was abnormally low compared to that of neighboring stations in the same year (6.72 at SU16 in May 1996). Box-whisker plots of the remaining data (Fig. 2a,c) reveal that despite a few outliers, year-to-year variations in the median surface lake \( pCO_2 \) had reasonable spatial coherence (i.e., do not appear to have been driven by noise in the observations). This indicates that year-to-year changes in \( pCO_2 \) estimated from EPA data represent actual temporal variability. For further discussion and comparison to atmospheric \( pCO_2 \) data, we calculated the standard deviation (SD) for each April and August field campaign and removed outliers (defined as greater or less than 3 SDs from the mean). The “greater-than criterion” eliminated a total of one point from all April data and two points from all August data, and the “less-than” criterion removed no points. This left at least 15 points for each April and at least 14 points for each August. Lake-wide mean \( pCO_2 \) was estimated for each year (Fig. 2b,d), and the long-term mean was calculated as the average of all years. In Figure 2 (b,d) and text, we also report the SDs for the August and April lake-wide mean values.

**Direct measurements of \( pCO_2 \)—**In addition to the long-term, low-frequency data from the EPA, we analyzed high-frequency direct measurements of \( pCO_2 \) in western Lake Superior taken in June-September 2001 as part of an independent study. A subsurface mooring was deployed 7.5 km offshore from Split Rock Light House near Duluth (47.19\degree N, 91.34\degree W; Fig. 1). The mooring was equipped with a Submersible Autonomous Moored Instrument for \( CO_2 \) (SAMI-CO\(_2\)) (DeGrandpre et al. 1995; Baehr and DeGrandpre 2002, 2004) and a temperature sensor. The SAMI was calibrated for \( pCO_2 \) measurements over the range of 20.3–30.4 Pa by dilution of a 304-Pa \( CO_2 \) standard with \( CO_2\)-free air (DeGrandpre et al. 1995, 1999). An infrared analyzer (LI-COR Environmental Company), calibrated with National Institute of Standards and Technology–traceable \( CO_2 \) gas standards, was used to verify the SAMI calibration. In situ data were corrected for the difference between the in situ and calibration temperatures (DeGrandpre et al. 1999). The \( CO_2 \) data were reported as wet \( pCO_2 \) using the water vapor pressure at the in situ temperature. The SAMI was deployed at 12 m in water of 250-m depth, and data were acquired half-hourly from 06 June 2001 through 11 September 2001. Lake Superior waters are relatively clear, such that the photic depth is 20 m or greater. Thus, the instrument resided inside the photic zone. We compare \( pCO_2 \) data from the SAMI location to \( pCO_2 \) from the nearest EPA location (SU19; Fig. 1) that is 64 km away. Although less than ideal with its deployment location and depth, these in situ data...
present a unique comparison opportunity for our EPA-based pCO₂ estimates. They are also the only in situ Lake Superior pCO₂ measurements resolving multiple continuous months of which we are aware.

**pCO₂ components**—Variability in temperature, DIC concentrations, pH, and alkalinity are the dominant influences on freshwater pCO₂. It is desirable to separate these multiple influences, as it helps us to better understand carbon cycling. We follow the approach of Takahashi et al. (2002) in separating the influence of temperature (pCO₂-T) from all other influences (pCO₂-nonT). In order to do so, we must know the isochemical effect of temperature on freshwater (ΔlnpCO₂/ΔT). Using CO2SYS (Lewis and Wallace 1998), we estimated this coefficient for Lake Superior by calculating pCO₂ across ranges of temperatures (0–20°C), DIC (800–920 µmol L⁻¹), and alkalinity (800–860 µmol L⁻¹) representative of the lake. We found 0.038 °C⁻¹ to be the optimal linear approximation. The two pCO₂ components were then calculated as follows:

\[ pCO₂ - T = \overline{pCO₂} \times \exp 0.038(T - T) \]  

\[ pCO₂ - nonT = pCO₂ \times \exp 0.038(T - T) \]  

where the overbars indicate the long-term mean.

**Statistical analysis**—We used Empirical Orthogonal Function (EOF) analysis to study spatial and interannual variability in Lake Superior pCO₂ captured in the EPA biannual survey. EOF analysis deconvolves the dominant spatial patterns in a three-dimensional (x, y, t) data set. It finds orthogonal patterns in the first two dimensions (space) and also provides a complementary set of structures in the sampling dimension (time). These complementary time series are called principle components and are related to the corresponding EOFs (von Storch and Zewirs 1999). The magnitude of an anomaly can be estimated at any point in time and space by multiplying EOFs (in Pa) with their corresponding principle components (unitless). We study the spatial variability of surface pCO₂ and temperature across the lake over the 11-yr period (1996–2006) for which we have the biannual EPA survey.

**Atmospheric observations of CO₂**—Observations of atmospheric CO₂ were taken from the nearby National Oceanic and Atmospheric Administration Greenhouse Gas Tall Tower Observatory site located at the WLEF television tower in Park Falls, Wisconsin (45°57'N, 90°16'W) (Bakwin et al. 1998). Calibrated in situ observations of CO₂ (uncertainty of ± 0.02 Pa) at 396 m above ground were averaged to the monthly timescale. Monthly observations should be reasonably representative of the
Results

Biannual survey of pCO$_2$—In the 11-yr April climatology, the lake had higher mean pCO$_2$ (47.1 ± 17.3 Pa) than in the August climatology (36.7 ± 6.7 Pa) (Figs. 2, 3). The 11-yr average atmospheric CO$_2$ for 1996–2006 was 37.7 ± 0.1 Pa and the April mean value was 38.3 ± 0.1 Pa, while the August mean was 36.4 ± 0.1 Pa. Given the uncertainty, we cannot distinguish the lake as a mean source or sink of CO$_2$ except in a few months (Fig. 2b,d), as follows: source April and August 1996, April 1997, April 1999, and April and August 2003; sink: August 1999 and April 2004.

During the 11-yr period, lake-wide mean pCO$_2$ in April ranged from 26 Pa (2004) to 91.8 Pa (1999) (Fig. 2a,b). High pCO$_2$ values in April 1999 were due to the mean pH (7.45) being substantially below the long-term mean pH (7.75). For the average April, the lake was a source of CO$_2$ to the atmosphere (pCO$_2$$_{lake}$ > pCO$_2$$_{atmos}$). Though an initial visual inspection of the April pCO$_2$ time series (Fig. 2b) may indicate a declining trend, the substantial overlap of the uncertainty bounds throughout the time series does not support such a conclusion. For the average August, the lake was barely a source of CO$_2$ to the atmosphere, but given the uncertainty, we can only clearly identify 1996 and 2003 as sources and 1999 as a sink. The lowest average August pCO$_2$ was 30.5 Pa (1997), and the highest average pCO$_2$ was 52.8 Pa (1996) (Fig. 2c,d). The lake-wide average values indicate substantial variability in the lake’s saturation state from year to year in both seasons, but there is significant uncertainty given the small sample sizes.

Direct, high-frequency pCO$_2$ measurements—A partial seasonal cycle (June–September) of pCO$_2$ in the western arm was captured with the SAMI (Fig. 4a). Average pCO$_2$ was the highest (39.9 Pa) for the 24 days of June and the lowest for the month of August (29.1 Pa). The lowest daily average pCO$_2$ was observed on August 28 (15.7 Pa) and the highest (44.5 Pa) on 07 September 2001.

At EPA site SU19 in April 2001, the surface temperature was 1.78°C and the SAMI June 2001 average was 3.36°C ± 0.01°C (Fig. 4b), indicating that the water column was inversely stratified. EPA surface (14.7°C) and 9.5-m (10.5°C) temperatures on 16 August were higher than the SAMI daily mean of 6.2°C on this date (Fig. 3b), though not inconsistent with the SAMI August mean of 10.6°C ± 3.1°C.

Since the water column should have been well mixed in April through June, we do not expect much change in pCO$_2$ through this time. pCO$_2$ estimated from EPA measurements on 26 April 2001 was 38.7 Pa at the surface at
location SU19, only 1.2 Pa less than the SAMI pCO$_2$ average for June 2001 (40 ± 0 Pa; Fig. 4a). If pH and alkalinity were the same at both sites, a 1.5°C increase in temperature could cause a 2.1-Pa increase in pCO$_2$, indicating an overall consistency between the EPA and SAMI pCO$_2$ observations in spring 2001, despite the fact that observations were completed more than a month apart. This comparison indicates that surface-water pCO$_2$ does not vary much with time in early spring in Lake Superior.

SAMI data indicate strong pCO$_2$ variations through summer (Fig. 4a) after warming from June through July (Fig. 4b). Rapid increases in temperature occurred at the same time as decreases in pCO$_2$ (Fig. 4a,b). For example, starting on 02 August, temperature declined dramatically and pCO$_2$ began to increase. On 16 August, EPA data indicated a surface pCO$_2$ of 34.3 Pa and 39.9 Pa at 9.5 m (Fig. 4a). At the same time, the SAMI measurement was 36.7 Pa at 12 m. The temperature discrepancy was also substantial, with EPA measurements higher at both depths (Fig. 4b). We further interpret these signals in the “Discussion” section.

The SAMI data offer an unprecedented opportunity to consider the diurnal timescale variations of pCO$_2$ (Fig. 4c,d). The daily range of pCO$_2$ steadily increased over the record from 2–3 Pa in June to 10–20 Pa in September (Fig. 4c). Analysis of the daily timing of the maxima and minima revealed variations on a timescale of approximately 17 h, with no tendency for the maxima to occur during the night and the minima to occur during the day. This indicates that it was not a daily cycle of in situ biological activity that directly drove these high-frequency pCO$_2$ variations.

$pCO_2$ components—Even though diurnal variations in pCO$_2$ do not appear to be directly biologically driven, the weekly timescale changes in SAMI pCO$_2$ generally follow its non-temperature component, indicating that larger-scale and longer-term pCO$_2$ change is driven primarily by changes in DIC and pH (Fig. 5). The effect of alkalinity is also incorporated into this term, but the EPA data indicate small alkalinity variability. DIC change over the seasonal cycle is primarily due to biological activity, with phytoplankton consuming CO$_2$ during photosynthesis and bacteria releasing CO$_2$ during respiration, as well as physically driven vertical resupply of DIC from the hypolimnion. pH can also be substantially modified in freshwater by algal production (Sawyer et al. 1994; Lynch et al. 2010), particularly in poorly buffered waters such as Lake Superior, where pH is very sensitive to DIC. As discussed below, the large excursions of pCO$_2$ in late summer at the SAMI location are speculatively interpreted to be attributable to cycles of upwelling and mixing followed by restratification and algal growth.

Nonlinearity in the pCO$_2$-nonT and pCO$_2$-T separation is illustrated in the late-August event in the SAMI by the fact that anomalies of the total pCO$_2$ are no longer the approximate sum of the anomalies in pCO$_2$-nonT and pCO$_2$-T. This is because during this bloom event, the DIC
has probably been driven to the low end of the range (800 μmolL−1) for which the coefficient of temperature sensitivity (0.038 °C−1) was derived.

Analysis of pCO₂ and its components estimated from EPA data also provides strong evidence for the control of variability in pCO₂ in Lake Superior by non-temperature factors (Fig. 6). There is a strong correlation between pCO₂ and pCO₂-nonT for all of the 216 observations made in spring and summer ($r^2 = 0.98$ in April; $r^2 = 0.76$ in August). Lack of correlation between pCO₂ and pCO₂-T ($r^2 = 0.00$ in April and $r^2 = 0.01$ in August) confirms that variation in pCO₂-nonT is the dominant influence on variation in pCO₂.

**Spatial and temporal variability in pCO₂ and temperature**—In order to understand the temporal and spatial patterns of interannual variability in open-water Lake Superior pCO₂ and temperature, as captured by the biannual EPA surveys, we applied EOF analysis to these data (Figs. 7, 8). A large percentage of the total pCO₂ (temperature) variance was explained by the first EOF: 87% (92%) in April and 70% (62%) in August. EOF results indicate that the dominant modes of year-to-year variability in lake pCO₂ and temperature were spatially homogeneous (i.e., of the same sign at all locations). This means that if one part of the lake was warmer than average in one year, it was most likely that all parts of the lake were also warmer than average, and similarly for pCO₂. This conclusion is consistent with the lake’s small size relative to the synoptic-scale meteorological systems forcing it, as it indicates that the open lake was responding as a whole to year-to-year changes in regional climate.

The principle components of EOF1 (PC1) provide the temporal evolution of the EOF1 pattern because multiplication of the PC1 for a particular year by the associated EOF pattern gives the total pattern for that year. In the temperature PC1 (Fig. 8b,d), we likely see the effect of the 1998 El Niño, which caused the warmest temperatures in both spring and summer of 1998. The PC1 of pCO₂ indicates somewhat depressed values in spring and summer of 1998, consistent with DIC control of pCO₂ variations, assuming enhanced biological activity with a warmer and more stratified lake. However, the relatively weak El Niño period of 2002–2004 was not particularly warm, and there is no correlation of the time series with the Southern Oscillation Index (Trenberth 1984; as updated at http://www.cgd.ucar.edu/cas/catalog/climind/soi.html) ($r^2 = 0.00$ and $p = 0.92$ for April; $r^2 = 0.01$ and $p = 0.76$ for August), so we cannot provide strong evidence for a connection to El Niño or Southern Oscillation variability. Similarly, we found no strong correlations between these time series and North Atlantic Oscillation ($r^2 = 0.00$ and $p = 0.83$ for April; $r^2 = 0.29$ and $p = 0.09$ for August) and Pacific Decadal Oscillation ($r^2 = 0.06$ and $p = 0.53$ April; $r^2 = 0.12$ and $p = 0.37$ for August). A weak correlation between the principle component of EOF1 for temperature and principle component of EOF1 for the pCO₂ ($r^2 = 0.35$ in April; $r^2 = 0.28$ in August) is consistent with the annual variability in pCO₂ being dominated by DIC change, as opposed to by temperature itself.

For temperature, and to a lesser degree for pCO₂, the spatial patterns (EOF1) and temporal patterns (PC1) are reasonably similar between the April and August analyses ($r^2 = 0.75$ for PC1 of temperature, $r^2 = 0.19$ for PC1 of pCO₂). Thus, there appears to be sufficient memory in the system to allow temperature anomalies created in winter and spring to persist through the summer. However, there is only a weak memory for pCO₂.

**Discussion**

Surface pCO₂ estimated from EPA temperature, alkalinity, and pH measurements indicates that Lake Superior was, on average for the 1996–2006 period, a source of CO₂ to the atmosphere in spring and approximately neutral in the summer and that this cycle was controlled by seasonal variation in surface lake DIC and pH. A SAMI instrument in the western arm in the spring and summer of 2001 indicated substantial variability in near-surface pCO₂ (up to 25 Pa at 12 m) on daily to weekly timescales. There is reasonable consistency between our two independent sources of data, particularly in spring, when the lake is vertically well mixed and when biological activity and heat fluxes are less able to modify surface lake pCO₂.
In situ pCO$_2$ data from the SAMI are consistent with the occurrence of a localized event of mixing or upwelling followed by restratification and a phytoplankton bloom, as detailed below. Temperature data from the SAMI indicate warming in late June through July (Fig. 4b) that should promote stratification and enhanced biological activity that, in turn, should result in DIC removal and pH increase, together leading to pCO$_2$ reduction, which is observed (Figs. 4a, 5). Once phytoplankton become nutrient limited or grazed by zooplankton with stratification in late July, pCO$_2$ should increase, as was observed. Because the lake surface pCO$_2$ was less than atmospheric pCO$_2$ at this time, an air-to-lake CO$_2$ flux should have also contributed to the rebound in lake pCO$_2$.

In early August 2001 at the SAMI, temperature declined dramatically and pCO$_2$ increased. This indicates a physical event that brought cold water with high DIC from depth to the surface. Analysis of North American Regional Reanalysis winds for this period of time and location indicates a reversal in wind direction from the dominant southwesterly flow (from the northeast) to a northeasterly flow (from the southwest), consistent with a coastal upwelling event. More normal conditions of southwesterly flow returned in late August, consistent with restratification and the observed surface warming. We suggest that the dramatic pCO$_2$ decline that then occurred in mid- to late August (Fig. 4b) may have been due to a phytoplankton bloom supported by nutrients supplied during the upwelling event. If phytoplankton production of 1.74 µmol L$^{-1}$ d$^{-1}$ (the maximum observed by Sterner 2010) occurred for 8 d, DIC would have decreased by 14 µmol kg$^{-1}$, and if pH (8.0) and alkalinity (840 µeq L$^{-1}$) remained constant, this would have resulted in a pCO$_2$ decrease of 0.8 Pa (T = 14°C). However, a DIC decrease of 14 µmol kg$^{-1}$ could have simultaneously induced a pH increase of 0.3 units and caused a pCO$_2$ decrease of 24.3 Pa. Thus, it is plausible that an algal bloom could have caused the observed pCO$_2$ change. At the very end of August and in early September, there appears to have been another upwelling (cooling with increase in pCO$_2$) followed by a bloom (warming with decline in pCO$_2$) before the record ends. The separation of pCO$_2$ into its components (Fig. 5) supports our interpre-

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**Fig. 6.** Relationships between pCO$_2$ and pCO$_2$-nonT in (a) April and (b) August and between pCO$_2$ and pCO$_2$-T in (c) April and (d) August.


Fig. 7. EOF results for (a) April and (c) August surface pCO$_2$ (Pa, top color bar; µatm, bottom color bar) and (b,d), corresponding principle components. pCO$_2$ estimates are based on biannual EPA direct measurements of temperature, alkalinity, and pH during the 1996–2001 period.

tation of the SAMI data, with pCO$_2$-nonT driven down (consistent with biological activity) at the same time that warming of the surface waters (consistent with stratification) drove pCO$_2$-T up. Change in pCO$_2$ was smaller than either component. This proposed sequence of events, while reasonable, is nonetheless speculative because we lack ancillary data with which to confirm the proposed upwelling or mixing and biological activity.

The discrepancies between the SAMI temperature data and the temperature from EPA station SU19 on 16 August 2001 at surface and depth measurements indicate that the EPA location did not experience the mixing or upwelling and bloom event that seems to have occurred at the SAMI location. At the SAMI location on 16 August, the pCO$_2$ was just beginning to be suppressed by what may have been increased biological activity. Only 2–3 d earlier, the SAMI pCO$_2$ at 12 m was consistent with the EPA observation at 9.5 m (Fig. 4a), indicating that just before the proposed increased biological activity, background conditions were consistent between SAMI and EPA observations. Though the two sites were close together on the scale of the lake, these limited data indicate that they were not uniformly affected by physical and biogeochemical processes.

The daily minima and maxima in the SAMI data (Figs. 4c, d) do not indicate that in situ biological productivity was the driving mechanism for this variability because there was no tendency for the maxima to occur during the night (a respiration signal) or for the minima to occur during the day (a photosynthesis signal). The approximately 17-h timescale of this variability is consistent with internal waves acting on the thermocline (J. Austin, pers. comm.). We posit that the increasing daily range from June to September occurred because the thermocline became increasingly stratified and the gradient of pCO$_2$ across it became larger. The observations of McManus et al. (2003) were consistent with this interpretation. They found the main gradient in the thermocline at locations in the vicinity of the SAMI site to be at 10–20 m in depth, and they found that the gradient of temperature became more pronounced over the course of the season. Their pCO$_2$ profile also indicated a strong gradient, greater than 10 Pa, in the surface 20 m in July 2001, but unfortunately, their profile did not resolve the near-surface pCO$_2$ gradient in September. The SAMI also recorded an increase in the daily range of temperatures over the course of the record that is positively correlated to daily ranges of pCO$_2$ ($r^2 = 0.4$).

EPA survey data indicate coherent spatial variability across the open waters of the lake, consistent with previous surveys (Munawar et al. 1978). SAMI data evidence short-term fluctuations, and comparison to the EPA’s SU19 data indicates that these occur over a limited spatial scale. Short-term upwelling events are typically confined to distinct zones along the coastline, as in Lake Michigan (Plattner et
Bias in the pCO$_2$ estimates due to the use of electrodes to measure pH is potentially significant. If we assumed a $-0.137$ pH unit bias (French et al. 2002) and applied this correction to all EPA data, we estimated an April lake-wide mean pCO$_2$ of 30.1 Pa and an August mean of 26.5 Pa. These values are substantially lower than our best estimates of 46.7 and 37.5 Pa and if correct would indicate that the open lake is a substantial CO$_2$ sink in both spring and summer. This would also make our EPA results inconsistent with the SAMI (Fig. 4), indicating that a large correction is not warranted. Co-location of in situ pCO$_2$ observations and EPA survey sampling would be one way to determine if a substantial pH bias correction is, in fact, required.

These results also indicate that spatio-temporal variability may be responsible for the apparent inconsistency in previous estimates of Lake Superior surface pCO$_2$. The direct pCO$_2$ observations of near surface water taken in the vicinity of Thunder Bay in 1990 (R. Hecky pers. comm.) by Kelly et al. (2001) give a pCO$_2$ value of 23.0 Pa from two samples in July and August 1990. This result is similar to the quite-low pCO$_2$ at the same time of year in the SAMI data. Additionally, the EPA survey indicates that mean lake-wide surface values could be as low as 30.4 Pa in summer. Furthermore, considering that Thunder Bay is a region of significant riverine inputs to the lake, it is quite possible that productivity enhanced by these inputs depresses pCO$_2$ in this area. Our mean estimates of lake-wide pCO$_2$ from the EPA survey are lower than those of Alin and Johnson (2007), in large part because of our application of the needed temperature correction to the EPA’s pH results (EPA procedures, http://www.epa.gov/greatlakes/monitoring/sop/chapter_5/LG500.pdf). Our open-lake values are consistent with those of Urban et al. (2004) in April and August within the error estimates.

These data do not resolve a full annual cycle of pCO$_2$. Nevertheless, for the sake of completeness, we wish to calculate a lake–air CO$_2$ flux estimate from them. To do so, we make the simplifying assumption that the mean pCO$_2$$_{\text{lake}}$ (average of both April and August for 1996–2006, 42.4 ± 11.1 Pa) persists throughout the year, and we use 3-h winds from North Atlantic Regional Reanalysis, annual mean WLEF pCO$_2$$_{\text{atmos}}$ (37.7 Pa), and the Wanninkhof (1992) flux parameterization to estimate an annual mean lake-to-air CO$_2$ flux of 1.3 ± 3.2 Tg C yr$^{-1}$. This very approximate flux estimate does not revise the flux estimate of Urban et al. (2005) of 3–8 Tg C yr$^{-1}$ from lake to atmosphere.

When interannual variability is taken into account, the data indicate that the lake can be a source or sink in either April or August and, further, that the open lake is not consistently respiring large amounts of terrestrial carbon, as has been found to be the case in many small inland lakes.
in the region (Hanson et al. 2004). However, this conclusion is compromised by the fact that the nearshore is poorly captured in these data and the fact that the full annual cycle is poorly resolved. Further, recent nearshore observations along the Keweenaw Peninsula (N. Urban unpubl.) indicate \( pCO_2 \) elevated above the atmospheric value for most of the year. There may be substantial respiration of terrestrial carbon close to the shore that these data sets do not capture.

The lake is undersampled for the purposes of constraining the net carbon budget and understanding variability. Nevertheless, springtime data from the EPA biannual survey are likely reasonably representative of this season in the open lake, largely because stratification has not yet occurred, and, thus, any temperature and biological influences on surface \( pCO_2 \) will be strongly damped by vertical homogenization of the water column. SAMI data indicate that there can be large short-term variability in \( pCO_2 \) (up to 20 Pa) at the depth of the thermocline in summer. But since the EPA intentionally does not sample upwelling regions, and because their surface observations are removed from strong thermocline gradients and are subject to air–lake heat and \( CO_2 \) exchange, it is also likely that data are reasonably representative of the true state of the majority of the lake’s surface in August. This conclusion is also consistent with those of previous studies (Munawar et al. 1978) that indicate large-scale biogeochemical homogeneity in open lake waters.

In summary, we find that the open waters of Lake Superior were, on average, a source of \( CO_2 \) to the atmosphere in spring and were approximately neutral in summer between 1996 and 2006. These data indicate that the open waters of the lake are not a source of \( CO_2 \) to the atmosphere at all times and that the lake is not respiring large amounts of terrestrial carbon. At diurnal timescales, we find significant variation (up to 20 Pa) in \( pCO_2 \) at 12 m that appears to have been driven by internal waves on the thermocline. At weekly timescales in summer, we find evidence of very large (up to 25-Pa) \( pCO_2 \) shifts that we speculate interpret as having been driven by mixing or upwelling events ending with restratification and a phytoplankton bloom that depressed DIC and increased pH. Interannual variations, as captured by the EPA survey data, indicate substantial lake-wide homogeneity in the lake’s response to variations in climate forcing. From weekly to interannual timescales, variations in \( pCO_2 \) were highly correlated with variations in \( pCO_2 \)-nonT, indicating that chemistry variability, through DIC and pH, is the primary driver of \( pCO_2 \) variability. Because we lack late-fall and winter observations, we cannot resolve the full seasonal cycle. Nevertheless, we use the data to make a rough estimate of the lake-to-air \( CO_2 \) flux of \( 1.3 \leq 3.2 \text{Tg C yr}^{-1} \), which does not revise the previous flux estimate (Urban et al. 2005) and so does not add a new constraint to the previously unbalanced carbon budget for Lake Superior (Cotner et al. 2004; Urban et al. 2005).

More data are clearly needed, particularly in the nearshore region and across the full seasonal cycle. At present we have no wintertime data. There also needs to be further determination regarding bias correction for electrode-measured pH values from the EPA. There are several ongoing efforts, including direct estimates of the air–sea \( CO_2 \) flux using eddy covariance (J. M. Mwangi unpubl.), that will yield valuable information about \( CO_2 \) saturation levels in the lake and net fluxes. Volunteer observing ship surveys of surface lake and atmospheric \( pCO_2 \), such as those air–lake \( CO_2 \) fluxes presently underway on Lake Michigan (H. Bootsma unpubl.) and in the global oceans (Takahashi et al. 2009), would also be invaluable to further progress in understanding \( pCO_2 \) and its relationship to carbon cycling in the lake and the carbon budget of the lake. Additionally, modeling efforts underway by several of these authors and others will assist in further elucidating the magnitude and mechanisms of temporal and spatial variability in Lake Superior \( pCO_2 \).

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