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Long-term pCO_2 trends in Adirondack Lakes

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Key Points:

- There are significant pCO_2 trends in 29% of Adirondack Lakes
- Trends are strongest in lakes recovering from acidification
- pCO_2 trends in 52% of Adirondack Lakes were greater than trends reported for the atmosphere and ocean

Supporting Information:

- Supporting Information S1

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Abstract Lakes are globally significant sources of CO_2 to the atmosphere. However, there are few temporally resolved records of lake CO_2 concentrations and long-term patterns are poorly characterized. We evaluated annual trends in the partial pressure of CO_2 (pCO_2) based on chemical measurements from 31 Adirondack Lakes taken monthly over an 18 year period. All lakes were supersaturated with CO_2 and were sources of CO_2 to the atmosphere. There were significant pCO_2 trends in 29% of lakes. The median magnitude of significant positive trends was 32.1 μatm yr^{-1}. Overall, 52% of lakes had pCO_2 trends greater than those reported for the atmosphere and ocean. Significant trends in lake pCO_2 were attributable to regional recovery from acid deposition and changing patterns of ice cover. These results illustrate that lake pCO_2 can respond rapidly to environmental change, but the lack of significant trend in 71% of lakes indicates substantial lake-to-lake variation in magnitude of response.

1. Introduction

Lake surface waters are supersaturated with CO_2 and are globally significant sources of CO_2 to the atmosphere [*Cole et al.*, 1994; *Raymond et al.*, 2013; *Ciais et al.*, 2013; *Butman et al.*, 2016]. CO_2 concentrations in lakes integrate the influence of physical, chemical, and biological factors with different characteristic scales of temporal variability [*Hanson et al.*, 2006; *Morales-Pineda et al.*, 2014]. For example, diel variations in lake CO_2 concentration result primarily from day-night patterns in metabolism [*Hanson et al.*, 2006; *Morales-Pineda et al.*, 2014]. Weekly scale and seasonal-scale variations relate to physical processes like weather, water temperature, thermal stratification, and presence of ice cover [*Cole et al.*, 1994; *Hanson et al.*, 2006; *Morales-Pineda et al.*, 2014]. Longer-term trends correspond with changes in organic and inorganic carbon inputs and climate change, including changes in ice duration [*Jones et al.*, 2003; *Hanson et al.*, 2006; *Finlay et al.*, 2015]. Understanding lake CO_2 concentrations at each of these scales is important to being able to generalize, extrapolate, and predict lake CO_2 response to different types of environmental change.

There are few long-term records of lake CO_2 [e.g., *Hanson et al.*, 2006]. This is in part because governmental monitoring programs typically do not measure key indicators of lake carbon cycling like CO_2 concentration or flux [*Seekell et al.*, 2014a]. Space-for-time substitutions have been used to predict long-term changes in CO_2 concentration [e.g., *Lapierre et al.*, 2013], but the accuracy of these predictions is uncertain because key correlates of lake CO_2 vary geographically in ways that are not clearly analogous to temporal variability [e.g., *Seekell et al.*, 2014b; *Lapierre et al.*, 2015]. Many long-term time series only include summer measurements, which do not reflect critical changes during ice off and mixing that account for the majority of annual CO_2 emissions [*Cole et al.*, 1994; *Riera et al.*, 1999; *Kelly et al.*, 2001; *Karlsson et al.*, 2013; *Finlay et al.*, 2015]. Collectively, these observations illustrate the need to characterize long-term trends and patterns in surface water CO_2.

Here we evaluate annual trends in the partial pressure of CO_2 (pCO_2) in lake surface waters based on long-term (1995–2012), monthly chemical monitoring for 31 temperate lakes in the Adirondack Mountains. We specifically evaluate annual trends because these are most likely to reflect broad-scale environmental change [*Hanson et al.*, 2006]. Lakes in the Adirondack region are subject to changes due to recovery from acid precipitation and climate warming [*Monteith et al.*, 2007; *Waller et al.*, 2012; *Beier et al.*, 2012]. Therefore, long-term monitoring of lake chemistry in this region gives a unique opportunity to evaluate lake pCO_2 response to these changes.

2. Methods

2.1. Study Region and Data Sources

The Adirondack Park is a large, mountainous region of northern New York (USA). It has a humid continental climate with short, cool summers and long, cold winters [*Newton*, 1990]. The landscape is lake rich (approximately

Table 1. Summary Statistics for Study Lake Characteristics[a]

Characteristic	Mean	Median	Range
Surface area (ha)	42.5	14.6	0.8–521.5
Watershed area (ha)	1601	194.2	1–14,282.9
Mean depth (m)	3.99	3.3	0.7–10.5
Elevation (m)	560.2	537	381–873
pH	5.7	5.9	4.3–6.9
DOC (mg L^{-1})	6.0	4.6	2.0–16
DIC (μM)	1.3	1.2	0.6–2.6
$p\mathrm{CO_2}$ (μatm)	1415.1	1128.6	725.4–3,106.6
Temperature (K)	283.4	283.7	280.5–284.4
ANC (μeq L^{-1})	38.36	31.9	−39.78–206.39
SO_4^{2-} (mg L^{-1})	3.65	3.8	1.37–5.27

[a] Statistics for chemical characteristics are, for each lake, based values averaged across months within a year and then averaged across years. Lake specific data are given in the supporting information Tables S1 and S2.

2800 lakes > 0.2 ha), with seepage, drainage, and chain drainage lakes being abundant [*Newton and Driscoll*, 1990; *Waller et al.*, 2012]. Most of these lakes are unproductive and have low concentrations of chlorophyll *a* in their surface waters [*Bukaveckas and Robbins-Forbes*, 2000].

Many Adirondack surface waters are poorly buffered and have been adversely impacted by acid deposition [*Baker et al.*, 1990]. A tremendous effort has been made to quantify the impacts of acid deposition [e.g., *Baker et al.*, 1990], as well as track recovery over time [e.g., *Driscoll et al.*, 2003; *Waller et al.*, 2012]. As part of these efforts, the Adirondack Lake Survey Corporation (ALSC) has made monthly measurements of surface water chemistry on 50 lakes for the period 1995–2012. For 34 of these lakes, there are consistent measurements of variables needed to calculate $p\mathrm{CO_2}$ (i.e., dissolved inorganic carbon, water temperature, and pH) across all months. Three of these lakes have a recent history of liming and are not considered in the present study. We used records from the remaining 31 lakes as the principle data source for evaluating $p\mathrm{CO_2}$ trends (Table 1 and Tables S1 and S2 in the supporting information). Sampling ceased in 2006 for one of these lakes. Each month's water samples were taken within a few days of each other. Water chemistry analyses, described in detail by *Driscoll and van Dreason* [1993], conformed to standard limnological methods. Briefly, dissolved inorganic carbon (DIC) was determined by infrared spectrophotometry. Dissolved organic carbon (DOC) was determined by CO_2 detection by infrared spectrophotometry after UV-enhanced persulfate oxidation. pH was measured potentiometrically with a glass electrode. Acid neutralizing capacity (ANC) was measured by strong acid titration and Gran plot analysis. Sulfate (SO_4^{2-}) concentrations were measured by ion chromatography. Field triplicates were taken during about 5% of lake visits (~1–2 lakes per month). For these lake visits, we calculated $p\mathrm{CO_2}$ for each of the triplicate samples and then used the average of the triplicates in our trend analysis. We did this because trend analyses (described below) can only be based on one value per lake per month. A detailed analysis of sampling variability based on these triplicate measures is found in *Schecher and Driscoll* [1988].

The chemical data used in our analysis are available on the ALSC website: www.adirondacklakessurvey.org. The ALSC also conducted a region-wide survey of 1469 lakes (surface areas between 0.5 and 700 ha) between 1984 and 1987. As part of this survey, lakes were classified in terms of their sensitivity to acidification based on surficial geology and hydrologic flow paths [*Driscoll and van Dreason,* 1993; *Driscoll et al.*, 2003]. We obtained lake classifications and morphometric data from this database to provide context for our trend analyses (retrieved from http://www.adirondacklakessurvey.org/historic.php).

2.2. $p\mathrm{CO_2}$ Calculations

We calculated $p\mathrm{CO_2}$ based on DIC (μM), pH, and in situ water temperature (K) from the ALSC data set following standard limnological approaches [*Weyhenmeyer et al.*, 2012]. Briefly, CO_2 (μM) is a function of DIC, temperature-adjusted equilibrium constants, and pH. $p\mathrm{CO_2}$ was then calculated from CO_2 concentration based on Henry's constant adjusted for water temperature and atmospheric pressure adjusted for lake elevation. Equations used for the calculations are given in the supporting information (Text S1).

Some Adirondack Lakes have relatively low pH (Table 1), and uncertainties in the measurement of pH at low values could impact our $p\mathrm{CO_2}$ estimates [*Driscoll and Newton*, 1985]. Direct measurements of $p\mathrm{CO_2}$ were not taken as part of the ALSC monitoring program, and therefore, we cannot directly validate the calculated values. However, we note that previous analyses have found $p\mathrm{CO_2}$ calculated based on pH, and DIC is unbiased relative to direct measurements [*Cole et al.*, 1994; *Riera et al.*, 1999]. This limitation related to calculated $p\mathrm{CO_2}$ is common to analyses of patterns in lake $p\mathrm{CO_2}$, and such uncertainty is a necessary concession to evaluate existing data sets because few were originally designed to evaluate lake carbon cycling [*Weyhenmeyer et al.*, 2012; *McDonald et al.*, 2013; *Seekell et al.*, 2014a].

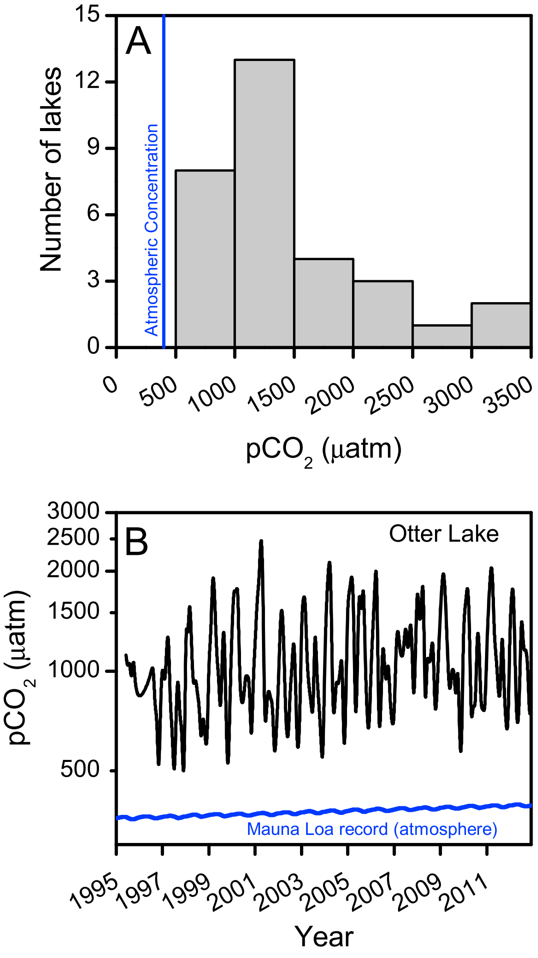

Figure 1. (a) Average pCO_2 was higher than atmospheric levels in all study lakes, indicating that they are net sources of CO_2 to the atmosphere. We give the atmospheric reference concentration of 400 µatm, although we recognize that this value changes seasonally and has increased over time. (b) pCO_2 time series from Otter Lake (black line), which is typical of Adirondack Lakes. There is tremendous seasonal variability, but the water is consistently supersaturated with CO_2 relative to atmospheric levels (blue line, based on the Mauna Loa record which was retrieved online from www.esrl.noaa.gov/gmd/ccgg/trends/).

2.3. Statistical Analysis

We evaluated annual trends based on the monthly data using the seasonal Kendall test [*Hirsch et al.*, 1982; *Hirsch and Slack*, 1984; *Marchetto et al.*, 2013]. The seasonal Kendall test is a rank-based test for monotonic trend that is robust to outliers and missing values. For each lake, an annual trend is calculated for each month. These month-specific trends are then combined to test for an overall annual trend. For each trend test, we report probability values corrected for serial correlation between months [*Hirsch and Slack*, 1984]. This approach has been widely applied to test for trends in water quality data, including previous analyses of environmental monitoring data from the Adirondack region [e.g., *Driscoll and Van Dreason*, 1993; *Stoddard et al.*, 1999; *Driscoll et al.*, 2003; *Hanson et al.*, 2006; *Seekell and Pace*, 2011]. The trend analyses were conducted using the "rkt" package for the *R* statistical application, version 3.2.2 [*Marchetto et al.*, 2013; *R Core Team*, 2015].

Subsequent to our trend analysis, we evaluated correlations between trends in pCO_2 and trends in DIC, DOC, Sulfate, ANC, water temperature, and pH. We also evaluated correlations between trends in pCO_2 and morphometric parameters including lake surface area, mean depth, maximum depth, watershed area, and elevation.

3. Results

3.1. Variation of pCO_2 Within and Between Lakes

Baseline pCO_2 (average of annual averages) for each of the study lakes and $>$ 98.7% of individual samples (see supporting information Text S2) were higher than the atmospheric levels, indicating that Adirondack Lakes are net sources of CO_2 to the atmosphere (Table 1 and Figure 1a). However, temporal variation within lakes was substantial. Figure 1b illustrates the typical characteristics of pCO_2 time series with the record from Otter Lake (43.18°N, 74.5°W). Seasonal variation in Otter Lake (coefficient of variation = 0.32) dominates interannual variation (coefficient of variation = 0.11). Variation in baseline pCO_2 between lakes (coefficient of variation = 0.46) exceeds both the seasonal and interannual variations within Otter Lake. This pattern of between-lake variability exceeding within-lake variability is consistent across 90% of the other study lakes (Table S2).

3.2. Trends in SO_4 and ANC

Detailed results of the seasonal Kendall trend analyses are given in Table 2. Briefly, sulfate concentrations declined significantly ($p \leq 0.05$) in all lakes, and this is consistent with previously reported region-wide declines in acid deposition [*Driscoll et al.*, 2003; *Waller et al.*, 2012]. All lakes had positive ANC trends, and these trends were significant in 71% of lakes. ANC is a key metric of lake acidification relative to chemical and biological impacts, and this result demonstrates a general recovery from acidification [*Driscoll et al.*, 2003].

Table 2. Summary Results of the Seasonal Kendall Trend Analyses

Measurement	Positive	Negative	No Trend	Positive $p < 0.05$	Negative $p < 0.05$
			Number of Trends		
pCO_2	18	13	0	6	3
DOC	24	5	2	17	3
DIC	24	7	0	10	1
pH	26	3	2	17	0
Temperature	10	1	20	3	0
ANC	31	0	0	22	0
SO_4^{2-}	0	31	0	0	31
			Median (Average) Magnitude of Trends		
pCO_2 (μatm yr^{-1})	5.36 (14.41)	−4.5 (−6.75)	NA	32.1 (33.3)	−15.9 (−16.2)
DOC (mg L^{-1} yr^{-1})	0.04 (0.06)	−0.06 (−0.06)	0 (0)	0.06 (0.07)	−0.07 (−0.09)
DIC (μM yr^{-1})	0.56 (0.86)	−0.28 (−0.47)	NA	1.03 (1.57)	−1 (−1)
pH (yr^{-1})	0.01 (0.01)	−0.002 (−0.002)	0 (0)	0.02 (0.02)	NA
Temperature (K yr^{-1})	0.02 (0.04)	−0.01 (−0.01)	0 (0)	0.08 (0.09)	NA
ANC (μeq L^{-1} yr^{-1})	0.79 (0.84)	NA	NA	0.92 (1.03)	NA
SO_4^{2-} (mg L^{-1}yr^{-1})	NA	−0.13 (−0.12)	NA	NA	−0.13 (−0.12)

Of the lakes without significant ANC trends ($n = 9$), 56% were classified by the ALSC as not acid sensitive and 33% were classified as moderately sensitive or sensitive but did not have low pH (average pH = 6.4). Hence, 89% ($n = 8$) of lakes without significant ANC trends did not show recovery, probably because they were never severely impacted by acid rain. The final lake with no ANC trend was a mounded seepage lake with high DOC. This type of lake is naturally acidic [*Driscoll and van Dreason*, 1993].

3.3. Trends in pCO_2

Across all 31 lakes, 58% had positive pCO_2 trends and 42% had negative trends. Twenty-nine percent of these trends (six positive and three negative) were significant ($p \leq 0.05$; see Table 2). The median magnitude of the significant positive trends was +32.1 μatm yr^{-1}, and median magnitude of significant negative trends was −15.9 μatm yr^{-1}. These values equate to changes of +578 μatm across the 18 year record for positive trends and −286 μatm for negative trends, both of which are considerable changes given the median lake pCO_2 of 1128.6 μatm (Table 1).

The lakes that did not have significant ANC trends also did not have significant pCO_2 trends. An additional lake (Clear Pond, 43.99°N, 73.83°W) was classified as not acid sensitive but had positive ($p = 0.03$) ANC trend. However, this lake was probably not strongly acidified because it had no significant trend in pCO_2, DIC, HCO_3^- (estimated based on DIC and pCO_2), or pH, which was circumneutral (average = 6.9). Collectively, these results indicate that lakes not strongly impacted by acidification do not have significant pCO_2 trends.

One exception to the above result is Sunday Pond (44.34°N, 74.3°W), an acid sensitive mounded seepage lake with a significant negative pCO_2 trend (supporting information Table S3). This negative trend was driven by significant (Mann-Kendall test $p < 0.01$) declines in April pCO_2 (−1395.9 μatm over the 18 year record) that corresponded with a significant (Mann-Kendall test $p < 0.01$) increase in April water temperatures (+4.9°C over the course of the record). While ice cover records for this lake are unavailable, April is the typical month for ice off in Adirondack Lakes, and we hypothesize that there has been a major shift in ice dynamics such that at the beginning of the record the lake was ice covered in April but that this ceased toward the end of the record [*Beier et al.*, 2012]. This type of shift in ice cover would decrease under ice CO_2 accumulation and can be substantial to the extent that it is reflected in annual trends [e.g., *Finlay et al.*, 2015].

Two additional lakes had significant negative annual pCO_2 trends. These trends could also have been triggered by changes in ice cover. Cascade Lake (43.79°N, 74.81°W) had decreases in April pCO_2 (−616 μatm over the 18 year period) associated with increased April water temperatures (+3°C), although the water temperature trend was not significant (supporting information Table S3). Little Hope Pond (44.51°N, 74.12°W) also witnessed rising April water temperatures. Decreased pCO_2 was not evident for April but during the following months (May and June). However, neither of these changes were statistically significant. An alternate explanation for the significant negative annual pCO_2 trends is based on chemistry. Specifically, we observed no significant change in DIC but significant increases in pH and HCO_3^-. It is possible in these lakes that pH recovered to the extent that the relative abundance of inorganic carbon species has shifted, driving down CO_2 concentrations while not substantially changing the total amount of DIC (supporting information Table S3).

Lakes with significant positive pCO_2 trends had consistent characteristics in that they all had significant positive trends in ANC, DIC, and DOC. Four of these lakes also had significant increases in pH, but the estimated percent of DIC comprised by CO_2 in these lakes was high (average = 94%, i.e., pH was low) indicating that most DIC remained in the form of CO_2.

We were unable to develop a consistent explanation for the lack of trend in the balance ($n = 13$) of the lakes. For these lakes, trends in ANC were positively correlated with DIC, which in turn was positively correlated with trends in pCO_2. It is possible that these factors simply have not changed enough to develop significant pCO_2 trends. We found no significant trends in April water temperature or April pCO_2 that might indicate changes in ice dynamics and no significant correlations between pCO_2 trends and a variety of morphometric measures.

4. Discussion

There were significant pCO_2 trends in over a quarter of the study lakes, and the rates of change in these systems were rapid relative to changes reported for oceans and the atmosphere. Specifically, the median rate of change in significant pCO_2 trends (both positive and negative) is positive and more than six times greater (12.19 μatm yr^{-1}) than the rates of change observed for the atmosphere (1.93 μatm yr^{-1}, years 2000–2006; 1.74 μatm yr^{-1}, years 1989–2008) and the oceans (1.84 μatm yr^{-1}, years 1989–2008) [*Canadell et al.*, 2007; *Doney et al.*, 2009]. When only considering significant positive trends, the median lake CO_2 trend (32.1 μatm yr^{-1}) is more than 17 times greater than atmospheric and oceanic trends. These contrasts suggest the potential for rapid change in lake contributions to landscape-scale carbon balances.

Acid deposition was decreasing during the study period, and many lakes exhibited recovery trajectories [*Driscoll et al.*, 2003]. However, the direction and magnitude of pCO_2 trends were highly variable between lakes. To some extent this reflects basin-specific susceptibility to acidification [*Driscoll and van Dreason*, 1993; *Driscoll et al.*, 2003]. Nine (29%) of the study lakes were not particularly susceptible to acid rain. The lack of recovery trend is reflected in no change in pCO_2 in eight of these systems. Six (19%) of the study lakes had significant positive trends. These lakes were known to be acid sensitive and exhibited significant changes in water chemistry (ANC, DIC, and DOC) associated with recovery trajectories.

The concurrent increases in pCO_2 and ANC in Adirondack Lakes contrast patterns in Earth's oceans where alkalinity is consumed as waters acidify and pCO_2 increases [*Omta et al.*, 2011]. One potential cause for this pattern in lakes is increasing catchment soil pCO_2 [*Norton et al.*, 2001]. Soil pCO_2 is not widely measured but is correlated with soil temperature and atmospheric CO_2 concentrations, both of which are increasing in the northern United States [*Rustad et al.*, 1986; *Hu and Feng*, 2003]. Model analyses suggest that rising soil pCO_2 increases aluminum export from catchments with low base saturation, like those in the Adirondack Mountains, even as sulfate concentrations decrease [*Norton et al.*, 2001; *Sullivan et al.*, 2006]. Hydroxide binds to aluminum in surface waters, and hydrogen ions to bicarbonate, forming CO_2 [*Norton et al.*, 2001]. Decreases in sulfate increase ANC in lakes by decreasing the concentration of strong anions [*Driscoll et al.*, 2007]. Previous analyses have revealed increasing concentrations of aluminum and significant declines in sulfate in Adirondack Lakes that are consistent with this mechanism as the cause of the concurrent increases in pCO_2 and ANC identified in our analysis [*Driscoll et al.*, 2003]. Further, a model analysis has found that this mechanism can create patterns of concurrently increasing ANC and pCO_2 that last on the order of decades, which is the same time scale as our trend analysis [*Norton et al.*, 2001]. Hence, there is a chemical route to explain concurrent increases in ANC and CO_2. Additionally, DOC concentrations increased, in part, because declines in sulfate deposition increase soil DOC solubility and export to lakes [*Monteith et al.*, 2007]. DOC serves as a substrate for CO_2 production through bacterial and photochemical mineralization and organic acids from DOC depress recovery in pH [*Munson and Gherini*, 1993]. Increasing DOC concentrations also contributed to increasing ANC, although this is a secondary factor relative to the changes in strong anion concentrations [*Waller et al.*, 2012]. Collectively, these results indicate that chemical recovery trajectories from acidification explain the significant pCO_2 increases observed in some lakes.

We could not identify a consistent explanation for lack of $p\mathrm{CO_2}$ trends in 35% ($n = 11$) lakes. Part of the challenge in explaining trends (or lack of trends) is the integrative nature of lake $\mathrm{CO_2}$. All of these lakes had significant increases in ANC, but trends in other factors (e.g., DIC) were inconsistent. It is possible that changes have been too small relative to variability in $p\mathrm{CO_2}$ and that significant trends will become apparent in the future. It is also possible that the lack of significant change is due to interactions with factors not monitored by the ALSC such as patterns of ice duration, stratification, or food web structure. One example of this is in Sunday Pond where declining spring ice cover is likely responsible for significant declines in $p\mathrm{CO_2}$. This relationship between ice cover and $p\mathrm{CO_2}$ has been observed in other regions [e.g., *Finlay et al.*, 2015], but ice cover is not tracked for all ALSC lakes. Changes in Adirondack Lake ice cover are not widespread, in part, because local snow conditions and lake morphometry influence how well ice off tracks rising spring air temperatures. This mechanism could only be identified for Sunday Pond because of the dramatic nature of the change [*Stager et al.*, 2009; *Beier et al.*, 2012]. This emphasizes the difficulty in discerning drivers from monitoring data when there are no dramatic or consistent changes.

Most variation in $p\mathrm{CO_2}$ is between lakes, and DOC concentration explains a substantial portion of this variation [*Sobek et al.*, 2003, 2005; *Lapierre et al.*, 2013]. DOC concentrations are increasing globally, and the between-lake $p\mathrm{CO_2}$-DOC relationship has been leveraged to suggest that $p\mathrm{CO_2}$ should increase in response to these changes [e.g., *Lapierre et al.*, 2013]. Our analysis is uniquely suited to test the assumption that geographic variation translates to temporal changes in $\mathrm{CO_2}$. We used the $p\mathrm{CO_2}$-DOC relationship (based on annual averages) between the study lakes to predict $p\mathrm{CO_2}$ time series based on the observed DOC time series. We then reran the seasonal Kendall analysis based on these hypothetical $p\mathrm{CO_2}$ time series and compared this to the results based on observed values. In general, the hypothetical and observed $p\mathrm{CO_2}$ time series are correlated, but predictions for individual lakes often produce trends (39% of the lakes) that were in the opposite direction of observed $p\mathrm{CO_2}$ trends (supporting information Text S3). There are likely many reasons for these deviations, and this limits the ability to broadly extrapolate temporal changes based on the strength of the between-lake relationships.

Currently, there are few monitoring programs that specifically evaluate lake carbon cycling [e.g., *Lapierre et al.*, 2013, 2015], and this is a major limitation to predicting lake responses to environmental change [*Weyhenmeyer et al.*, 2012; *Seekell et al.*, 2014a]. Both the variability in direction and magnitude of changes identified in our trend analysis, and the observation that space-for-time analyses may not provide satisfactory predictions of $p\mathrm{CO_2}$ change, emphasize the need for wider-spread carbon monitoring in inland waters.

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Geophysical Research Letters

Supporting Information for

Long-term pCO$_2$ trends in Adirondack lakes

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Contents of this file

Introduction

This supplemental material contains additional text figures, and tabular results that are referred to in the main text. Data collection and statistical analyses are described in detail in the main text.

Text S1. pCO$_2$ calculations

We calculated pCO$_2$ (µatm) based on DIC (µM), pH, and *in situ* water temperature (T, in K) from the ALSC dataset following the approach of *Weyhenmeyer et al.* [2012]. First, we calculated the water temperature adjusted equilibrium constants K_1 and K_2:

$$\log_{10} K_1 = -356.3094 - 0.06091964T + \frac{21834.37}{T} + 126.8339 \log_{10} T - \frac{1684915}{T^2}$$

$$\log_{10} K_2 = -107.8871 - 0.03252849T + \frac{5151.79}{T} + 38.92561 \log_{10} T - \frac{563713.9}{T^2}$$

We then calculated the CO$_2$ concentration (µM):

$$\mathrm{CO_2} = \frac{\mathrm{DIC}}{\frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} + 1}$$

where

$$[H^-] = 10^{-\mathrm{pH}}$$

Finally, we determined pCO$_2$ based on elevation (E, in meters above sea level) adjusted atmospheric pressure (P, bar), and Henry's constant (K_H) adjusted for in situ water temperature.

$$pCO_2 = \frac{CO_2}{0.987 K_H P}$$

where

$$\log_{10} K_H = 108.3865 + 0.01985076T - \frac{6919.53}{T} - 40.45154 \log_{10} T - \frac{669365}{T^2}$$

and

$$P = 0.001(1013 - 0.1E)$$

Reference

Weyhenmeyer, G. A., et al. (2012), Carbon dioxide in boreal surface waters: A comparison of lakes and streams, *Ecosystems, 15,* 1295-1307.

Text S2. Occurrence of under-saturation

There were 6140 total samples and only 78 (< 1.3%) were under-saturated relative to atmospheric CO_2 concentrations from the Mauna Loa record (http://www.esrl.noaa.gov/gmd/ccgg/trends/data.html). Under-saturation was observed in all months, except for February. When occurrences were summed across lakes, under-saturation was most prevalent in the summer, and the seasonality is significantly different from a null hypothesis of under-saturation occurring equally across the seasons (df = 11, $\chi 2=53.38$, $p < 0.01$). However, under-saturation was still uncommon in the summer, occurring in only 41 of 1599 June/July/August samples (~2.6%). Two lakes were the source 51% of all under-saturated samples and under-saturation occurred during the summer months in these lakes. These two lakes mostly drove the overall seasonal pattern. In fact, 58% of lakes were never under-saturated when sampled, and even in the two lakes with the most common occurrence of under-saturation, only 8 and 11% of samples were under-saturated. Even in the lake and month where under-saturation was most common, it was observed in less than half the samples (44%). Hence under-saturation was rare in the Adirondack lakes, especially compared to lakes in regions subject to nutrient pollution from agriculture [e.g. *Balmer and Downing*, 2011]. Under-saturation was too rare in our analysis to explain variation in its occurrence. However, it is likely partly a function of factors such as weather, stratification patterns, and food web structure, which cannot be resolved solely through chemical monitoring [*Vachon and del Giorgio*, 2014; *Schinder et al*, 1997].

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Text S3. Do space-for-time analyses adequately for predict temporal changes in $p\mathrm{CO}_2$?

The $p\mathrm{CO}_2$-DOC relationship for study lakes was: $p\mathrm{CO}_2 = 518 + 149.4$ DOC, $r^2 = 0.62$ (Figure S1).

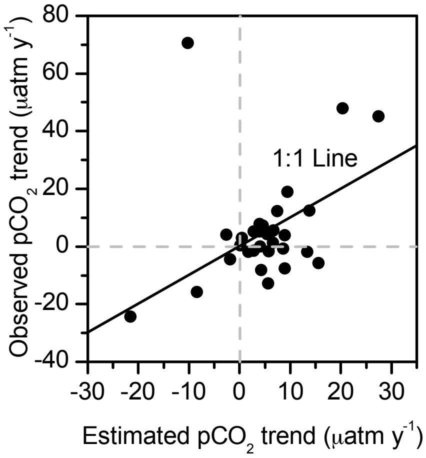

Figure S1. The relationship between observed $p\mathrm{CO}_2$ trends and hypothetical trends generated by applying the between-lake $p\mathrm{CO}_2$-DOC relationship to observed DOC time series.

Lake Name	Latitude	Longitude	Surface area (ha)	Watershed area (ha)	Elevation (m)	Mean depth (m)
Little Hope Pond	44.515833	-74.125278	2.8	38.1	521	3.5
Big Hope Pond	44.511944	-74.125	8.9	194.2	522	5.8
Little Echo Pond	44.305556	-74.3575	0.8	1	482	2.9
East Copperas Pond	44.311944	-74.372222	3.6	15	479	4.1
Middle Pond	44.336944	-74.371944	24.3	181.9	484	1.5
Sunday Pond	44.344722	-74.300556	4	108.9	485	5.4
Sochia Pond	44.352222	-74.294722	1.6	9.6	500	3.1
Owen Pond	44.323056	-73.903333	7.6	1139.2	514	3.7
Heart Lake	44.179722	-73.9675	10.7	62.9	661	5.1
Marcy Dam Pond	44.158889	-73.953056	1.2	1142.4	720	0.7
Grass Pond	44.657222	-74.495833	1.6	35.7	381	4.2
Black Pond	44.436667	-74.301389	29	344.2	495	6.2
Lake Rondaxe	43.756389	-74.916389	90.5	14282.9	524	3
Moss Lake	43.781111	-74.853056	45.7	1314.7	536	5.7
Cascade Lake	43.789167	-74.812778	40.4	474.8	557	4.2
Bubb Lake	43.774722	-74.846944	18.2	185.8	554	2.1
Dart Lake	43.793333	-74.871111	51.8	10756.5	537	7.3
Windfall Pond	43.805	-74.831389	2.4	43.7	591	3.2
Big Moose Lake	43.651111	-74.855278	512.5	9643.8	558	6.8
West Pond	43.811389	-74.883333	10.4	108.1	581	1.5
Squash Pond	43.825556	-74.886389	3.3	41.3	653	1.4
Constable Pond	43.830556	-74.8075	20.6	945.1	580	2.1
Limekiln Lake	43.713333	-74.813056	186.9	1393	575	6.1
Willis Lake	43.371389	-74.246389	14.6	139.4	400	1.6
Clear Pond	43.993889	-73.827778	70.4	600.6	584	9.2
Long Pond	43.8375	-74.480556	1.7	26.2	574	2
Arbutus Lake	43.982778	-74.235833	48.9	354	516	2.8
Lake Colden	44.119167	-73.983056	15.4	645.4	843	2.3
Avalanche Lake	44.130833	-73.970278	4.4	115.2	873	3.3
Sagamore lake	43.765833	-74.628611	68	4946.2	580	10.5
Otter Lake	43.181111	-74.503333	14.8	340.8	505	2.3

Table S1. Lake location and morphometry.

Lake Name	Mean $p\mathrm{CO}_2$ (μatm)	Seasonal variation $p\mathrm{CO}_2$	Mean DOC (mg l^{-1})	Mean Water Temperature (K)	Mean DIC (μM)	Mean pH	Mean SO_4^{2-} (mg l^{-1})	Mean ANC (μeq l^{-1})
Little Hope Pond	1597.59	0.20	11.68	283.68	1.30	5.77	3.25	43.76
Big Hope Pond	924.29	0.34	8.31	283.66	0.95	6.20	3.33	50.48
Little Echo Pond	2768.58	0.17	15.95	283.42	1.82	4.34	1.86	-39.78
East Copperas Pond	2066.73	0.23	10.95	283.29	1.37	4.58	1.82	-18.04
Middle Pond	1733.25	0.65	5.31	283.70	2.45	6.58	4.20	113.32
Sunday Pond	932.74	0.41	2.04	283.99	0.67	5.13	2.30	-1.59
Sochia Pond	1704.50	0.42	4.23	283.99	0.67	5.13	1.62	-8.78
Owen Pond	1116.06	0.11	5.12	282.58	1.89	6.66	5.27	115.73
Heart Lake	1016.04	0.24	2.48	283.45	1.11	6.37	3.35	46.59
Marcy Dam Pond	764.22	0.34	3.21	280.53	0.72	5.87	3.50	26.80
Grass Pond	1776.10	0.21	8.97	283.74	1.19	4.58	1.37	-17.90
Black Pond	1069.36	0.35	3.72	283.93	2.54	6.45	4.74	206.39
Lake Rondaxe	986.16	0.16	4.07	283.70	1.09	6.23	4.10	48.79
Moss Lake	1086.19	0.25	3.93	283.82	1.47	6.47	4.50	76.61
Cascade Lake	1023.65	0.45	3.34	283.85	1.18	6.37	4.56	52.89
Bubb Lake	1256.55	0.49	3.46	283.96	1.32	6.28	3.80	48.95
Dart Lake	766.54	0.14	4.45	283.58	0.60	5.70	4.07	17.88
Windfall Pond	1133.57	0.28	3.85	283.79	1.85	6.67	4.37	105.26
Big Moose Lake	880.86	0.30	4.59	283.33	0.68	5.60	4.07	15.12
West Pond	2004.03	0.70	6.83	284.33	1.50	5.26	3.53	10.30
Squash Pond	2328.62	0.27	8.91	282.95	1.56	4.55	3.28	-21.09
Constable pond	1240.24	0.20	5.78	283.48	0.83	4.99	4.46	-0.12
Limekiln Lake	944.84	0.23	3.28	283.95	0.88	6.13	3.90	33.36
Willis Lake	3053.33	0.20	8.35	284.40	2.57	6.00	3.62	70.54
Clear Pond	725.41	0.34	3.39	283.69	1.53	6.87	4.11	103.45
Long Pond	3106.62	0.30	14.27	283.79	2.05	4.64	3.29	-11.46
Arbutus Lake	1064.29	0.36	4.94	283.33	1.36	6.48	4.88	70.44
Lake Colden	1077.53	0.42	4.40	281.26	0.80	5.20	3.48	7.23
Avalanche Lake	1405.66	0.33	5.96	281.25	1.00	5.06	3.19	5.29
Sagamore lake	1187.28	0.17	7.78	283.24	1.05	5.92	4.84	31.90
Otter Lake	1128.61	0.31	2.63	283.84	0.80	5.36	4.44	6.72

Table S2. Average chemical characteristics for the study lakes (averaged across months within a year, then across years). Seasonal variation of $p\mathrm{CO}_2$ is the coefficient of variation of monthly averages.

Lake Name	$p\mathrm{CO}_2$ trend (µatm y^{-1})	DOC trend (mg l^{-1} y^{-1})	Water Temp. Trend (K y^{-1})	DIC Trend (µM y^{-1})	pH trend (y^{-1})	$\mathrm{SO_4}^{2-}$ trend (mg l^{-1} y^{-1})	ANC Trend (µeq l^{-1} y^{-1})	April Water Temp. trend (K y^{-1})	April $p\mathrm{CO}_2$ trend (µatm y^{-1})
Little Hope Pond	-24.39**	-0.14*	0.01	0.04	0.039**	-0.14**	1.80**	0.05	-56.41*
Big Hope Pond	5.07	0.02	0.03	1.67**	0.024**	-0.14**	2.03**	0.14	22.72
Little Echo Pond	7.83	0.03	0.00	0.21	0.005**	-0.07**	0.68**	0.03	-44.86
East Copperas Pond	45.16*	0.18**	0.00	2.08*	0.003	-0.10**	0.48*	0.08	-28.99
Middle Pond	0.35	0.00	0.00	-0.27	-0.002	-0.11**	0.51	0.15	35.47
Sunday Pond	-15.93**	-0.06*	0.08*	-0.97**	0.000	-0.05**	0.07	0.24**	-64.29**
Sochia Pond	-7.76	0.06**	0.01	-0.42	0.008*	-0.06**	0.64**	0.20	-40.84
Owen Pond	-1.58	0.02	0.00	0.47	0.003	-0.18**	0.79	-0.01	18.93
Heart Lake	4.08	-0.02	0.00	0.22	-0.001	-0.10**	0.24	0.07	7.59
Marcy Dam Pond	2.91	0.00	0.00	0.33	0.013**	-0.10**	0.65**	0.02	-5.26
Grass Pond	-5.82	0.10**	0.00	-0.28	0.001	-0.06**	0.12	0.24	-41.11
Black Pond	-12.88	0.04	0.16*	-1.11	0.006	-0.12**	0.20	0.24	15.64
Lake Rondaxe	4.28	0.04*	0.00	1.02**	0.015*	-0.13**	1.36**	0.27*	-24.90
Moss Lake	-2.01	0.01	0.01	0.75	0.008	-0.11**	1.37**	0.14	-7.06
Cascade Lake	-8.21*	0.03*	0.00	0.30	0.014*	-0.13**	0.95**	0.13	-20.39
Bubb Lake	-4.50	-0.01	0.02	-0.01	0.006	-0.08**	0.42	0.18	-50.56
Dart Lake	4.82*	0.04*	0.02*	0.79**	0.033**	-0.14**	1.23**	0.02	-1.38
Windfall Pond	7.24	0.03*	0.00	0.56	0.001	-0.15**	0.48	-0.04	15.13
Big Moose Lake	1.22	0.04**	0.00	0.53	0.035**	-0.14**	1.24**	0.05	20.52
West Pond	18.95*	0.06*	0.00	0.95*	0.012*	-0.15**	0.79**	0.10	-22.77
Squash Pond	-1.97	0.09*	0.00	-0.22	0.011**	-0.13**	1.10**	0.07	-15.76
Constable pond	12.32	0.09**	0.00	0.76*	0.012*	-0.16**	0.82**	0.10	-9.08
Limekiln Lake	-1.78	0.04**	0.01	0.83**	0.025**	-0.14**	1.44**	0.18	-17.64
Willis Lake	70.53**	-0.07*	-0.01	4.63**	0.000	-0.13**	1.09*	0.33*	-8.31
Clear Pond	-0.10	0.03*	0.01	0.17	0.003	-0.13**	0.49*	0.07	-22.54
Long Pond	47.94**	0.14*	0.00	1.92*	0.014**	-0.15**	1.27**	0.12	102.87
Arbutus Lake	5.23	0.03	0.00	0.56	-0.002	-0.15**	0.40	0.15	25.02
Lake Colden	-0.85	0.06**	0.00	0.14	0.020**	-0.13**	0.72**	0.00	1.81
Avalanche Lake	3.85	0.06*	0.00	0.19	0.017**	-0.14**	0.86**	0.02	10.85
Sagamore lake	5.48	0.05	0.00	0.52	0.011	-0.16**	0.90**	0.01	14.20
Otter Lake	12.19*	0.05**	0.00	1.04**	0.024**	-0.15**	0.84**	0.18*	-8.88

Table S3. Lake specific trends. * Denotes statistical significance at the $p \leq 0.05$ level. ** Denotes statistical significance at the $p \leq 0.01$ level.