

## Regulation of spatial and temporal variability of carbon flux in six hard-water lakes of the northern Great Plains

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### Abstract

Six hard-water lakes were sampled May–August for 14 yr in a 52,000 km<sup>2</sup> catchment to identify the mechanisms that regulate the spatial and temporal variability of net atmospheric exchange of CO<sub>2</sub> of lakes on the Northern Great Plains. Annual mean daily fluxes ranged from  $-100$  to  $>200$  mmol C m<sup>-2</sup> d<sup>-1</sup>, while *p*CO<sub>2</sub> values varied between 0.3 and 5500 Pa. We observed periods of net CO<sub>2</sub> uptake (1995, 2000) and release (1998, 2006) resulting in synchronous variations in net CO<sub>2</sub> flux among lakes. Furthermore, *p*CO<sub>2</sub>, pH, and chemical enhancement of CO<sub>2</sub> influx all varied coherently among sites. Interannual variation in net CO<sub>2</sub> flux and *p*CO<sub>2</sub> was correlated strongly with pH, correlated weakly with other physical and chemical conditions, and was uncorrelated to algal biomass, productivity, or ecosystem respiration. In contrast, spatial variability of water-column *p*CO<sub>2</sub> was correlated negatively to concentrations of soluble reactive phosphorus, total dissolved nitrogen, pH, and gross primary productivity, suggesting an important role of lake metabolism at large spatial scales. Finally, comparison with an additional 20 saline lakes demonstrated that changes in mean annual pH, *p*CO<sub>2</sub>, and CO<sub>2</sub> flux during 2002–2007 were coherent in diverse lakes within a region of  $>100,000$  km<sup>2</sup> and suggest that climatic control of pH and *p*CO<sub>2</sub> had an unexpectedly great effect on net CO<sub>2</sub> flux through productive hard-water lake ecosystems.

Lakes are important components of the global carbon budget, owing to their disproportionate rates of carbon processing relative to their integral surface area (Cole et al. 2007; Prairie 2008). On average, freshwater lakes export half of the carbon that comes in from the watershed, while the remainder is either buried in the sediments or released as CO<sub>2</sub> to the atmosphere (Cole et al. 2007). However, rates of CO<sub>2</sub> exchange with the atmosphere vary substantially in time and space ( $<-250$  to  $>3000$  mmol C m<sup>-2</sup> d<sup>-1</sup>) (Schindler et al. 1997; Cole and Caraco 1998; Duarte et al. 2008) as a result of differences in lake metabolism and food-web structure (Schindler et al. 1997; Prairie et al. 2002), subsidies of terrestrial dissolved organic matter (DOM) (Kelly et al. 2001; Rantakari and Kortelainen 2005), geological and edaphic controls of dissolved inorganic carbon (DIC) content (Dean 1999; Myrbo and Shapley 2006), salinity (Duarte et al. 2008), and climatic variability (Hanson et al. 2006) (Fig. 1). Improved understanding of the patterns and causes of this spatial and temporal variation is needed to accurately estimate the role of lakes to the global carbon budget (Cole et al. 2007).

Empirical evidence to date suggests that spatial and temporal differences in partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>) arise mainly from changes in primary production (P) and ecosystem respiration (R), factors that are strongly influenced by subsidies of inorganic nutrients and organic material from the catchment (Prairie et al. 2002; Hanson et al. 2003) (Fig. 1). In general, lakes are heterotrophic, *p*CO<sub>2</sub> exceeds 37 Pa, and CO<sub>2</sub> evades to the atmosphere when dissolved organic carbon (DOC) concentrations in lakes exceed 5–6 mg L<sup>-1</sup> (Prairie et al. 2002; Hanson et al. 2004).

However, the strength of metabolic control of CO<sub>2</sub> flux may be scale dependent, with respiration and production regulating short-term (diel-seasonal) CO<sub>2</sub> exchanges (Schindler and Fee 1973; Dillon and Molot 1997; del Giorgio et al. 1999), while climate regulates differences in solute influx and CO<sub>2</sub> concentration among years (Kelly et al. 2001; Rantakari and Kortelainen 2005; Hanson et al. 2006). Similarly, while continental gradients of lake metabolism can be used to predict large-scale patterns of CO<sub>2</sub> exchange (Alin and Johnson 2007), much less is known of the controls of spatial variability within and among lake regions (Duarte et al. 2008). To date, there have been few comparisons of relative importance of metabolism, chemistry, and climate in regulating CO<sub>2</sub> flux, particularly for eutrophic, hard-water, and saline lakes in which chemically enhanced CO<sub>2</sub> fluxes can be important (Duarte et al. 2008).

Chemical controls of CO<sub>2</sub> flux are most pronounced in lakes with elevated pH. For example, freshwater lakes with pH  $>8$  have low concentrations of dissolved CO<sub>2</sub> relative to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> and are often sites of in-gassing of atmospheric carbon (Schindler et al. 1997; Bade and Cole 2006). Reactions can be more complex in lakes with elevated concentrations of DIC or intense primary production, since thermal or biotic initiation of CaCO<sub>3</sub> precipitation (Brunskill 1969; Müller et al. 2006) can result in net increases in dissolved CO<sub>2</sub> concentrations while reducing total DIC content (McConnaughey et al. 1994). Similarly, because climatic variability can alter influx of DIC and DOC from catchments (Kelly et al. 2001; Rantakari and Kortelainen 2005), and because the magnitude and character of these inputs will also depend on local vegetation, soils, and geology (Dean 1999), it has proven difficult to evaluate the hierarchical relationships among

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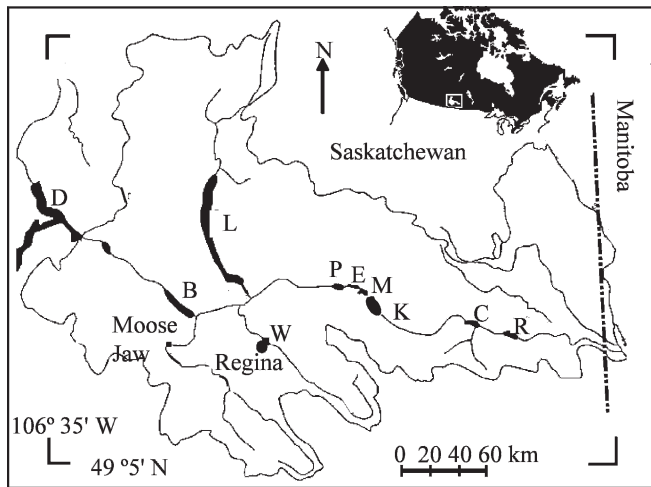


Fig. 2. Map of the study lakes in the Qu'Appelle Valley of southern Saskatchewan. Lakes included in this study, from upstream to downstream, are Diefenbaker (D), Buffalo Pound (B), Last Mountain (L), Wascana (W, situated in the city of Regina), Katopwa (K), and Crooked (C). Other lakes include Pasqua (P), Echo (E), Mission (M), and Round (R).

Pound, Wascana), 6 m (Crooked), or 15 m (other sites). Integrated water was used for analyses of dissolved C species, nutrient content, chlorophyll *a* (Chl *a*) concentrations, and algal production (*see below*). In contrast, pH was measured immediately below the water surface using a calibrated (three standard) handheld pH meter (accuracy  $\pm 0.1$  unit); lake transparency (m) was measured using a 20-cm diameter Secchi disk; and temperature ( $^{\circ}\text{C}$ ), conductivity ( $\mu\text{S cm}^{-1}$ ), and oxygen profiles ( $\text{mg O}_2 \text{ L}^{-1}$ ) were measured using a YSI model 85 meter deployed at 1-m depth intervals. Wind measurements were taken 1 m above the surface of the water at the time of sampling using a Dwyer handheld wind meter. All sampling was conducted between 10:00 h and 15:00 h over the deepest point in the lake as determined using fixed global positioning system (GPS) coordinates.

Depth-integrated water samples were filtered through 0.45- $\mu\text{m}$  pore membrane filters and were used to determine concentrations of dissolved substances in each lake (Leavitt et al. 2006). Soluble reactive phosphorus (SRP,  $\mu\text{g P L}^{-1}$ ), total dissolved nitrogen (TDN),  $\text{NH}_4^+$ , and  $\text{NO}_3^-$  (all  $\mu\text{g N L}^{-1}$ ) were all analyzed at the University of Alberta Water Chemistry Laboratory following procedures of Stainton et al. (1977). Analysis of DIC and DOC concentrations followed standard procedures (Environment Canada 1979) using a Shimadzu model 5000A total carbon analyzer. Detailed analysis of depth profiles of DIC, conductivity, and pH revealed little variation with depth over the sampling interval, consistent with the polymictic status of the lakes. All samples were stored at  $4^{\circ}\text{C}$  in the dark in sterile, gas-tight containers until analysis. Because of high sample pH ( $>8.0$ ) and lack of headspace, we assumed that there was little effect of storage on DIC measurements. Finally, particulate organic matter from prescreened (243- $\mu\text{m}$  mesh), depth-integrated water samples was filtered onto washed GF/C glass-fiber filters and frozen ( $-10^{\circ}\text{C}$ ) until

Table 1. Morphometric, chemical, and biological characteristics of Qu'Appelle Valley lakes. Data are mean values (standard deviations in parentheses) of measurements taken between May and August, 1994–2007. Variables include soluble reactive phosphorus (SRP), total dissolved nitrogen (TDN), dissolved organic and inorganic carbon (DOC, DIC), and chlorophyll *a* (Chl *a*).

Lake	Area (km <sup>2</sup> )	Volume (m <sup>3</sup> 10 <sup>-6</sup> )	Water residence (yr)	Mean depth (m)	SRP ( $\mu\text{g L}^{-1}$ )	TDN ( $\mu\text{g L}^{-1}$ )	DOC (mg L <sup>-1</sup> )	DIC (mg L <sup>-1</sup> )	Conductivity ( $\mu\text{S cm}^{-1}$ )	Secchi (m)	Chl <i>a</i> ( $\mu\text{g L}^{-1}$ )
Diefenbaker	500.0	9400.0	1.3	33.0	16.6 (36.0)	325.2 (135.2)	5.6 (5.0)	33.8 (7.2)	419.9 (341.2)	3.3 (1.3)	4.8 (4.3)
Buffalo Pound	29.1	87.5	0.7	3.0	50.5 (250.3)	493.4 (216.5)	6.5 (3.9)	30.9 (9.7)	528.1 (513.7)	1.2 (1.0)	28.3 (39.7)
Last Mountain	226.6	1807.2	12.6	7.9	30.96 (73.4)	948.27 (195.6)	12.8 (5.8)	60.4 (11.6)	1794.5 (325.0)	2.2 (0.7)	12.3 (10.2)
Wascana	0.5	0.7	0.05	1.5	201.4 (168.7)	1353.8 (766.5)	16.0 (4.3)	40.5 (14.2)	917.7 (414.6)	0.8 (0.5)	35.1 (50.7)
Katopwa	16.2	233.2	1.3	14.3	112.1 (96.8)	943.6 (229.2)	11.3 (2.9)	50.6 (10.2)	1096.5 (234.6)	1.8 (0.9)	22.5 (16.2)
Crooked	15.0	120.9	0.5	8.1	110.6 (143.5)	874.9 (237.3)	11.0 (3.7)	51.5 (10.0)	1185.7 (279.6)	1.4 (0.7)	27.4 (31.7)

analysis for Chl *a* by standard spectrophotometric procedures (Jeffrey and Humphrey 1975).

Water-column estimates of net production by the plankton (NP), gross primary production (GPP), and respiration (R) were determined from a combination of laboratory assays of changes in oxygen content during light and dark incubations (Howarth and Michaels 2000) and biweekly measures of lake transparency and day length. Unlike samples from oligotrophic lakes, changes in dissolved O<sub>2</sub> were substantial in all trials (>2 mg O<sub>2</sub> L<sup>-1</sup>) and are reasonable estimates of algal and bacterial metabolic processes in productive lakes (Howarth and Michaels 2000). Briefly, three 250-mL bottles were filled with 243- $\mu$ m screened, depth-integrated water and were wrapped in aluminum foil to exclude light. An additional three bottles were left exposed to light at 450  $\mu$ mol quanta m<sup>-2</sup> s<sup>-1</sup>, which is comparable to the irradiance measured in situ at the Secchi depth using a Satlantic OCI-200 radiometer on several dates in 2007. Oxygen content of each bottle was measured initially using a YSI model 85 meter and again after 24 h incubation in the laboratory at observed ambient surface-water temperatures and a 12-h photoperiod equivalent to that of an average summer day. NP was estimated from changes in O<sub>2</sub> concentrations in the light bottles and was converted to mg C m<sup>-3</sup> d<sup>-1</sup> assuming a photosynthetic quotient of 1.0 (Wetzel 2001). The decline in O<sub>2</sub> content of dark bottles was used to calculate cellular respiration, while GPP was estimated as NP + R. Because our study lakes are polymictic, algae experience a light regime that is both variable and difficult to estimate. Consequently, we approximated water-column metabolic processes by multiplying lab-based estimates of productivity with the fraction of the day spent in the euphotic zone, defined as the ratio of the euphotic volume (Secchi depth) to total lake volume. Because incubator irradiance was equivalent to that measured at Secchi depth and because Secchi depth varied seasonally from ~10 cm to ~8 m, we assumed that our estimates captured a high proportion of spatial and temporal variation in productivity attributable to changes in light regimes.

*Estimation of CO<sub>2</sub> flux*—CO<sub>2</sub> concentration (mmol m<sup>-3</sup>) was calculated on each sampling date from depth-integrated DIC concentrations and surface-water pH values, with correction for ionic strength and water temperature at 1-m depth (Stumm and Morgan 1996). DIC has only been measured since 1998 and was not estimated during 2002; therefore we used the correlation between DIC and conductivity ( $r = 0.66$ ,  $p < 0.001$ ,  $n = 331$ ) to estimate DIC during periods with missing data. Independent tests revealed that CO<sub>2</sub> concentrations calculated using conductivity as a proxy for DIC compared very well with those estimated directly from measured DIC values ( $r = 0.988$ ,  $p < 0.001$ ,  $n = 317$ ). Partial pressure of CO<sub>2</sub> (Pa) was estimated using Henry's Law constant and accounted for changes in temperature (Kling et al. 1992).

Chemically enhanced CO<sub>2</sub> flux (mmol m<sup>-2</sup> d<sup>-1</sup>) was calculated for each sampling date following the boundary-layer equations presented in Cole and Caraco

(1998):

$$\text{net daily CO}_2 \text{ flux} = \alpha k ([\text{CO}_2]_{\text{lake}} - [\text{CO}_2]_{\text{sat}}) \quad (1)$$

where [CO<sub>2</sub>]<sub>lake</sub> is the concentration of CO<sub>2</sub> in the surface water ( $\mu$ mol L<sup>-1</sup>); [CO<sub>2</sub>]<sub>sat</sub> is the concentration of CO<sub>2</sub> at equilibrium with the atmosphere ( $\mu$ mol L<sup>-1</sup>);  $\alpha$  is the chemical enhancement of CO<sub>2</sub> flux at high pH (Hoover and Berkshire 1969) and was calculated using the equations in Wanninkhof and Knox (1996); and  $k$  is piston velocity (cm h<sup>-1</sup>) determined from eq. 5 in Cole and Caraco (1998) relating  $k$  to wind speed, and accounting for temperature (Wanninkhof 1992). Atmospheric *p*CO<sub>2</sub> was assumed to be 37 Pa, the average value recorded at the Mauna Loa Observatory during 1994–2007 (<http://www.esrl.noaa.gov>). Wind speeds (m s<sup>-1</sup>) were averaged over all sampling dates for each lake because there were no significant differences in wind speed by month or year at a given site. In contrast, mean ( $\pm$ SD) wind speed differed among Diefenbaker (3.4  $\pm$  2.8), Buffalo Pound (4.1  $\pm$  2.6), Last Mountain (4.3  $\pm$  2.7), Wascana (2.8  $\pm$  2.0), Katepwa (3.3  $\pm$  2.7), and Crooked Lakes (4.2  $\pm$  3.2), likely because of differences in the density of urban trees (Wascana) or lake orientation (Katepwa, Diefenbaker) relative to the direction of prevailing winds. Mean daily CO<sub>2</sub> flux for each lake and year was estimated for the May–August sampling period by averaging biweekly measurements. Although biweekly sampling will miss some variability associated with severe weather (e.g., storms), this sampling regime is comparable to that used in most other determinations of CO<sub>2</sub> flux (Hanson et al. 2006).

*Survey of saline lakes*—Estimates of *p*CO<sub>2</sub> and net daily CO<sub>2</sub> flux from the Qu'Appelle Valley lakes were compared with those determined for a series of 20 saline lakes spanning an additional area of 100,000 km<sup>2</sup> in southern Saskatchewan to determine whether the characteristics of productive freshwater lakes could be extrapolated to regional endorheic systems. As detailed in Pham et al. (2008), these survey lakes lacked visible surface-water inflow and exhibited elevated pH (8.4–9.3) and carbon content (DOC = 10–159 mg C L<sup>-1</sup>; DIC = 18–500 mg C L<sup>-1</sup>) but differed greatly in size (area = 0.5–60.0 km<sup>2</sup>;  $Z_{\text{max}}$  = 1.3–30 m), mean nutrient concentrations (total Kjeldahl N = 0.7–8.0 mg N L<sup>-1</sup>; SRP = 9–610  $\mu$ g P L<sup>-1</sup>), and salinity (0.4–50.7 g total dissolved solids L<sup>-1</sup>). All sites were sampled using standard protocols (*see* above) three times (May, July, September) during 2003–2005, and twice during 2002 and 2007 (June, August). CO<sub>2</sub> concentration was calculated accounting for changes in temperature and ionic strength using equations for both freshwater (Stumm and Morgan 1996) and saline ecosystems (Millero 2007), and CO<sub>2</sub> flux was calculated as described above for the Qu'Appelle Valley lakes. In general, intra-annual variation in chemical parameters in these lakes is substantially less than that observed among years (Pham et al. 2008); therefore we hypothesized that both Qu'Appelle and saline lakes should exhibit synchronous changes in chemical parameters related to CO<sub>2</sub> flux.

*Numerical analyses*—Temporal variation in net daily CO<sub>2</sub> flux was estimated by calculating both annual

variation around mean estimates (coefficient of variation, CV) and by estimating the temporal synchrony ( $S$ ) of net CO<sub>2</sub> flux among lakes. In the latter case,  $S$  was estimated from annually resolved time series of mean CO<sub>2</sub> flux as the average Pearson correlation coefficient for all possible lake pairs ( $n = 14$ ) following Patoine and Leavitt (2006). Mean lake-pair synchrony takes a value of 1.0 when gas flux covaries perfectly among sites,  $-1.0$  when fluxes are perfectly inversely correlated, and 0.0 where fluxes lack temporal coherence among lakes. The sensitivity of  $S$  to the effects of individual lakes or years was estimated by removing each lake or year, recalculating  $S$ , and comparing the whole and censored data sets (Rusak et al. 1999). Analysis of temporal coherence was also conducted for annual time series of mean  $p\text{CO}_2$ ,  $\alpha$ , and pH to evaluate the relative modes of temporal variability of the key factors influencing the calculation of net CO<sub>2</sub> flux. Finally, unreplicated linear regression was used to compare mean annual  $p\text{CO}_2$  and mean CO<sub>2</sub> flux of lakes in the Qu'Appelle catchment with saline survey lakes. In all cases, summary analyses are presented in this paper, while complete statistical analyses for each year and site are available on request from the authors.

Time series of environmental variables thought to influence Qu'Appelle lake chemistry, production, or CO<sub>2</sub> flux were compared to those of net CO<sub>2</sub> flux and  $p\text{CO}_2$  to identify potential mechanisms regulating the differences in carbon dynamics among lakes and years. First, biweekly determinations of  $p\text{CO}_2$  and net CO<sub>2</sub> flux ( $n = 672$ ) were correlated with concomitant estimates of lake-water conditions (pH, DIC, temperature), nutrient status (SRP, TDN, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, DOC), and productivity (NP, GPP, R, Chl  $a$ , O<sub>2</sub>) to quantify catchment-scale patterns in C dynamics. Second, annual averages of  $p\text{CO}_2$  and net C flux ( $n = 84$ ) were regressed against the annual averages of the aforementioned predictors, as well as with estimates of local climatic conditions (air and water temperature, precipitation, ice out date, evaporation, river discharge) to identify the best correlates of temporal variability in CO<sub>2</sub> flux. In addition, ANOVA was used to determine whether there were significant differences among years, while stepwise multiple regression was used to identify possible interactions among predictor variables, such as seen elsewhere (Prairie 2008). Finally, mean  $p\text{CO}_2$  and CO<sub>2</sub> fluxes during 1994–2007 were calculated for each lake ( $n = 6$ ) and correlated to equivalent means of the environmental predictors above to identify possible mechanisms underlying spatial variation in CO<sub>2</sub> flux among lakes. ANOVA was used to quantify whether among-site differences were significant. In all cases, there was no significant temporal autocorrelation in time series, although most chemical variables required log<sub>10</sub>-transformation to normalize variance before analysis. Similarly, the critical alpha for correlation analyses was adjusted for the number of comparisons using a Bonferroni correction (Zar 1999). All statistical analyses were performed using SYSTAT version 10.

The modified Monte Carlo model error analysis of Cuddington and Leavitt (1999) was used to determine whether correlations between  $p\text{CO}_2$  and environmental

conditions (pH, DIC, temperature, wind speed) arose solely because predictors are components of the calculations used to determine  $p\text{CO}_2$  and CO<sub>2</sub> flux (see above). In this procedure, we obtained 500 random values each of pH, DIC, temperature, and wind speed from distributions of each predictor in which the mean was obtained from field observations (biweekly observations for 14 yr) but variability was set at a uniform 50% of each mean. These random data sets were then used to calculate  $p\text{CO}_2$  and to determine the strength of correlation between predictors and  $p\text{CO}_2$  expected if correlations arose by chance. In instances where observed correlations were substantially greater than modeled correlations, we inferred the presence of an underlying causal mechanism.

Predictor time series were obtained from relevant local, regional, and national sources. Seasonal precipitation and air temperature data for each lake were obtained from the Environment Canada database (<http://www.climate.weatheroffice.ec.gc.ca/>). Evaporation rates at each site and river discharge rates for several sites along the Qu'Appelle River (Fig. 1) were obtained from the Saskatchewan Watershed Authority (B. Oegema and T. Chamulak pers. comm.). Calendar day of year (DOY) of ice cover melt was obtained from direct observation of all lakes except Crooked Lake. Missing ice-melt dates for each lake and approximate dates for Crooked Lake were obtained using a multiple regression model ( $R_{\text{adj}}^2 = 0.754$ ,  $n = 58$ ,  $p < 0.001$ , SE 3.8 d) based on log-transformed lake mean depth (standard coefficient +0.576), average March air temperature ( $-0.510$ ), March precipitation ( $-0.419$ ), and log-transformed upstream winter flow (+0.215) (I. Dröscher and P. R. Leavitt unpubl. data). Indices of atmospheric-ocean systems known to influence regional climate included the Pacific Decadal Oscillation (<http://jisao.washington.edu/pdo/PDO.latest>), winter North Atlantic Oscillation (<http://www.cgd.ucar.edu/cas/jhurrell/indices.html>), and Southern Oscillation Index (SOI) (<http://www.cpc.noaa.gov/data/indices/soi>).

## Results

*Magnitude of C flux*—Mean net CO<sub>2</sub> flux varied significantly among years (Fig. 3), with most sites exhibiting a high degree of synchrony. For example,  $p\text{CO}_2$  lake exceeded 37 Pa during 1995–1997 and 1999–2000, leading to substantial net losses of CO<sub>2</sub> from all lakes during many of those years. In contrast, all sites exhibited a net influx of CO<sub>2</sub> during 1998 and 2006 (Fig. 3), while the magnitude of C efflux from lakes generally declined through time ( $r_{\text{Cflux-year}} = -0.05$  to  $-0.735$ ). As a result of these trends, annual means of CO<sub>2</sub> flux were synchronous among lakes during the 14-yr study period ( $S = 0.61$ ,  $p < 0.05$ ). Removal of both 2002 (residual  $S = 0.72$ ,  $p < 0.01$ ) and 2006 (residual  $S = 0.51$ ,  $p > 0.05$ ) indicated that these years had pronounced effects on temporal coherence. When variation associated with all observations was partitioned into time and lake effects, ANOVA revealed that 56.7% ( $p < 0.001$ ) of variation could be attributed to differences among years. Mean C flux also differed significantly among lakes ( $r_{\text{ANOVA}}^2 = 0.147$ ,  $p = 0.03$ ), although the explained

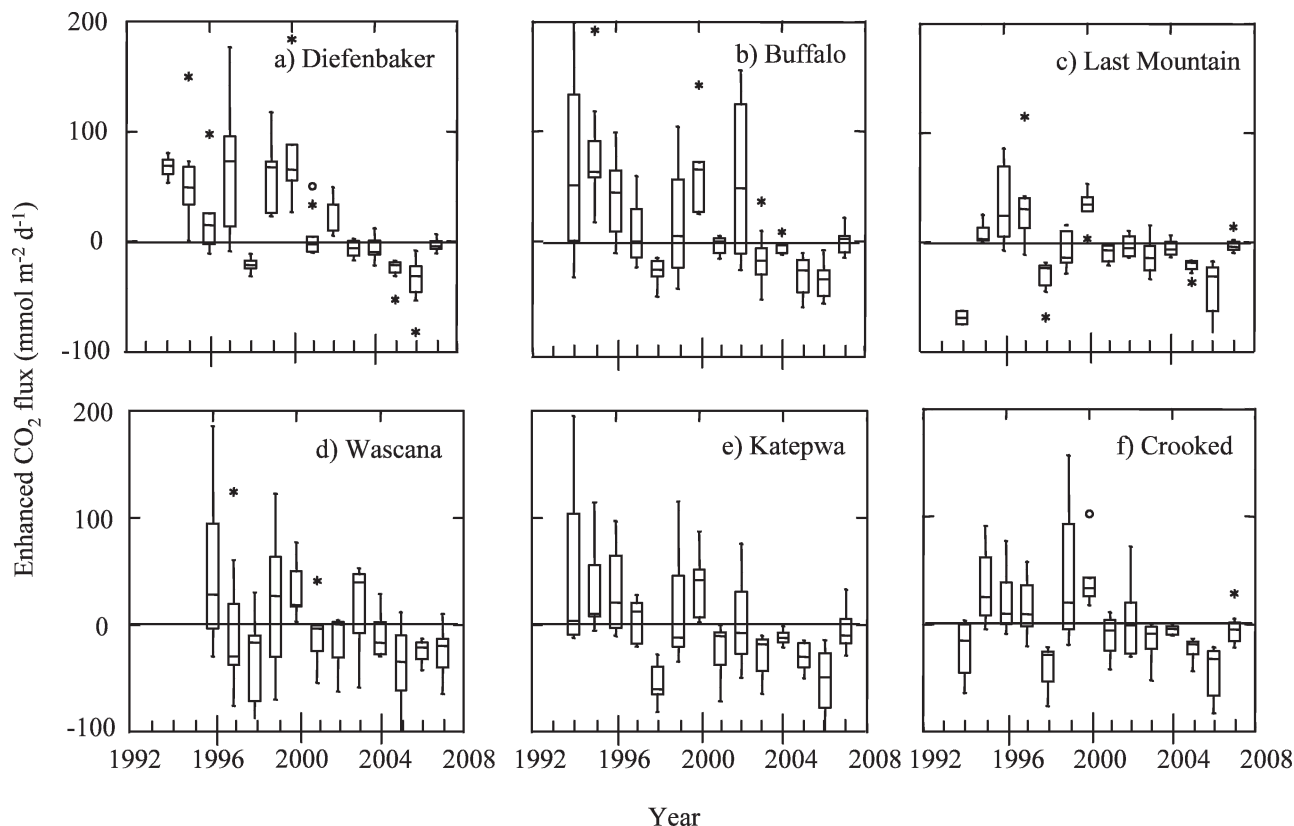


Fig. 3. Chemically enhanced  $\text{CO}_2$  flux at the air–water interface for the six study lakes in southern Saskatchewan from 1994 to 2007. Boxes represent values measured biweekly from May to August for a given year. The horizontal line indicates atmospheric equilibrium. Positive values represent net  $\text{CO}_2$  efflux to the atmosphere, while negative values represent influx of  $\text{CO}_2$  from the atmosphere into the lake.

variation was much lower than that attributable to differences among years. Specifically, headwater lakes (Diefenbaker, Buffalo Pound) tended to release  $\text{CO}_2$  more often than did downstream lakes, while large deep lakes (Diefenbaker, Last Mountain) usually exhibited lower intra-annual variability in  $p\text{CO}_2$  (not shown) and net  $\text{CO}_2$  flux than did smaller lakes (Fig. 3). Not surprisingly, synchrony in net C flux increased from  $S = 0.61$  to  $S = 0.67$  when either shallow lake (Buffalo Pound, Wascana) was removed from calculations.

Variability in  $p\text{CO}_2$  and net  $\text{CO}_2$  flux was correlated mainly with variation in lake-water pH rather than other chemical, physical, or biological parameters when all lakes, years, and dates were considered. For example,  $p\text{CO}_2$  was correlated strongly and inversely with pH ( $r = -0.995$ ,  $p < 0.001$ ,  $n = 609$ ), but only weakly with variations in DOC ( $r = -0.233$ ,  $p < 0.001$ ), TDN ( $r = -0.217$ ,  $p < 0.001$ ),  $\text{NO}_3^-$  ( $r = 0.186$ ,  $p = 0.001$ ), water temperature ( $r = -0.162$ ,  $p < 0.001$ ), DIC ( $r = 0.129$ ,  $p = 0.03$ ), or SRP ( $r = -0.125$ ,  $p = 0.01$ ). Monte Carlo error analysis revealed that the observed correlation of  $p\text{CO}_2$  and pH was much stronger than that expected to arise solely as a result of the calculations used ( $r = -0.703$ ), whereas that of  $p\text{CO}_2$  and DIC was much weaker than expected by chance ( $r = 0.647$ ). Observed changes in  $p\text{CO}_2$  were uncorrelated with variations in water-column metabolism as recorded by algal biomass, productivity, or respiration ( $r = -0.01$  to

$-0.092$ ,  $p > 0.05$ ). Similar strong correlations between pH and  $p\text{CO}_2$  were obtained when analyses were conducted on individual lakes using all years and dates ( $n = 50\text{--}80$ ). However, although there were occasionally significant correlations with other factors for individual lakes (e.g., in Wascana Lake,  $r_{p\text{CO}_2\text{DIC}} = 0.433$ ,  $p = 0.002$ ), there was no consistency among lakes in which factor was correlated with  $p\text{CO}_2$ . Similarly, pH was by far the strongest correlate of net  $\text{CO}_2$  flux in analyses that included all lakes, years, and dates, or in those focusing on individual basins. Overall, correlations between pH and net  $\text{CO}_2$  flux explained  $\sim 13\%$  (range 7–28%) less variation than did those with  $p\text{CO}_2$ .

*Correlates of temporal variability*—Interannual variation in mean annual  $p\text{CO}_2$  and  $\text{CO}_2$  flux were correlated strongly with changes in mean annual pH ( $r = -0.977$  and  $-0.944$ ,  $p < 0.001$ , respectively) and SOI ( $r = 0.521$  and  $r = 0.321$ ,  $p < 0.001$ ) but not with annual averages of predictors related to water-column production and respiration, nutrient content, river discharge, or regional climate (all  $p > 0.05$ ). Although variation in  $p\text{CO}_2$  was correlated with changes in mean respiration ( $r = -0.290$ ), TDN ( $r = -0.390$ ), and DOC ( $r = -0.375$ ), none of these relationships were statistically significant when  $p$  was adjusted using the Bonferroni correction. Similarly, mean annual  $p\text{CO}_2$  was uncorrelated with any variable except pH in

analysis of individual lake basins. Overall, such strong correlations of pH,  $p\text{CO}_2$ , and net CO<sub>2</sub> flux may reflect the wide range of mean annual pH observed in these lakes (8.1–9.7).

Strong temporal coherence of annual lake means was observed for all parameters that influence calculation of net CO<sub>2</sub> flux in alkaline lakes (Fig. 4), since pH ( $S = 0.88$ ,  $p < 0.01$ ), chemical enhancement of C flux ( $S = 0.73$ ,  $p < 0.01$ ), and  $p\text{CO}_2$  ( $S = 0.78$ ,  $p < 0.01$ ) all exhibited strong synchrony among lakes. Overall, chemical enhancement was greatest in Wascana and Buffalo Pound Lakes (Fig. 4b), two shallow sites with particularly high pH and intra-annual variability in net C flux (Fig. 3).

*Correlates of spatial variability*—Among-lake differences in  $p\text{CO}_2$  and net CO<sub>2</sub> flux were correlated strongly with spatial variability in lake parameters related to algal metabolism when averaged over 14 yr (Fig. 5). Specifically, differences in  $p\text{CO}_2$  among lakes were correlated with average concentrations of total dissolved phosphorus ( $r = -0.854$ ,  $p = 0.031$ ), TDN ( $r = -0.957$ ,  $p = 0.003$ ),  $\text{NH}_4^+$  ( $r = -0.842$ ,  $p = 0.03$ ), and DOC ( $r = -0.981$ ,  $p = 0.001$ ), while weaker correlations were recorded for GPP ( $r = -0.679$ ,  $p = 0.06$ ), respiration ( $r = 0.857$ ,  $p = 0.029$ ), and annual precipitation ( $r = 0.753$ ,  $p = 0.058$ ). Because pH is also correlated to SRP ( $r = 0.888$ ,  $p = 0.018$ ), TDN ( $r = 0.921$ ,  $p = 0.009$ ), and GPP ( $r = 0.780$ ,  $p = 0.067$ ), it is difficult to isolate the unique effects of metabolic process; however, in general, pH increased as a function of algal biomass and production in seasonally resolved time series of most lakes and years (analysis not shown). As in other lakes (Prairie 2008), multiple regression analysis demonstrated a highly significant relationship ( $r = 0.970$ ,  $p = 0.015$ ) between  $p\text{CO}_2$ , DOC, and Chl *a* when based on 14-yr means:

$$\log p\text{CO}_2 = -0.041 \times \text{DOC} - 0.106 \times \log \text{Chl } a + 1.594 \quad (2)$$

However, the relationship between  $p\text{CO}_2$  and DOC is negative, contrary to previous studies (Prairie et al. 2002; Hanson et al. 2003; Sobek et al. 2005).

*Saline lake survey*—Mean annual pH and  $p\text{CO}_2$  were highly correlated among saline and freshwater lakes during 2002–2007 (Fig. 6), despite the large area surveyed (>100,000 km<sup>2</sup>). The correlations among lake districts were significant for pH ( $r = 0.951$ ,  $p = 0.013$ ),  $p\text{CO}_2$  ( $r = 0.939$ ,  $p = 0.018$ ), and CO<sub>2</sub> flux ( $r = 0.948$ ,  $p = 0.014$ ) with values falling on the 1 : 1 line when the  $p\text{CO}_2$  of saline lakes was estimated using corrections for ionic strength (Millero 2007). Taken together, these results suggest that similar mechanisms regulate variability in pH,  $p\text{CO}_2$ , and net CO<sub>2</sub> flux over a large geographic area, irrespective of the hydrology and ionic composition of lake basins.

## Discussion

Analysis of chemical and physical properties of six hard-water lakes for 14 yr and 20 saline lakes for 5 yr revealed that  $p\text{CO}_2$  and, to a lesser extent, net atmospheric exchange

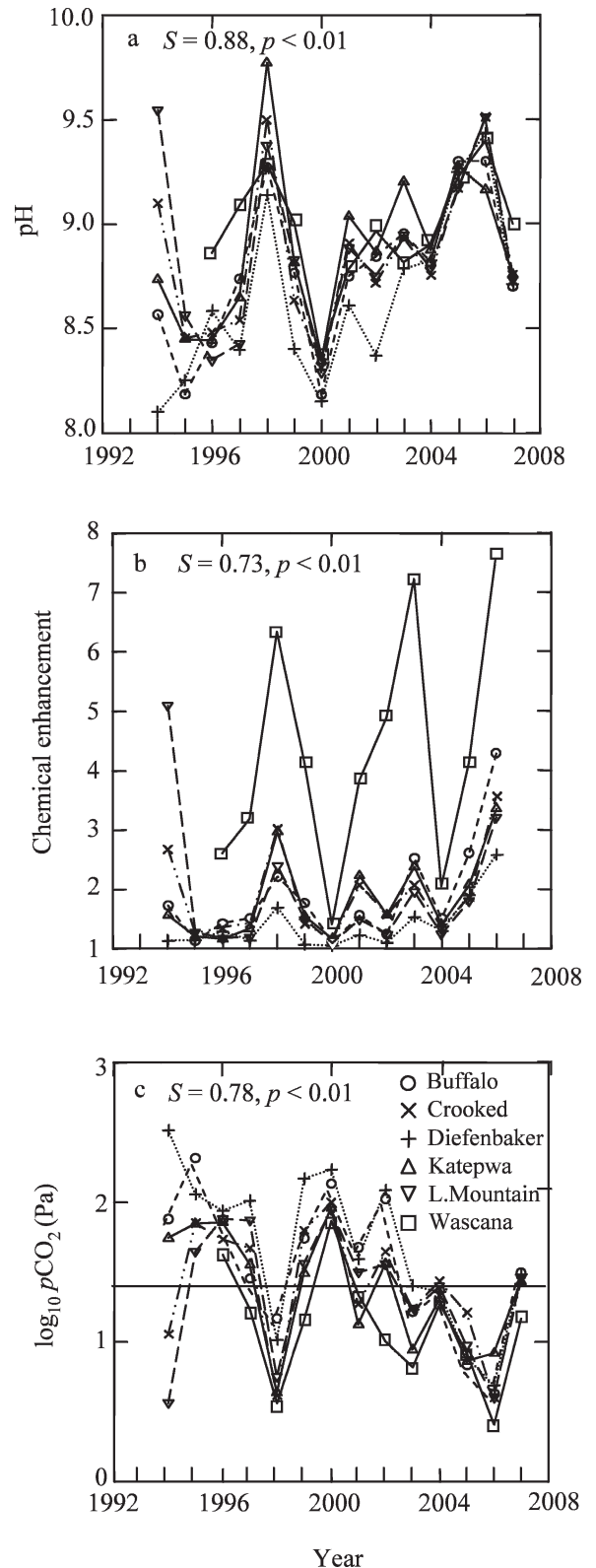


Fig. 4. Annual average (a) pH, (b)  $p\text{CO}_2$ , and (c) chemical enhancement factor ( $\alpha$ ) of the six study lakes from 1994 to 2007. The horizontal line in panel (c) represents atmospheric  $p\text{CO}_2$ .

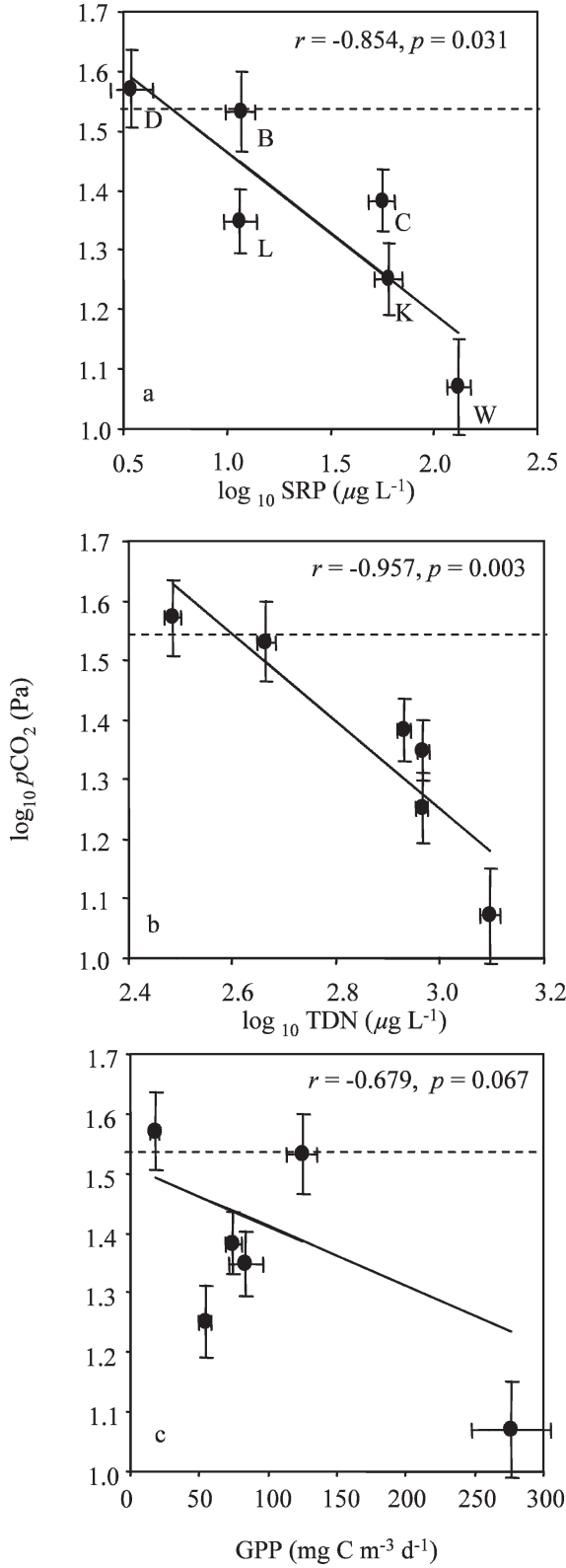


Fig. 5. Relationships between mean  $p\text{CO}_2$  within all Qu'Appelle lakes and (a) soluble reactive phosphorus (SRP), (b) total dissolved nitrogen (TDN), and (c) gross primary production (GPP). Circles are labeled by the first letter of the lake they represent. Error bars represent the standard error of the mean. Solid lines represent results of regression analyses, and dashed lines represent atmospheric  $p\text{CO}_2$ .

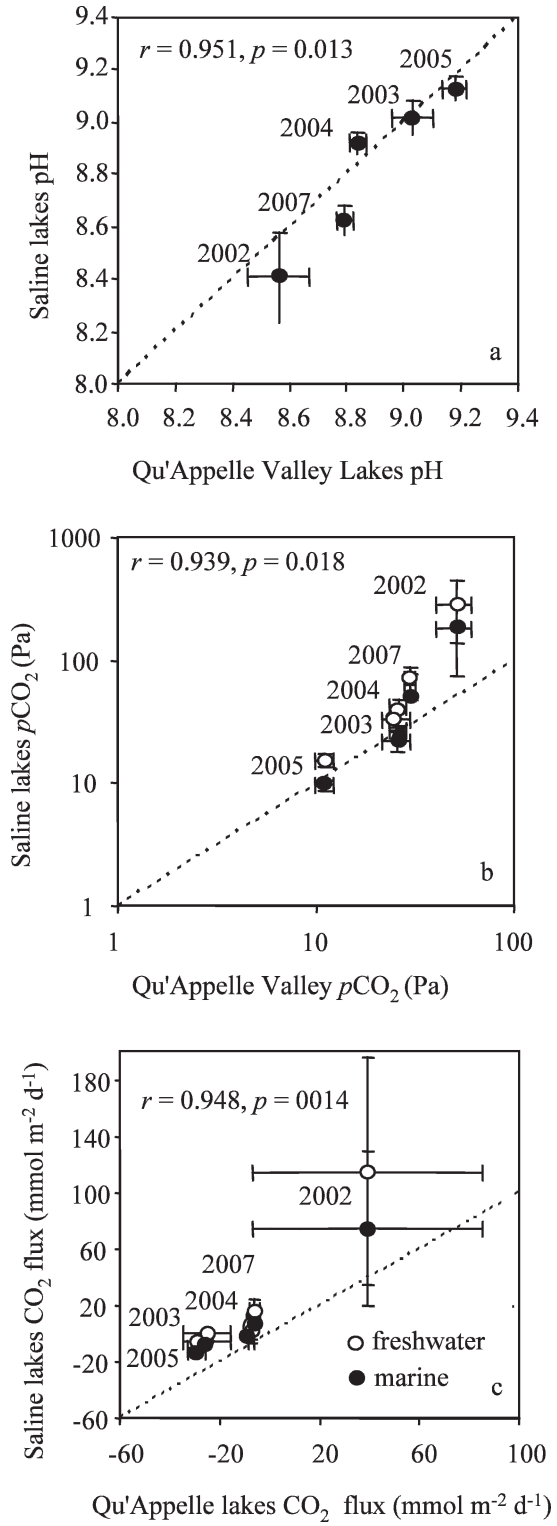


Fig. 6. Comparison of annual average (a) pH, (b)  $p\text{CO}_2$  (Pa), and (c)  $\text{CO}_2$  flux ( $\text{mmol m}^{-2} \text{d}^{-1}$ ) for 20 saline lakes in southern Saskatchewan and the six study lakes of the Qu'Appelle Valley.  $p\text{CO}_2$  and  $\text{CO}_2$  flux rates were calculated for the saline lakes both using the freshwater equations (open symbols) in Stumm and Morgan (1996) and marine estimates (filled symbols) in Millero (2007). The dashed line represents the 1 : 1 line.

of CO<sub>2</sub> varied coherently among diverse lakes over an area >100,000 km<sup>2</sup> (Figs. 3, 6). Rates of CO<sub>2</sub> flux (−100 to +200 mmol C m<sup>−2</sup> d<sup>−1</sup>) and *p*CO<sub>2</sub> levels (up to 5500 Pa) observed for Qu'Appelle lakes were greater than those recorded for most boreal lakes (−15 to 60 mmol C m<sup>−2</sup> d<sup>−1</sup>; up to 2000 Pa) (Cole et al. 1994; Cole and Caraco 1998; del Giorgio et al. 1999), consistent with the view that hard-water lakes are hot spots for C exchange (Duarte et al. 2008). Unexpectedly, productive Qu'Appelle lakes exhibited both years of substantial CO<sub>2</sub> uptake (1995, 2000) and release (1998, 2006), patterns that were strongly correlated with the high interannual variation in pH ( $r_{p\text{CO}_2 - \text{pH}} = 0.995$ ,  $p < 0.0001$ ) and its effects on chemical enhancement of CO<sub>2</sub> uptake (Fig. 4). In contrast, temporal variation of both *p*CO<sub>2</sub> and net daily CO<sub>2</sub> flux was uncorrelated with algal biomass, productivity, or ecosystem respiration ( $r = -0.092$  to  $-0.01$ ,  $p > 0.05$ ), although differences in mean annual *p*CO<sub>2</sub> among lakes were inversely correlated with nutrient status and algal production (Fig. 5), such as seen elsewhere (Prairie et al. 2002). Similar synchronous patterns in saline and freshwater lakes (Fig. 6) suggest a common climatic mechanism that regulates pH and *p*CO<sub>2</sub> independent of runoff features (e.g., discharge, solute content, suspended particle load), residence time (Table 1), ionic composition (Pham et al. 2008), or drainage characteristics (exorheic, endorheic) (Magnuson et al. 1990; Baines et al. 2000).

*Temporal variability of CO<sub>2</sub> flux*—Temporal variability of *p*CO<sub>2</sub> and net CO<sub>2</sub> flux was more highly correlated with changes in pH than expected solely on the basis of their mathematical relationship, in part because of the high interannual variation in mean annual pH (range 8.1 to 9.7). For example, variation in pH resulted in nearly 10-fold more variation in *p*CO<sub>2</sub> ( $r = -0.995$ ) than did any other dissolved compound (DOC, TDN, NO<sub>3</sub>, DIC; all  $r < 0.233$ ) or temperature ( $r = -0.162$ ) when all dates are included ( $n > 600$ ), and 3.5-fold more than all other variables when considering annual mean values ( $n > 50$ ). The disproportionate effect of pH on *p*CO<sub>2</sub> and net CO<sub>2</sub> flux arises in part because of substantial chemical enhancement of CO<sub>2</sub> uptake ( $\alpha$ ) (Fig. 4b), which is negligible below pH 8.0 but increases exponentially under more alkaline conditions (Duarte et al. 2008) and reached over 20-fold in shallow Wascana Lake during 2003 (data not shown). Since similar levels of interannual variation of pH were also recorded for our saline survey lakes (Fig. 6) (Pham et al. 2008), and other hard-water systems in the northern United States (Myrbo and Shapley 2006), we infer that pH may be an easily measured indicator of CO<sub>2</sub> flux in productive alkaline lakes, irrespective of other ionic and hydrologic characteristics.

Strong predictive relationships between pH and *p*CO<sub>2</sub> allow us to identify critical thresholds around which alkaline lakes switch from CO<sub>2</sub> uptake to gas release. According to the regression,

$$\log p\text{CO}_2 - \text{lake} = -1.091 \times \text{pH} + 10.993 \quad (r^2 = 0.977) \quad (3)$$

*p*CO<sub>2</sub> lake exceeded 37 Pa and CO<sub>2</sub> was released when the pH of Qu'Appelle lakes was less than 8.6. This threshold differs slightly with that inferred from a survey of diverse saline lakes (pH 9.0) (Duarte et al. 2008), possibly because mean concentrations of DIC are often substantially greater in saline lakes (global mean ~700 mg C L<sup>−1</sup>) than in those of the Qu'Appelle catchment (45 mg C L<sup>−1</sup>). Interestingly, *p*CO<sub>2</sub> values in our saline lakes were similar to those of the Qu'Appelle Valley, despite DIC concentrations typical of other saline ecosystems (Pham et al. 2008, 2009), suggesting that other, as yet unmeasured, processes may influence water-column concentrations of CO<sub>2</sub> (e.g., benthic production and respiration in shallow lakes) (Vadeboncoeur et al. 2001).

Several lines of evidence suggest that interannual variation in *p*CO<sub>2</sub> and pH was derived from climatic variability associated with winter temperature rather than metabolic controls of the solute and gas contents of prairie lakes. For example, variation in the SOI climate system was strongly and positively correlated ( $r = 0.321$  to  $0.521$ ,  $p < 0.05$ ) with both *p*CO<sub>2</sub> and annual mean CO<sub>2</sub> flux, while neither variable was correlated ( $p > 0.10$ ) to water-column Chl *a* concentrations ( $r = -0.056$  to  $0.104$ ), GPP ( $r = -0.018$  to  $0.098$ ), NP ( $r = -0.215$  to  $-0.092$ ), or respiration ( $r = -0.290$  to  $-0.068$ ). In the Canadian Prairies, the positive phase of the SOI system (La Niña) is associated with cold snowy winters, during which a southern displacement of the winter jet stream leads to longer ice cover (Bonsal et al. 2006) and, as shown elsewhere, an increased accumulation of CO<sub>2</sub> and a decline of pH under ice (Striegl and Michmerhuizen 1998; Striegl et al. 2001; Baehr and DeGrandpre 2002). Although we did not find a correlation between ice cover duration and spring *p*CO<sub>2</sub> (data not shown), additional factors, such as productivity during the previous season (Anderson et al. 1999) and overwinter benthic temperature (which would affect bacterial respiration rates) may interact to affect spring *p*CO<sub>2</sub> and pH. We infer that climatic variability did not regulate *p*CO<sub>2</sub> levels by altering the alkalinity or DIC content of these lakes, since the DIC content of study lakes varied relatively little among years (Table 1) and observed correlations between variables ( $r_{\text{CO}_2 - \text{DIC}} = 0.129$ ) were much weaker than expected by chance ( $r = 0.646$ ). Instead pronounced effects of climate on interannual variation in *p*CO<sub>2</sub> are consistent with previous observations that short-term (diel to seasonal) variation in CO<sub>2</sub> flux in soft-water lakes is due to ecosystem respiration (Dillon and Molot 1997; del Giorgio et al. 1999; Prairie 2008), whereas climate regulates differences among years (Kelly et al. 2001; Rantakari and Kortelainen 2005; Hanson et al. 2006). In our case, we infer that variation in CO<sub>2</sub> does not arise from reactions involving borate (~180 μg B L<sup>−1</sup>) or alkalinity generation (pH should rise in winter when NO<sub>3</sub>, SO<sub>4</sub> are reduced) but recognize that further research is required to quantify the potential roles of groundwater influx (Striegl and Michmerhuizen 1998), benthic respiration (Andersson and Kumblad 2006), and other unmeasured regulatory mechanisms.

*Spatial variability of CO<sub>2</sub> flux*—When averaged over 14 yr, differences in mean *p*CO<sub>2</sub> among lakes were

correlated negatively to lake trophic status and productivity (Fig. 5). In general, lower mean  $p\text{CO}_2$  in productive lakes is consistent with other spatial analyses of  $p\text{CO}_2$  and  $\text{CO}_2$  flux, including Dillon and Molot (1997), Duarte and Agusti (1998), and Duarte and Prairie (2005). However, unlike those surveys, the large differences in productivity among our study lakes ( $\sim 200 \mu\text{g SRP L}^{-1}$ ,  $\sim 30 \mu\text{g Chl } a \text{ L}^{-1}$ ) (Table 1) did not translate into substantial differences in  $p\text{CO}_2$  among sites. This relatively muted response to water-column metabolism is consistent with ANOVA of annual mean values, which demonstrated that differences in lake productivity accounted for <3% of variation among basins.

Weak effects of microbial metabolism on  $\text{CO}_2$  fluxes were also revealed by analysis of the relationship between mean annual DOC content and  $p\text{CO}_2$  (see Eq. 2 above). Several previous studies have demonstrated that bacterial respiration and  $p\text{CO}_2$  increase as a function of DOC concentrations, with net heterotrophy and  $\text{CO}_2$  evasion common in lakes with more than 5–6 mg DOC  $\text{L}^{-1}$  (Prairie et al. 2002; Hanson et al. 2003; Sobek et al. 2007). Instead, we found a significant negative relationship between DOC and  $p\text{CO}_2$  and prolonged episodes of  $\text{CO}_2$  undersaturation despite DOC concentrations  $>5 \text{ mg L}^{-1}$  at all sites (Table 1). Several factors may interact to alter the relationship between DOC and  $p\text{CO}_2$  in Qu'Appelle Valley lakes, including the observations that midsummer DOC is  $\sim 600$  yr old and refractory (P. R. Leavitt unpubl. data), that this weakly colored DOC allows damaging ultraviolet radiation to penetrate several meters into the lake (Curtis and Adams 1995), and that DIC concentrations are 400% greater than those of DOC (Table 1) and may overwhelm the effects of DOC. Therefore, although microbial activity is unquestionably intense in these lakes, it appears that there is insufficient variation through time and space to regulate net  $\text{CO}_2$  fluxes in the same manner as in boreal freshwater systems.

*Caveats to C flux estimates*—A variety of methods are available to estimate  $\text{CO}_2$  flux from lakes, each with its relative merits (Anderson et al. 1999; Matthews et al. 2003; Soumis et al. 2008). In this study, gas flux estimates were derived from well-established boundary-layer equations (Cole and Caraco 1998) and observed wind speed but did not account for the effects of precipitation or convective mixing (Anderson et al. 1999; Eugster et al. 2003). Within the Qu'Appelle Valley, lakes are generally polymictic because of the low topographic relief, frequent summer storms, and high mean wind speeds on the subhumid northern Great Plains (precipitation – evaporation =  $-40$  to  $-60 \text{ cm yr}^{-1}$ ). In such systems,  $\text{CO}_2$  flux is regulated mainly by wind and physical mixing rather than precipitation or convective forces; therefore the use of floating chambers (Duchemin et al. 1995; Galy-Lacaux et al. 1999), which remove wind effects (Matthews et al. 2003), is at least in principle inappropriate. Similarly, although we recognize that estimates of  $k_{600}$  based on wind speed can be unreliable for sheltered water bodies (Matthews et al. 2003; Soumis et al. 2008), our wind speeds are sufficiently great (2.8–4.3  $\text{m s}^{-1}$ ) to avoid commonly identified problems (low

sensitivity, spatial patchiness). Finally, this study could have been improved by the use of eddy covariance techniques to better estimate  $\text{CO}_2$  flux (Anderson et al. 1999); however, this technique would be impractical for our comparison of 26 ecosystems. Instead, by using common boundary-layer equations to estimate  $\text{CO}_2$  fluxes, our findings can be compared directly with most published research, while providing novel insights on the patterns and causes of spatial and temporal variation in  $\text{CO}_2$  exchange.

Given the strong correlations between  $p\text{CO}_2$  and pH among lakes, it is reasonable to evaluate whether this result is influenced by the methodologies used to estimate the contrasting regulatory mechanisms. Several lines of evidence demonstrate that spatial synchrony did not arise from common systematic drift in field determinations of pH, including the fact that pH was determined using multiple sets of gear in any given summer, saline lakes were sampled independently (Pham et al. 2008, 2009) yet remained coherent, seasonal pH change was poorly correlated among lakes (K. Finlay unpubl. data), and the fact that meters were calibrated regularly with three laboratory standards. Similarly, while we recognize that the application of laboratory measurements of productivity to the field is less suitable than in situ determinations over a range of depths and irradiances, we point out that no method is universally suited to polymictic lakes in which algae rapidly experience widely divergent environments. Furthermore, we note that robust estimates of both algal abundance (Chl *a*) and respiration ( $\text{O}_2$  consumption) were also poor predictors of  $p\text{CO}_2$ . Similarly, while the combined use of surface-water pH and integrated water-column DIC could introduce errors in well-stratified lakes, none of the Qu'Appelle lakes demonstrate substantial vertical variability over the depth of integration (Dröscher et al. 2009). Instead, these observations suggest the widespread patterns of lake synchrony of  $p\text{CO}_2$  and pH are robust to the methodologies employed in this study, while the unusually high correlation of  $p\text{CO}_2$  and pH ( $r = -0.995$ ,  $p < 0.0001$ ) but not other variables used in the calculation of  $p\text{CO}_2$  (DIC, wind, temperature) suggest an underlying mechanism that requires further study.

*Hard-water lakes and global carbon cycling*—Rates of  $\text{CO}_2$  flux recorded in our study were among the highest observed for freshwater lakes. Previously comprehensive global estimates suggest that  $\text{CO}_2$  flux ranges from  $-15$  to  $60 \text{ mmol C m}^{-2} \text{ d}^{-1}$  (Schindler et al. 1997; Cole and Caraco 1998; del Giorgio et al. 1999), while  $p\text{CO}_2$  ranges from 1 to 2000 Pa (Cole et al. 1994; Sobek et al. 2005). In contrast, Qu'Appelle lakes varied from  $-100$  to  $200 \text{ mmol C m}^{-2} \text{ d}^{-1}$ , with  $p\text{CO}_2$  values up to 5500 Pa. Recently, Duarte et al. (2008) noted that saline lakes exhibit even greater rates of C processing, with  $\text{CO}_2$  fluxes ranging from  $-275$  to  $3123 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $p\text{CO}_2$  values of greater than 8000 Pa. Taken together, these patterns suggest that it is the uniformly great DIC concentrations that cause these lakes to contribute disproportionately to the global carbon budget; however, the high synchrony among lakes also cautions investigators against extrapolation from short-term studies to global patterns. Instead, future studies should

incorporate better estimates of spatial and temporal variability of  $p\text{CO}_2$  and its potential regulatory variables to more fully evaluate the role of lakes in the global carbon budget.

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