

Magnitudes and controls of organic and inorganic carbon flux through a chain of hard-water lakes on the northern Great Plains

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Abstract

Whole-lake carbon (C) mass-balance budgets were constructed for a chain of six hard-water lakes to quantify the relative importance of organic carbon (OC) and inorganic carbon (IC) exchanges between atmosphere, water column, sediments, and rivers. Mean summer C fluxes were calculated for each lake during the ice-free periods (May to September) of 1995–2007 by measuring deposition of IC and OC in lake sediments, export of C to outflow rivers, lotic C influxes, and atmospheric exchange of CO₂. Unlike soft-water lakes, IC in rivers accounted for 68.2–85.6% of total C (TC) influx to these hard-water lakes, CO₂ efflux accounted for 0–44.5% of total C export (median 2.8%), and sedimentation buried similar amounts of OC and IC. Deposition of C in sediments accounted for 1.8–61.7% of total export and was correlated to water residence time, while C efflux through rivers accounted for 32.6–98.2% of total export, mainly as IC (69.6–85.1% of TC). Unexpectedly, estimates of net ecosystem production based on OC mass balances suggested that all lakes were autotrophic (production > respiration) during summer, despite elevated dissolved organic carbon content (5.6–16.1 mg C L⁻¹), pCO₂ values, and net CO₂ emissions to the atmosphere from three lakes. We conclude that C fluxes within and among these hard-water lakes are regulated by hydrologic inputs of dissolved IC rather than by lake metabolism, IC and OC pathways are only loosely coupled, and future climate variability will alter C fluxes in similar lakes mainly through regulation of mass transfer from land.

Analysis of global carbon (C) fluxes has focused historically on terrestrial and oceanic processes (Falkowski et al. 2000); however, the presence of mass imbalances within continental C budgets (Fan et al. 1998) has stimulated research into the role of lakes as missing C sinks (Dean and Gorham 1998; Cole et al. 2007). Lakes can be important nodes of C processing because they receive most of their C from terrestrial sources (Cole et al. 2007), have high water residence times compared with rivers, permanently bury particulate C (Downing et al. 2008), and exhibit intense microbial processing of dissolved compounds, which exchanges C between organic carbon (OC) and inorganic carbon (IC) pools (Prairie 2008; Tranvik et al. 2009). Early attempts to synthesize the role of lakes in C balances have focused on the common features of dilute boreal aquatic systems (reviewed in Cole et al. 2007), whereas more recent analyses suggest that the mechanisms regulating C fluxes and in-lake processing may differ in saline (Duarte et al. 2008) and hard-water lakes (Finlay et al. 2009; Stets et al. 2009). Improved understanding of the patterns and causes of variability among lentic systems is needed to accurately quantify the role of lakes in global C budgets, as well as to forecast their responses to anticipated future climate change (Benoy et al. 2007; Tranvik et al. 2009).

Synthesis of C flux studies of ion-poor lakes and reservoirs suggests that most C enters as allochthonous dissolved OC (DOC) (Dillon and Molot 1997; Benoy et al. 2007). These studies also show that DOC predominates the total C pool of most boreal lakes (Sobek et al. 2006;

Tranvik et al. 2009) and that only ~ 50% of total C influx is exported from lakes (Cole et al. 2007). On average, ~ 80% of processed C is lost to the atmosphere through CO₂ evasion, whereas the remainder is sequestered for thousands of years in profundal lake sediments (Cole et al. 2007). Daily and seasonal variation in atmospheric CO₂ exchange appears to be regulated mainly by the metabolic activity of autotrophic and heterotrophic microbes (algae and bacteria) in the water column (del Giorgio et al. 1999) and sediments (Ask et al. 2009), and, consequently, is sensitive to changes in the influx of inorganic nutrients and dissolved organic matter (DOM) (Schindler et al. 1997). However recent evidence suggests that allochthonous inputs of dissolved IC (DIC) may decouple metabolic control of CO₂ flux on longer timescales (Hanson et al. 2006), whereas whole-lake experiments show that autotrophic and heterotrophic microbes differentially exploit IC and OC pools (Cole et al. 2006; Pace et al. 2007). As yet, comparatively little is known of how the magnitude and regulation of these processes may differ in saline and hard-water lakes (Duarte et al. 2008), despite the observation that such systems account for ~ 50% of inland water volume (Hammer 1986).

Limited empirical evidence to date suggests that the C content of hard-water and saline lakes is regulated by subsidies of terrestrial IC rather than OC (Dean et al. 2006; Stets et al. 2009) and that most dissolved C exists as IC species (HCO₃⁻, CO₃²⁻) at elevated pH (> 8) despite high concentrations of DOC (> 5 mg C L⁻¹) (Duarte et al. 2008; Finlay et al. 2009). Unexpectedly, pCO₂ in these DIC-rich systems often exceeds atmospheric levels (37 Pa), reflecting intense rates of heterotrophic metabolism (Finlay et al.

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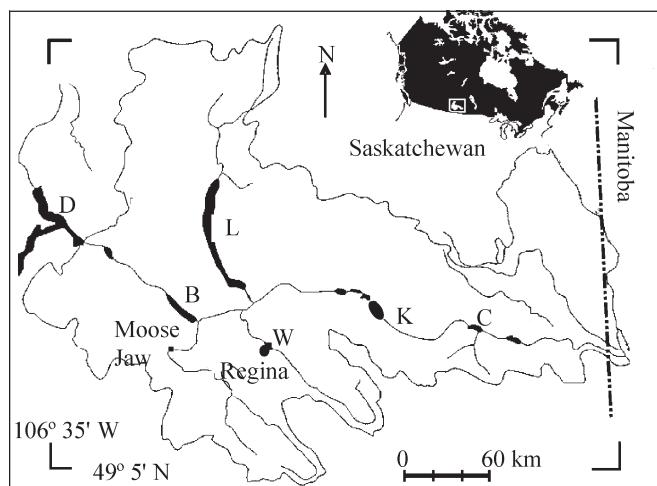


Fig. 1. Map of the study lakes in the Qu'Appelle valley of southern Saskatchewan, Canada. From upstream to downstream, study lakes include: Diefenbaker (D), Buffalo Pound (B), Last Mountain (L), Wascana (W, situated in the city of Regina), Katepwa (K), and Crooked (C).

2009) and generation of free CO_2 through precipitation of CaCO_3 at elevated temperatures or high rates of photosynthesis (McConnaughey et al. 1994). As a result, rates of CO_2 evasion can be 10-fold greater than those observed in DIC-poor systems (Duarte et al. 2008) despite evidence that both photosynthesis and sedimentation rates are also elevated in hard-water systems (Dean et al. 2006; Downing et al. 2008). Little is known of how the importance of CO_2 release varies among years or in relation to other C fluxes, but recent observations indicate that CO_2 evasion varies as a function of river influx of DIC (Stets et al. 2009) rather than microbial metabolism (Finlay et al. 2009), suggesting further that OC and IC pathways are not well integrated in DIC-rich lakes.

In this study, we quantified the main C fluxes through a chain of six hard-water lakes of the northern Great Plains during summers of 1995–2007 to measure the relative importance of IC and OC to whole-lake mass balances of C and to test the hypothesis that atmospheric exchange of CO_2 in hard-water lakes is regulated by IC influx rather than lake metabolism (Stets et al. 2009). Consistent with this hypothesis, we found that lotic influx of IC accounted for 71.6–85.6% of total C influx to lakes, that atmospheric CO_2 exchange was a minor component of C fluxes despite elevated $p\text{CO}_2$ and DOC concentrations, and that IC and OC pathways were only weakly coupled in these hard-water lakes.

Methods

Study sites—The six study lakes are situated within the Qu'Appelle River catchment, a lotic system that drains 52,000 km^2 (50°00'N–51°30'N, 101°30'W–107°10'W) in southern Saskatchewan, Canada, and extends over 400 km from headwaters near Lake Diefenbaker to its confluence with the Assiniboine River in Manitoba (Fig. 1). More than 75% of the drainage area of the Qu'Appelle River is

composed of agricultural fields and pastures on calcareous till (Christiansen 1960), while the cities of Regina and Moose Jaw are main point sources of nutrients (Hall et al. 1999). The regional climate is subhumid continental and is characterized by short warm summers (mean 19°C in July), cold winters (mean –16°C in January), and an average of 105 frost-free days (Leavitt et al. 2006).

Under natural conditions, the Qu'Appelle River arises east of Lake Diefenbaker and flows east through Buffalo Pound Lake, a central chain of four lakes (Pasqua, Echo, Mission, and Katepwa) and two downstream lakes (Crooked and Round). Reservoirs were created by impoundment of the South Saskatchewan River (Lake Diefenbaker), Wascana Creek (Wascana Lake), and the outflow of Buffalo Pound Lake. Water from Last Mountain Lake and Wascana Lake flows into the Qu'Appelle River via Last Mountain Creek and Wascana Creek, respectively. In addition, ca. 1.4% of outflow water from Lake Diefenbaker is transferred into the Qu'Appelle catchment above Buffalo Pound Lake (M. Grajczyk, Saskatchewan Watershed Authority, pers. comm.). River flow is monitored in the catchment at five locations, including the headwaters on the South Saskatchewan River, three sites in the central reaches of the Qu'Appelle River, and one downstream site (Dröschner et al. 2009).

Study lakes range from mesotrophic upstream basins (Diefenbaker, Buffalo Pound, Last Mountain) to eutrophic downstream sites (Katepwa, Crooked), with hypereutrophic Wascana Lake situated within the city of Regina (Table 1). Lakes vary in mean depth from 2 to 33 m, but all exhibit low relative depths (ratio of maximum depth to mean diameter) of 0.09–0.51% (Wetzel 2001) and, with the exception of occasionally dimictic Katepwa Lake, lakes are polymictic in all years. DIC and DOC concentrations are high (30–60 mg L^{-1} and 5–16 mg L^{-1} , respectively) and tend to increase downstream, with the exception of subsaline Last Mountain Lake, which has elevated levels of both DIC and DOC. Similarly, all lakes have moderate to high flushing rates (water residence time < 1.5 yr), except for Last Mountain Lake (~12.6 yr). In general, lakes have high conductivity (400–1800 $\mu\text{S cm}^{-1}$) and elevated mean summer pH (Table 1).

Limnological sampling—Diefenbaker, Buffalo Pound, Last Mountain, Katepwa, and Crooked Lakes were sampled biweekly between 01 May and 31 August during 1995–2007, whereas Wascana Lake was sampled similarly during 1996–2007. Depth-integrated water samples were collected by pooling Van Dorn water bottle casts taken each meter below the surface for polymictic lakes to a maximum depth of 3 m (Buffalo Pound, Wascana), 6 m (Crooked), or 15 m (other sites), and in the epilimnion of Katepwa Lake when it was stratified. Depth-integrated water was used for analysis of dissolved C species, whereas pH was measured immediately below the water surface using a calibrated (three standard) handheld pH meter (accuracy ± 0.1 unit). Lake transparency (m) was measured using a 20-cm diameter Secchi disk. Temperature (°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 (Yellow

Table 1. Morphometric and chemical characteristics of lakes of the Qu'Appelle River drainage basin. Values include water residence time (WRT), total dissolved phosphorus (TDP), total dissolved nitrogen (TDN), DOC, DIC, conductivity (Cond), and algal abundance as chlorophyll *a* (Chl *a*).

Lake	Area (km ²)	Volume (m ³ ×10 ⁶)	Mean depth (m)	WRT (yr)	TDP (μg L ⁻¹)	TDN (μg L ⁻¹)	DOC (mg L ⁻¹)	DIC (mg L ⁻¹)	Cond (μS cm ⁻¹)	Chl <i>a</i> (μg L ⁻¹)	pH
Diefenbaker	500	9400	33.0	1.3	22.5	333.2	5.6	33.8	422.5	4.8	8.4
Buffalo Pound	29.1	87.5	3.0	0.7	30.0	492.2	6.2	30.9	481.8	29.3	8.5
Last Mountain	226.6	1807.2	7.9	12.6	50.3	957.3	12.8	60.4	1787.7	12.6	8.7
Wascana	0.5	0.7	1.5	0.7	351.6	1381.2	16.1	40.5	917.7	35.1	9.0
Katepwa	16.2	233.2	14.3	1.3	163.0	958.7	11.5	50.6	1094.7	22.9	8.7
Crooked	15	120.9	8.1	0.5	124.2	861.0	11.0	51.5	1180.5	27.6	8.7

Springs) deployed at 1-m depth intervals. Wind measurements were taken 1 m above the lake surface during 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-μm pore membrane filters immediately after collection and were used to determine concentrations of dissolved substances in each lake. Analysis of DIC and DOC concentrations followed standard procedures using a Shimadzu model 5000A total carbon analyzer (Finlay et al. 2009). 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°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 (Finlay et al. 2009). Total dissolved phosphorus (μg P L⁻¹), total dissolved nitrogen, NH₄⁺, and NO₃⁻ (all μg N L⁻¹) were analyzed at the University of Alberta Water Chemistry Laboratory following procedures of Stainton et al. (1977). Particulate organic matter (POM) from prescreened (243-μm mesh), depth-integrated water samples was filtered onto washed GF/C glass-fiber filters and frozen (-10°C) until analysis for chlorophyll *a* (Chl *a*) by standard spectrophotometric procedures (Jeffrey and Humphrey 1975). All samples were analyzed within 4 months of collection.

Sediment cores were taken using a Glew gravity corer from the central region of Diefenbaker, Buffalo Pound, Last Mountain, and Crooked Lakes in the summer of 2007 and from Katepwa Lake in 2008. For Wascana Lake, we used sediment cores taken in 2003, since the lake was dredged and deepened in 2004. Each core was sectioned at 5-mm intervals and frozen (-10°C) until analysis. Each section was freeze-dried, and subsamples were acidified using 0.3 mol L⁻¹ HCl. Each organic (acidified) and bulk (unacidified) sample was analyzed for C stable isotope ratios (δ¹³C) and content (% dry weight) using isotope ratio mass spectrometry at the University of Regina following Leavitt et al. (2006).

Sediment chronology was based on ²¹⁰Pb activity measured by gamma spectrometry using an Ortec high-purity germanium (HPGe) coaxial well photon detector system following standard procedures (Appleby et al. 1986; Schelske et al. 1994). In brief, 15 evenly spaced samples were selected from each core, freeze-dried (72 h, 0.1 Pa), and homogenized before transfer into preweighed polyethylene tubes (15 × 80 mm). Tubes were filled to a height of 55 mm (equivalent to the depth of the HPGe well), reweighed, sealed with epoxy resin, and set aside for 21 d to achieve equilibrium of the native ²²⁴Ra and its decay products. Supported ²¹⁰Pb activity, expressed as ²²⁶Ra activity, was based on average activities of ²¹⁴Pb (295.1 keV and 351.9 keV) and ²¹⁴Bi (609.3 keV). Unsupported ²¹⁰Pb activity was calculated by subtracting proxy estimates of supported ²¹⁰Pb from the total ²¹⁰Pb activities (46.5 keV), while ¹³⁷Cs activity was measured at 661.7 keV. Depth-age

relationships were estimated for each core using the constant rate of supply (CRS) calculation (Binford 1990; Appleby 2001). Errors in age determination were based on estimates of counting errors of total ^{210}Pb and ^{226}Ra counts, background activities, and detector efficiency (Schelske et al. 1994). Bulk sediment mass accumulation rates (MAR) ($\text{g cm}^{-2} \text{yr}^{-1}$) were computed using the CRS-derived sediment chronology and dry densities of each sediment section (Appleby 2001).

Carbon budgets—The carbon budgets for each lake were estimated by quantifying seasonal CO_2 flux at the air–water interface of lakes, deposition of IC and OC in sediments, and C fluxes associated with surface water flows. Groundwater and methane (CH_4) fluxes were not included in these mass-balance calculations, although potential effects of neglecting these fluxes were addressed by comparing independent estimates of influx and losses both within lakes (mass balance) and between pairs of adjacent lakes (mass transfer) (see below). CO_2 exchanges were estimated for each year, mean sedimentation rates were calculated for the period 1990–present, while continuous monitoring at weirs was used to calculate annual and 13-yr averages for water residence time, inflow, and export at each site. Based on these data, mean C budgets were calculated for the summer sampling period only (01 May to 31 August) during 1995–2007. These budgets did not include CO_2 fluxes between the air and the water immediately after ice-off (Striegl et al. 2001), since preliminary analysis demonstrated that these factors altered the relative importance of estimated CO_2 fluxes less than 10% (analysis not shown).

CO_2 concentration (g C m^{-3}), $p\text{CO}_2$ (Pa), and CO_2 flux ($\text{g C m}^{-2} \text{d}^{-1}$) were estimated for 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, as described in Finlay et al. (2009). Briefly, chemically enhanced CO_2 flux ($\text{mmol m}^{-2} \text{d}^{-1}$) was calculated for each sampling date following the boundary layer equations of 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 $[\text{CO}_2]_{\text{lake}}$ is the concentration of CO_2 in the surface water ($\mu\text{mol L}^{-1}$), $[\text{CO}_2]_{\text{sat}}$ is the concentration of CO_2 at equilibrium with the atmosphere ($\mu\text{mol L}^{-1}$), α is the chemical enhancement of CO_2 flux at high pH (Hoover and Berkshire 1969), and k is piston velocity (cm h^{-1}) determined from eq. 5 in Cole and Caraco (1998) relating k to wind speed and accounting for temperature (Wanninkhof 1992). Atmospheric $p\text{CO}_2$ was assumed to be 37 Pa, the average value recorded at the Mauna Loa Observatory during 1995–2007 (<http://www.esrl.noaa.gov>). Chemically enhanced CO_2 flux was then estimated for all other days during summer by multiplying the mean daily CO_2 flux on successive sampling events with the time interval (days) between sampling events. Total summer fluxes were estimated as the sum of daily fluxes standardized to the 120-d sampling period (01 May to 31 August) and multiplied by lake surface area.

Carbon export from the water column to sediments was estimated from mean MAR ($\text{g C cm}^{-2} \text{yr}^{-1}$) and mean C content (% dry weight) in the top 10 cm of each core (ca. 1990–present). Deposition of OC was estimated as the product of %C following acidification (no carbonates) and MAR, whereas IC deposition was calculated as the difference between total C and OC deposition. Sedimentation rates during summer (day of year (DOY) 122–242) were estimated as a fixed fraction of total annual C deposition by assuming that sedimentation was constant throughout the average ice-free period (mid-April to mid-October). Although we recognize that this may not be entirely accurate, the absence of thermal stratification is expected to reduce elevated deposition seen during spring in many dimictic lakes. Furthermore, sediments in Qu'Appelle lakes lack the fine structure (laminae) needed to quantify seasonal deposition (Leavitt et al. 2006), thus constraining more highly resolved estimates of seasonal deposition. Finally, we further assumed that single core estimates of MAR adequately captured mean lakewide sedimentation rates because all Qu'Appelle lakes have panlike morphology with steep littoral zones and large flat central bottoms (relative depth < 1%) (Table 1) and because a previous comparison of > 30 cores taken from both Pasqua and Wascana lakes revealed that C content and sedimentation rates varied < 25% among profundal sites (Leavitt et al. 2006; P. R. Leavitt unpubl. data).

Carbon export to rivers was estimated as the product of water-column C concentration (sum of DIC, DOC, algal C) and outflow river discharge rates ($\text{m}^3 \text{s}^{-1}$) during the sampling period (DOY 122–242) estimated from continuous weir estimates of river discharge averaged for lake and year, although mean site-specific values for the entire 13-yr sampling period were used for decadal budgets. In this case, algal C (mg L^{-1}) was estimated from biweekly estimates of chlorophyll *a* (Chl *a*) standing stock in each lake and year, and by assuming a C:Chl *a* ratio of 50 (Reynolds 1984). No attempt was made to quantify other sources of particulate C because prior microscopic analysis revealed little nonmicrobial mass (Graham 1997). Similarly, lotic C influx to each lake was estimated as the product of mean summer river discharge and the 13-yr mean of annual mean water-column concentrations of DIC, DOC, and algal C in the receiving lake because the C content of river water was not routinely available. The accuracy of this estimate of C influx was tested independently by comparing measured OC and IC export from upstream sites with estimated C influx to immediately downstream basins. Specifically, we compared the Qu'Appelle River–specific outflow of Lake Diefenbaker with the inflow to Buffalo Pound, the outflow of Katepwa with the inflow to Crooked Lake, and the sum of lotic export from Wascana, Buffalo Pound, and Last Mountain Lakes to the C input to Katepwa Lake (Fig. 1). In all cases, mean summer river discharge rates ($\text{m}^3 \text{s}^{-1}$) were based on direct weir estimates obtained from the Saskatchewan Watershed Authority (T. Chamulak, Saskatchewan Watershed Authority, pers. comm.).

Net ecosystem production (NEP)—Mass balances of both IC and OC were also used to estimate NEP following

the procedures of Stets et al. (2009) to evaluate the relationship between diverse estimates of lake metabolism and the magnitude and direction of atmospheric CO₂ exchange. Most often NEP is calculated by direct measurement as the difference between gross primary production (GPP) and respiration (R) of a given lake. However, Stets et al. (2009) point out that NEP can also be estimated from whole-lake mass flux of either OC or IC as

$$\text{NEP}_{\text{OC}} = E_{\text{OC}} + \Delta_{\text{OC}} - I_{\text{OC}} \quad (2)$$

$$\text{NEP}_{\text{IC}} = I_{\text{IC}} - E_{\text{IC}} - \Delta_{\text{IC}} \quad (3)$$

where E is the export of C in surface or groundwater; I is the influx of C to the lake from atmospheric, lotic, or subterranean sources; and Δ is the net change in sediment and water-column C content (i.e., storage). In both mass balances, NEP takes a positive value when lakes convert IC into OC and are net autotrophic.

Estimates of the NEP of planktonic communities (NEP_P) were also determined from biweekly estimates of lake transparency, day length, and microbial GPP and R determined in light and dark bottle assays following Finlay et al. (2009). Briefly, three 250-mL bottles were filled with 243- μm screened, depth-integrated water and were wrapped in aluminum foil to exclude light. An additional three bottles were incubated in the laboratory at lake-specific temperatures in light fields (450 $\mu\text{mol quanta m}^{-2} \text{s}^{-1}$) equivalent to the irradiance measured in situ at Secchi depth. 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. Planktonic NEP was estimated from changes in O₂ concentrations in the light bottles and was converted to $\text{mg C m}^{-3} \text{d}^{-1}$ assuming a photosynthetic quotient of 1.0 (Wetzel 2001). The decline in O₂ content of dark bottles was used to calculate community respiration, while planktonic GPP was estimated as $\text{NEP}_P + R$. Finally, we approximated whole water-column metabolic processes in these polymictic lakes 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 (as 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 (Finlay et al. 2009).

Mass-balance estimates of NEP_{IC} and NEP_{OC} were compared with bioassay estimates of NEP_P and calculated net CO₂ flux to quantify the relationship between lake metabolism (autotrophy, heterotrophy) and the magnitude and direction of CO₂ exchange with the atmosphere. Previous research demonstrates that many soft-water lakes exhibit net CO₂ efflux to the atmosphere as a result of bacterial metabolism of allochthonous DOM (Cole et al. 2007). However, while many hard-water and saline lakes also exhibit elevated $p\text{CO}_2$ and net gas evasion (Duarte et al. 2008), mass-balance studies suggest that net CO₂

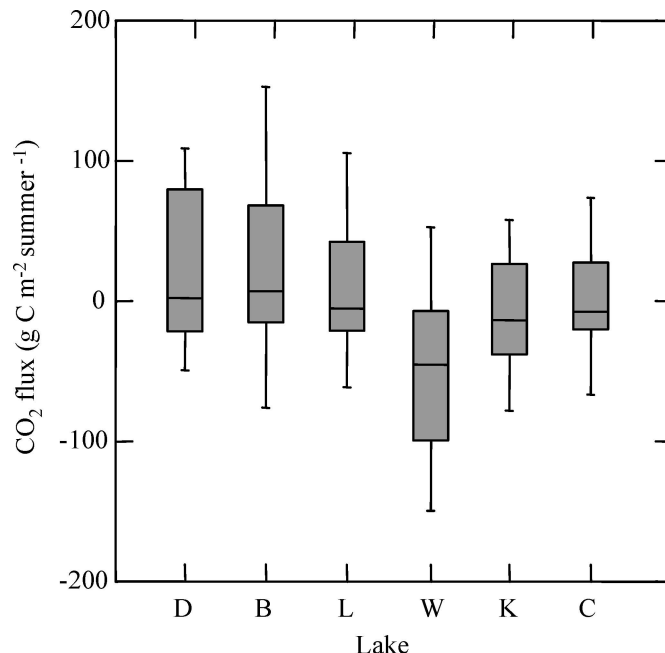


Fig. 2. Chemically enhanced net CO₂ flux at the air-water interface for the six study lakes in southern Saskatchewan, Canada, from 1995 to 2007. Positive values represent net CO₂ efflux to the atmosphere, while negative values represent influx of CO₂ from the atmosphere into the lake. Boxes represent the range within which 50% of values fall, the center line represents the median of the values, the box edges represent the first and third quartiles, and the whiskers represent the range of observations.

exchange can be decoupled from metabolism in hard-water lakes because of unusually high influx of IC and subsequent chemical reactions that produce CO₂ (Stets et al. 2009). Because algal biomass is elevated at all Qu'Appelle lakes (Table 1) and water-column DOC is colorless and recalcitrant (Leavitt et al. 2006), we hypothesized that all study lakes are net autotrophic. However, because the chemistry of Qu'Appelle lakes is similar to those of Stets et al. (2009), we also expected that these lakes could release CO₂ in a manner unrelated to lake metabolism (Finlay et al. 2009).

Results

C fluxes—Atmospheric exchange of CO₂ varied considerably between years, ranging from an influx of $-149.6 \text{ g C m}^{-2} \text{ summer}^{-1}$ to an efflux of $152.9 \text{ g C m}^{-2} \text{ summer}^{-1}$ (Fig. 2). In contrast, mean CO₂ flux over all 13 yr was not significantly different from zero for any lake (-47.0 to $53.9 \text{ g C m}^{-2} \text{ summer}^{-1}$) despite chemical enhancement at high pH, and only Wascana Lake exhibited mean summer CO₂ flux that differed significantly from other basins (ANOVA $p = 0.022$, Tukey's post hoc test).

Total carbon sedimentation ranged from $17.6 \text{ g C m}^{-2} \text{ summer}^{-1}$ (Wascana) to $68.1 \text{ g C m}^{-2} \text{ summer}^{-1}$ (Diefenbaker) (Fig. 3) as a result of variation among lakes in the density of bulk sediments ($0.089\text{--}0.281 \text{ g cm}^{-3}$), linear sedimentation rate ($0.35\text{--}0.69 \text{ cm yr}^{-1}$), and total C content ($5.1\text{--}12.6\%$). Unlike the case of soft-water lakes, a high

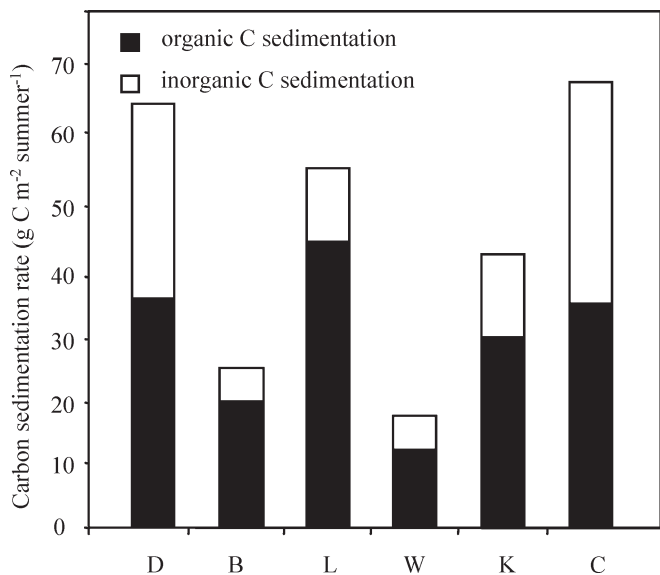


Fig. 3. Mean inorganic (white boxes) and organic carbon (black boxes) sedimentation rates ($\text{g C m}^{-2} \text{ summer}^{-1}$) of the six study lakes for the period ca. 1990–2007.

proportion of total C sedimentation (20.0–50.0%) in these hard-water systems was attributable to the deposition of inorganic C (Fig. 3).

Inorganic C accounted for the highest proportion of C efflux in rivers (Fig. 4). In all lakes, export of DIC in rivers ($18\text{--}3718 \text{ g C m}^{-2} \text{ summer}^{-1}$) was significantly and substantially (69.6–85.1% of TC) greater than that of DOC ($4\text{--}1370 \text{ g C m}^{-2} \text{ summer}^{-1}$), while algal particulate organic carbon (POC) accounted for < 3% of total lotic efflux at all sites (Table 2). Areal rates of efflux via rivers also differed significantly among lakes (ANOVA $p < 0.001$), with upstream lakes (Diefenbaker, Buffalo Pound, Last Mountain) generally exhibiting lower areal lotic efflux than did downstream lakes (Wascana, Katopwa, Crooked) (Fig. 4). Overall, C export in rivers accounted for between 32.6% (Last Mountain) and 98.2% (Crooked) of total C export from the water column (Table 2).

Estimated influx of DIC ($25\text{--}3718 \text{ g C m}^{-2} \text{ summer}^{-1}$) was also substantially greater (71.6–85.6% of TC) than that of DOC ($5\text{--}1370 \text{ g C m}^{-2} \text{ summer}^{-1}$) in all Qu'Appelle lakes when calculated as the product of river discharge and in-lake C content (Fig. 4). For Crooked Lake, this estimate agreed to within 10% of the influx calculated from measured outflow from Katopwa Lake (Table 3), the site immediately upstream of Crooked Lake (Fig. 1). Agreement was lower, but still within 50%, for similar comparisons of Buffalo Pound Lake, a reservoir with domestic water withdrawals, and Katopwa Lake, a site that received riverine inputs from Buffalo Pound, Wascana, and Last Mountain Lakes via the chain of linked Pasqua, Echo, and Mission Lakes (see Fig. 1).

Carbon budgets—Comparison of the major C fluxes revealed that whole-lake C budgets of Qu'Appelle Valley lakes were regulated mainly by fluxes of inorganic C within and among lakes (Fig. 5; Table 2). For example, DIC in

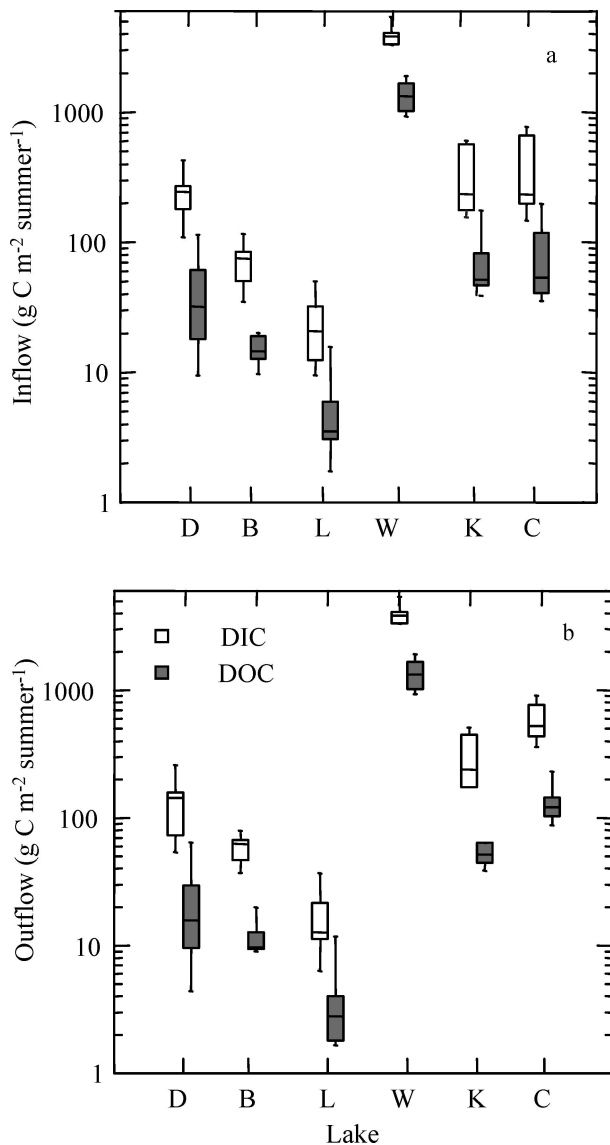


Fig. 4. Seasonal (a) inflow and (b) outflow ($\text{g C m}^{-2} \text{ summer}^{-1}$) of dissolved inorganic carbon (DIC, open boxes) and dissolved organic carbon (DOC, gray boxes) of the six study lakes from 1995 to 2007. Boxes represent the range within which 50% of values fall, the center line represents the median of the values, the box edges represent the first and third quartiles, and the whiskers represent the range of observations.

rivers accounted for 68.2–85.6% of total C inputs to these hard-water lakes during summer, while lotic losses of DIC ranged from 28.3% to 75.1% of total C export. Similarly, IC fluxes accounted for 20.0–50.0% of C deposition in lake sediments, although sedimentation itself accounted for < 25% of total C export in all lakes except subsaline Last Mountain Lake (61.7%). Overall, atmospheric exchange of CO_2 accounted for < 5% of total C fluxes in downstream lakes, whereas CO_2 evasion was more important in headwater Diefenbaker (15% of total efflux) and Buffalo Pound Lakes (44.5%).

Although IC was the main component of most C fluxes in lakes, organic C was the predominant component of

Table 2. Mean C budgets for lakes of the Qu'Appelle catchment during 1995–2007. All C fluxes as Mg C lake⁻¹ summer⁻¹. Values in parentheses represent percentages that each component contributes to either total inputs or outputs. For estimation of relative (%) magnitudes, positive atmospheric CO₂ exchange (evasion) is considered an efflux, while negative CO₂ exchange (invasion) is considered an influx (% in *italic*). POC is assumed to be negligible within inflowing river waters.

	Diefenbaker	Buffalo Pound	Last Mountain	Wascana	Katepwa	Crooked
River influx						
DIC	135,318	1768	3005	338	5801	6045
DOC	22,673	371	638	134	1291	1265
Total dissolved C input	157,991 (100)	2138 (100)	3643 (100)	472 (95.3)	7092 (97.8)	7311 (99.8)
Enhanced atmospheric CO ₂ exchange	21,170 (15.0)	1571 (44.5)	1149 (5.7)	-24 (4.7)	-162 (2.2)	-16 (0.2)
River efflux						
DIC	74,864	996	5385	338	5959	10,486
DOC	12,544	209	1143	134	1326	2195
POC	536	46	55	14	131	262
Total C outflow	87,943 (62.1)	1251 (35.5)	6583 (32.6)	485 (98.2)	7416 (91.6)	12,943 (92.7)
Carbon sedimentation						
IC	13,986	141	2637	2.4	204	511
OC	18,435	5645	9821	6.4	471	511
Total carbon deposition	32,421 (22.9)	706 (20.0)	12,458 (61.7)	8.8 (1.8)	675 (8.4)	1021 (7.3)
Influx–outflux (outflux as % influx)	16,456 (89.6)	-1390 (165.0)	-16,546 (554.3)	1.2 (99.7)	-837 (111.5)	-6638 (190.6)

total C export to lake sediments (Fig. 5). When compared among lakes, organic C fluxes appeared to be influenced by lake hydrology, since both mean annual deposition of OC in sediment (g C m⁻² summer⁻¹) ($r = 0.854$, $p = 0.03$) and log₁₀-transformed OC export in rivers (g C m⁻² summer⁻¹) ($r = -0.783$, $p = 0.06$) were correlated with log₁₀-transformed mean water retention time. In contrast, both IC sedimentation and outflow were uncorrelated with lake hydrology ($p > 0.10$), suggesting that the controls of OC export are different than those regulating IC losses.

Estimates of total C loss (rivers, sediments, atmosphere) agreed to within ~ 10% of estimates of total C influx for lakes Diefenbaker ($C_{\text{out}} = 0.896 \times C_{\text{in}}$), Wascana ($C_{\text{out}} = 0.997 \times C_{\text{in}}$), and Katepwa ($C_{\text{out}} = 1.15 \times C_{\text{in}}$) (Table 2). In contrast, C losses from Last Mountain Lake exceeded total C influx by over 500%, whereas C_{out} was 165% and 190% of C_{in} in Buffalo Pound and Crooked Lakes, respectively. We infer that groundwater is likely the “missing” source of C input to Crooked Lake because

Table 3. Comparisons of C outflows (Mg C lake⁻¹ summer⁻¹) from upstream lakes with calculated inflows based on water discharge rates and lake concentrations of IC or OC. On average, 1.4% of the outflow from Lake Diefenbaker flows into the Qu'Appelle valley and into Buffalo Pound, whereas the sum of the outflows from Buffalo Pound, Last Mountain, and Wascana Lakes flow into Katepwa Lake through three closely joined lakes. The outflow from Katepwa Lake flows into Crooked Lake. Numbers in parentheses represent calculated outflow as a percentage of IC or OC inflow from upstream lakes.

Lake	Outflow from upstream lakes		Calculated inflow	
	IC	OC	IC	OC
Buffalo	1048	183	1768 (59.2)	371 (49.4)
Katepwa	6719	1600	5800 (115.8)	1291 (123.9)
Crooked	5959	1457	6045 (98.6)	1265 (115.2)

measured surface water influx was in close agreement to lotic C export from immediately upstream Katepwa Lake (Table 3). At present, we cannot evaluate the nature of additional C sources to Buffalo Pound and Last Mountain Lakes, although we note that the latter has several unmonitored creeks and wetlands that contribute saline and freshwaters to the lake's north basin in spring and early summer, while Buffalo Pound also serves as the drinking water reservoir for both Regina and Moose Jaw.

NEP and lake metabolism—The mean magnitude and direction of net CO₂ flux from Qu'Appelle lakes during the summers of 1995–2007 was not consistently related to estimates of NEP based on bottle assays of planktonic microbial metabolism (NEP_P), IC mass balances (NEP_{IC}), or organic C production (NEP_{OC}), even in lakes with well-balanced mass budgets (Diefenbaker, Wascana, Katepwa). For example, CO₂ evasion accounted for ~ 15% of C loss from headwater Lake Diefenbaker (Fig. 5), yet both IC and OC mass balances suggested that the lake was net autotrophic (Table 4), while bottle bioassays suggest that Diefenbaker was only slightly heterotrophic (Table 5). Similarly, mass-balance estimates of NEP were consistent with observed CO₂ invasion into Wascana and Katepwa Lakes, yet bottle bioassays suggested Katepwa Lake was heterotrophic (negative NEP_P). Overall, NEP_{OC} was positive (autotrophic) for all lakes, while mean net heterotrophic conditions were indicated for several lakes based on NEP_{IC} (Buffalo Pound, Last Mountain, Crooked), NEP_P (Diefenbaker, Last Mountain, Katepwa, Crooked), and net CO₂ exchange (Diefenbaker, Buffalo Pound, Last Mountain).

Discussion

Comparison of C fluxes within and among lakes during the summers of 1995–2007 demonstrates that net C balance

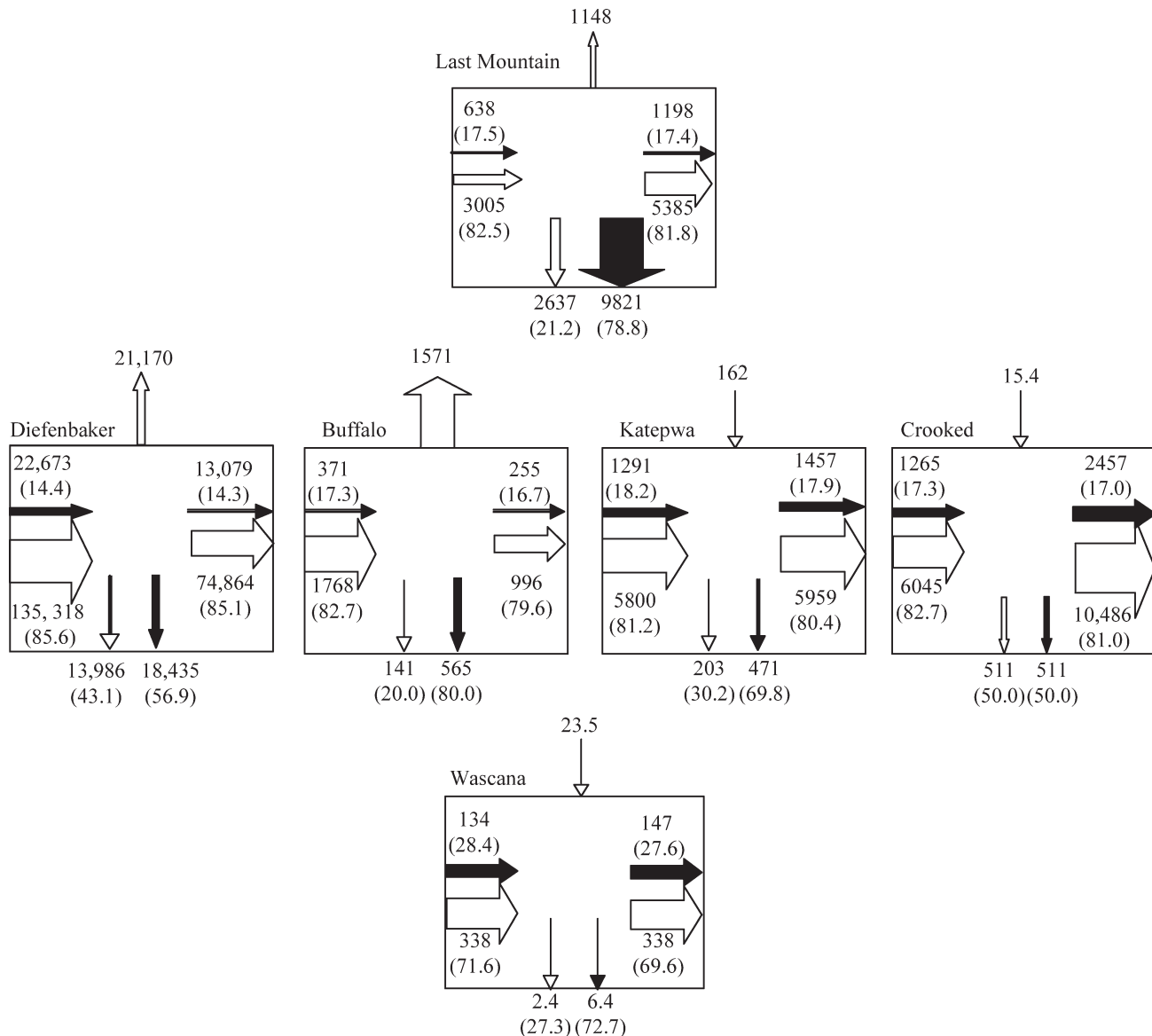


Fig. 5. Average organic (OC, solid) and inorganic (IC, open) carbon (C) fluxes in Qu'Appelle study lakes from 1995 to 2007. For each lake box, uppermost arrows represent atmospheric CO₂ exchange, lowermost arrows represent sedimentation of IC and OC, while horizontal arrows represent the inflows (left) and riverine outflow (right) of DIC and DOC. Arrow size represents the relative quantity of C in each pool within each lake. In contrast, values adjacent to arrows represent whole-lake average C fluxes (Mg C lake⁻¹ summer⁻¹), while values in parentheses represent relative (%) proportions of IC and OC fluxes for individual processes (e.g., sedimentation). POC accounted for < 3% of POC export (*see text*) and is not included in the figure but was included in estimates of relative (%) contribution of IC and OC flow.

in these hard-water systems is regulated mainly by subsidies of allochthonous IC (Fig. 5; Table 2) but suggests that IC and OC fluxes may be controlled by different mechanisms (Table 4). For example, DIC in rivers accounted for 68.2–85.6% of all C influx and 28.1–75.1% of total C export, similar to other hard-water systems (Stets et al. 2009), but unlike most boreal lakes in which allochthonous C arrives mainly as DOC (Cole et al. 2007; Prairie 2008). As a result, atmospheric CO₂ exchange was a minor C flux in most Qu'Appelle lakes (Fig. 5), despite elevated concentrations of DOC (5.6–16.1 mg C L⁻¹) and algae (4.8–35.1 μg Chl *a* L⁻¹) (Table 1), intense chemical enhancement at high pH,

and mean annual *p*CO₂ and daily CO₂ fluxes in individual years that exceeded values recorded for many other freshwater systems (Finlay et al. 2009). Although IC was also an important component of C storage in sediments of all lakes (20.0–50.0%), deposition of OC but not IC was correlated with lake hydrology ($r^2 = 0.731$, $p = 0.03$), suggesting that sedimentation of organic and inorganic C were under partially independent regulation. Consistent with this viewpoint, estimates of NEP based on OC mass balances suggested that all lakes were net autotrophic (Table 4), whereas those based on IC mass balances and atmospheric CO₂ exchanges revealed a mixture of hetero-

Table 4. Calculation of NEP based on mass balance of OC (NEP_{OC}) and IC (NEP_{IC}) following procedures of Stets et al. (2009). Export = E, Import = I, and Δ is change in lake storage in water column and sediment samples calculated for the summer sampling period ($Mg\ season^{-1}$). NEP estimates are expressed both per lake ($Mg\ C\ lake^{-1}$) and on an areal basis ($g\ C\ m^{-2}$). Positive NEP indicates that lakes are net autotrophic (OC is produced; IC is consumed).

	Diefenbaker	Buffalo Pound	Last Mountain	Wascana	Katepwa	Crooked
Organic carbon						
E_{OC} ($Mg\ season^{-1}$)						
River discharge	13,079	255	1198	147	1457	2457
ΔOC ($Mg\ season^{-1}$)						
Sedimentation	18,435	565	9821	6	471	511
Water column	-7661	265	1247	1	242	494
Net accumulation (sediment+water)	10,774	830	11,069	7	713	1004
I_{OC} ($Mg\ season^{-1}$)						
Input from upstream	22,673	371	638	134	1291	1265
NEP_{OC} ($Mg\ C\ lake^{-1}$)	1180	714	11,629	20	879	2196
NEP_{OC} ($g\ C\ m^{-2}$)	2.4	24.5	51.3	40.9	54.3	146.4
Inorganic carbon						
E_{IC} ($Mg\ season^{-1}$)						
River discharge	96,034	2567	6533	338	5959	10,486
ΔIC ($Mg\ season^{-1}$)						
Sedimentation	13,986	141	2637	2.4	203	511
Water column	-26,320	156	4355	-1	10,089	-91
Net accumulation (sediment+water)	-12,334	298	6992	1	-617	420
I_{IC} ($Mg\ season^{-1}$)						
Input from upstream	35,318	1768	3005	361.5	5962	6060
NEP_{IC} ($Mg\ C\ lake^{-1}$)	51,618	-1097	-10,520	22	620	-4846
NEP_{IC} ($g\ C\ m^{-2}$)	103.2	-37.7	-46.4	44.8	38.3	-323.1

trophic and autotrophic status (Tables 2, 4). Although inaccuracies in mass-balance calculations may contribute to these inconsistencies (*see* below), other well-constrained C budgets also suggest that IC fluxes can be decoupled from organic matter production in hard-water lakes (Stets et al. 2009; Tranvik et al. 2009), while whole-lake stable isotope additions suggest only a loose coupling between DIC and DOC fluxes within boreal lakes (Cole et al. 2006; Pace et al. 2007).

C fluxes—Mean daily rates of CO_2 flux to the atmosphere were greater than those observed for DOC-rich boreal systems (Cole et al. 1994; del Giorgio et al. 1999) and less than those of some saline lakes (Duarte et al. 2008), but accounted for only a small proportion of C flux in whole-lake mass-balance budgets (median 2.8% of total C efflux) (Table 2). For example, mean CO_2 flux during individual years ranged from -149.6 to $152.9\ g\ C\ m^{-2}$

Table 5. Mean (\pm SD) gross primary production (GPP), respiration (R), and net primary production ($NPP = NEP_P$) rates ($mg\ C\ m^{-3}\ d^{-1}$) of lakes in Qu'Appelle River catchment, Saskatchewan, during 1995–2007, as determined by bottle bioassays (Finlay et al. 2009).

Lake	GPP	R	NPP
Diefenbaker	17.6 ± 24.8	-85.6 ± 412.7	-70.3 ± 411.6
Buffalo	124.9 ± 100.9	-112.1 ± 414.1	13.5 ± 434.0
Last Mountain	83.7 ± 110.7	-144.7 ± 485.4	-59.1 ± 485.9
Wascana	276.5 ± 252.4	-229.9 ± 571.0	46.5 ± 590.5
Katepwa	54.2 ± 45.7	-205.0 ± 528.9	-164.0 ± 521.4
Crooked	74.7 ± 50.6	-86.5 ± 347.5	-10.3 ± 355.5

summer⁻¹ (Fig. 2), with individual daily exchange of -100 to $200\ mmol\ C\ m^{-2}\ d^{-1}$ (Finlay et al. 2009). These values have a much greater magnitude than those observed for other hard-water lakes ($2\text{--}49\ g\ C\ m^{-2}\ yr^{-1}$) (Stets et al. 2009) and DOC-rich boreal systems ($< 18\ g\ C\ m^{-2}\ yr^{-1}$) (Dillon and Molot 1997; Algesten et al. 2003; Rantakari and Kortelainen 2005) but are lower than those from tropical floodplains ($803\ g\ C\ m^{-2}\ yr^{-1}$) (Melack and Engle 2009) or saline lakes (-275 to $3123\ mmol\ m^{-2}\ d^{-1}$) (Duarte et al. 2008). Despite such intense C processing, Qu'Appelle lakes were not a significant source of CO_2 to the atmosphere (net CO_2 flux $\sim 0\ g\ C\ m^{-2}\ summer^{-1}$) when averaged over 13 yr (Fig. 2) because generally high pCO_{2-lake} and CO_2 evasion rates during 1995–2000 were balanced by pCO_{2-lake} values $< 37\ Pa$ and net CO_2 invasion thereafter (Finlay et al. 2009). This conclusion was not altered by including estimates of rapid CO_2 loss in spring after ice melt (Striegl et al. 2001; Kortelainen et al. 2004) or elevated CO_2 evasion at night (Maberly 1996; Cicerone et al. 1999) (calculations not shown), likely because these effects were overwhelmed by the substantial interannual variation in CO_2 flux (Fig. 2). Instead, because net CO_2 flux also varied coherently among years over regions $> 100,000\ km^{-2}$ (Finlay et al. 2009), our study cautions that short-term (subdecadal) gas exchange studies may not capture the true range of variability in CO_2 flux and may obscure the role of lakes in global carbon balances.

Rates of OC sequestration in Qu'Appelle lake sediments were greater than those recorded for small boreal lakes ($< 6\ g\ OC\ m^{-2}\ yr^{-1}$) (Algesten et al. 2003) and unproductive large lakes ($5\text{--}18\ g\ OC\ m^{-2}\ yr^{-1}$) (Dean and Gorham 1998; Downing et al. 2008) but were less than

those seen in small eutrophic impoundments (up to 2122 g OC m⁻² yr⁻¹) (Downing et al. 2008) or reservoirs (400 g OC m⁻² yr⁻¹) (Dean and Gorham 1998). However, unlike DOC-rich lakes, IC sedimentation also contributed 32.0% ± 12.1% of total C deposition in Qu'Appelle lakes (Fig. 3), consistent with stable isotope analyses (Leavitt et al. 2006; P. R. Leavitt unpubl. data), which demonstrates that mean (± SD) δ¹³C values of whole sediments (-19.8‰ ± 2.1‰) in these lakes are substantially enriched relative to that of sedimentary OC (-27.6‰ ± 1.2‰) due to high carbonate content in the Qu'Appelle River (δ¹³C_{river-water} = -3.0‰ to -7.0‰) (*see below*). Taken together, combined IC and OC sedimentation rates in the Qu'Appelle catchment over the entire ice-free period (20–66 g OC m⁻² yr⁻¹, 7–52 g IC m⁻² yr⁻¹) were comparable to those seen in other hard-water ecosystems (12 g OC m⁻² yr⁻¹, 28 g IC m⁻² yr⁻¹) (Stets et al. 2009) and were greater than global estimates for other productive lakes (72–94 g C m⁻² yr⁻¹) (Dean and Gorham 1998; Downing et al. 2008). Furthermore, because modern sediment MAR is similar to those documented during the past 2000–6000 yr (Rusak et al. 2004; Michels et al. 2007), these sedimentary deposits represent carbon sinks that are substantially more permanent than those in regional soils.

The predominance of lotic IC fluxes in whole-lake mass balances (Table 2; Fig. 5) is consistent with observations that soils within the Qu'Appelle catchment are derived mainly from calcareous glacial till overlying carbonate-rich Pleistocene bedrock (Christiansen 1960). Although IC content was not directly measured in rivers, stable isotope analysis of 0.45-μm filtered whole water from three stations in the Qu'Appelle River (each *n* = 14) during 2001–2002 (Leavitt et al. 2006; P. R. Leavitt unpubl. data) revealed that δ¹³C values ranged -3.0‰ ± 3.1‰ to -7.0‰ ± 5.3‰, similar to that of sedimentary IC (-2.9‰ to -10.9‰) estimated for each lake from Keeling regressions of whole-sediment δ¹³C vs. C:N⁻¹ (*y*-intercept = δ¹³C_{IC}) (Keeling 1958). Similarly, direct measurement of the IC content of each lake, combined with observed water residence times, revealed that IC accounted for 69.6–85.1% of lotic C export. These findings are similar to those recorded by Stets et al. (2009) for other hard-water lakes of the northern Great Plains but contrast sharply with many boreal forest lakes where OC influx is threefold to 15-fold greater than that of IC (Dillon and Molot 1997; Sobek et al. 2006; Tranvik et al. 2009). Interestingly, annual OC loading to the Qu'Appelle lakes (up to 1400 g C m⁻² summer⁻¹) were also 10-fold greater than those of typical boreal lakes (up to 40 g OC m⁻² yr⁻¹) (Dillon and Molot 1997), likely reflecting the very high catchment-to-lake area ratios (> 1000:1) and OC content of surface waters (Patoine et al. 2006; Pham et al. 2009). Thus while overall mass budgets were heavily influenced by allochthonous subsidies of IC, these prairie lakes remained hotspots for processing of terrestrial DOC (Cole et al. 2007).

Carbon budgets—Mass-balance budgets are intended to provide robust insights on the main C fluxes between lakes and their catchments (Andersson and Sobek 2006), yet this approach usually has assumptions, imbalances, and errors

that constrain the accuracy of this approach (Stets et al. 2009). In the present study, we focused on decadal means of the major C fluxes during summer and did not conduct a detailed error propagation analysis because our earlier biogeochemical investigations in these and other regional lakes revealed that all mass influxes (water, solutes, particles) varied up to 10-fold among years because of snowmelt and runoff prior to the monitoring period (Leavitt et al. 2006; Patoine et al. 2006; Pham et al. 2009). Instead, we focused on comparisons of long-term mean summer conditions to provide insights on the pathways and mechanisms regulating C flux within and among Qu'Appelle lakes.

As with other mass budgets (Sobek et al. 2006), our estimates of C export to sediments, rivers, and the atmosphere were better constrained than our determinations of C influx. For example, C export to rivers was measured using digital morphometric maps (Dröscher et al. 2009), daily estimates of river discharge, and biweekly determinations of DOC, DIC, and POC content of each lake. As we demonstrated earlier with similar whole-lake budgets of nitrogen and energy, this temporal resolution is sufficient to capture all significant seasonal variability in lake chemistry and pelagic community composition (Patoine et al. 2006; Dröscher et al. 2009). Similarly, summer fluxes of CO₂ are believed to be well constrained for Qu'Appelle lakes because these net CO₂ fluxes are regulated mainly by seasonal and interannual changes in pH, rather than more difficult to measure changes in DIC, temperature, wind speed, or microbial metabolism (Finlay et al. 2009). Although CH₄ fluxes were not measured in these basins, we infer that they should account for a minor C flow in most lakes because all sites are polymictic, have limited littoral zones, and few submerged or floating macrophytes (Hall et al. 1999; but *see* McGowan et al. 2005), all factors that limit CH₄ production and evasion (Tranvik et al. 2009). Finally, although estimates of MAR in sediments were based only on a single central sediment core, comparison of 30 short cores (~ 10–15 cm) each from Wascana and Pasqua Lakes (Leavitt et al. 2006; P. R. Leavitt unpubl. data) and longer cores spanning up to 250 yr (Hall et al. 1999; Leavitt et al. 2006) reveal that C deposition varies < 25% among profundal sites, a range that is similar to observed spatial variation within other lakes (Downing et al. 2008). Together, these findings suggest that comparisons of C efflux within and among lakes are robust to measurement errors, particularly when averaged over the 13 yr of study.

Estimates of C influx from the catchment were less well constrained than those of C export because we lacked the IC and OC content of inflowing rivers, estimates of overland flow, and groundwater influx. Previous mass balances constructed for nitrogen demonstrate that both effective catchment area (catchment area contributing runoff to lake) and peak river discharge during spring vary 10-fold among years (Patoine et al. 2006). Consequently, influx of dissolved and particulate IC during spring should be disproportionately enhanced during years of greatly elevated discharge, as seen in studies of other particle-associated elements (Bennett et al. 2001). Such potentially high but unmonitored spring influxes could alter subse-

quent summer mass balances if vernal C inputs altered in-lake C fluxes during summer (e.g., C release from sediments). Similarly, we expect that groundwater may represent an important C influx to Last Mountain Lake, where long water residence time (> 12 yr) and limited surface water outflow create conditions similar to those seen in other hard-water lakes with restricted drainage (Stets et al. 2009). Fortunately, despite these potential errors, total C influx and efflux during summer agreed to within ~ 10% for three lakes (Diefenbaker, Wascana, Katepwa) (Table 2), while comparison of C outflow and influx in adjacent lakes agreed to within ~ 20% for both Katepwa and Crooked Lakes (Table 3). Therefore, while mass budgets of some lakes appeared to be missing significant C sources (Last Mountain, Buffalo Pound, Crooked) (Tables 2, 3), the high overall similarities among lakes (Fig. 5) suggested that insights concerning the relative magnitude of summer C fluxes, particularly exports, were robust to errors of measurement or omission.

Despite potential omissions, comparison of mass-balance budgets among Qu'Appelle lakes confirmed that these lakes were sites of intense C processing (Tables 2, 4), consistent with research findings from soft-water (Benoy et al. 2007; Cole et al. 2007) and saline lakes (Duarte et al. 2008). However, unlike previous studies, we found that these hard-water lakes sequestered far more C in sediments than was released to the atmosphere (Fig. 5), despite individual years of intense CO₂ invasion or loss (Fig. 2). Interestingly, this pattern holds even if budgets are constructed only with organic or inorganic C fluxes (Fig. 5; Table 2). In fact, we infer that sediment sequestration of C may overwhelm atmospheric CO₂ exchange in many hard-water and saline lakes of the northern Great Plains both because pH, *p*CO₂, and net summer CO₂ flux vary coherently within this region of > 100,000 km² (Finlay et al. 2009) and because the hydrology, and therefore C influx, of these closed-basin lakes is regulated by the same spring snowmelt mechanism that occurs in Qu'Appelle lakes (Pham et al. 2009). Furthermore, because OC deposition varies with water residence time, we anticipate that C sedimentation should be proportionately more important in closed-basin lakes than in the Qu'Appelle catchment, although we recognize that validation of this hypothesis will require complete mass balances in saline lakes.

A new model of C flux in lakes—Comparison of mass budgets suggests a new model of ecosystem function in which the processing of IC and OC influxes by lakes occurs through parallel but weakly coupled mechanisms. For example, estimates of NEP_{OC} suggest that all study lakes produce OC (net autotrophic), whereas estimates based solely on IC flux (NEP_{IC}, NEP_P) suggest a variable metabolic status among lakes, a pattern that is more consistent with observed patterns of net CO₂ exchange (Fig. 2; Table 2) and with other mass balances in hard-water lakes (Stets et al. 2009). Similarly, previous statistical analysis demonstrates that CO₂ exchange is largely uncorrelated with the intensity of microbial metabolism or DOC content in Qu'Appelle lakes (Finlay et al. 2009),

unlike many boreal systems (Prairie 2008). Finally, we suggest that differential effects of hydrology on IC and OC fluxes may arise because the mechanisms converting dissolved C into particulate matter differ between IC and OC. In the Qu'Appelle lakes, sedimentation and lotic export of OC may be correlated with water residence time ($r^2 = 0.613-0.729$, $p \sim 0.05$) because most OC in these lakes is dissolved (Tables 1, 2), DOM flocculation is slow and light dependent (von Wachenfeldt et al. 2008; von Wachenfeldt and Tranvik 2008), and sinking of particulate OM is slower in these polymictic lakes than in stratified systems. In contrast, permanent deposition of particulate IC (CaCO₃) depends mainly on changes in the solubility of DIC species arising from seasonal variation in temperature, pH, total DIC content, and biological productivity both in the water column and at the sediment surface (Stumm and Morgan 1996). Because these latter factors exhibit landscape gradients that are independent of mean water residence time (Table 1), sedimentation of IC varies little as a function of hydrology in Qu'Appelle lakes (Fig. 3).

Synthesis of whole-lake C studies suggests that IC and OC fluxes are weakly coupled in most lakes but that the nature of the mechanism coupling IC and OC pathways may be dependent on the relative magnitude of organic and inorganic subsidies from land. For example, experimental addition of ¹³C-DIC to small boreal lakes reveals that DOC is used readily by aquatic heterotrophic bacteria but that algae process CO₂, while fish metabolize mainly terrestrial POC (Cole et al. 2006; Pace et al. 2007). In those systems, most C is derived from terrestrial DOC, while IC and OC pathways are coupled mainly by planktonic (Cole et al. 2007; Prairie 2008) and benthic metabolism (Ask et al. 2009), particularly at subannual timescales (Hanson et al. 2006). In contrast, external inputs of IC appear to regulate the C content of hard-water lakes at all timescales (Table 2) (Stets et al. 2009), while mainly chemical mechanisms (pH, precipitation) provide the weak linkage between IC and OC fluxes (Duarte et al. 2008; Finlay et al. 2009). Although this weakly coupled dual flux model is tentative and requires validation, we note that it is consistent with predictions of the *Em* flux framework of Leavitt et al. (2009) in which the relative effects of energy (*E*) or mass (*m*) influx on ecosystem function are greatest when influx composes a high proportion of lake content.

Implications for climate effects on lakes—Modest extrapolation of the findings of the whole-lake C budgets suggests that future climate variability will affect C flux through prairie lakes mainly by altering influx of water and solutes, as suggested elsewhere for studies of nitrogen influx (Patoine et al. 2006; Bunting et al. 2010). Although *E* influx during summer (irradiance, atmospheric heat) causes synchronous seasonal changes in lake chemistry (evaporative concentration) that can alter CO₂ fluxes over large spatial extents (Duarte et al. 2008; Finlay et al. 2009), mass-balance studies suggest that atmospheric CO₂ exchange represents only a small component of total C flux in hard-water lakes (Fig. 5; Table 2) despite substantial chemical enhancement. Instead, stable isotope analyses ($\delta^2\text{H}$, $\delta^{18}\text{O}$) demonstrate that lakes of the northern Great Plains are

sustained over decades by the influx of meltwater derived from winter precipitation (Pham et al. 2009), the same mechanism that regulates IC and OC influx to Qu'Appelle lakes through rivers. Unfortunately, regional snow packs have declined ~ 30% since 1970 (Akinremi et al. 1999), whereas human consumption of river water has increased to a historical maximum (Schindler and Donahue 2006). Taken together, these patterns suggest that the influx of IC to prairie lakes will decline in a future warmer-drier climate, while OC sedimentation should increase due to prolonged water retention, leading to a reduction in total C content of hard-water lakes.

At present, it is difficult to forecast how future climate change will alter the role of hard-water lakes in global C balances (Downing et al. 2008; Tranvik et al. 2009). For example, while reduced water influx should decrease DIC content and the intensity of CO₂ evasion, nutrient input to lakes should also decline (Schindler and Donahue 2006; Leavitt et al. 2009; Bunting et al. 2010), constraining autotrophic production and consumption of CO₂, while evaporative concentration of lakes may partly offset reduced subsidies of allochthonous IC (Duarte et al. 2008). On the other hand, declining winter runoff should also reduce influx of allochthonous OC and its processing by heterotrophic bacteria. Ultimately, we believe that this conundrum can be best resolved by developing decade-long time series of annual mass-balance budgets such that the consequences of interannual variation in hydrology and atmospheric CO₂ exchange can be more clearly identified.

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