Multidecadal carbon sequestration in a headwater boreal lake

Britt D. Hall,* Raymond H. Hesslein, Craig A. Emmerton, Scott N. Higgins, Patricia Ramlal, Michael J. Paterson

Abstract

Dissolved organic carbon (DOC) was measured continuously since 1970 in a pristine headwater boreal lake and its catchment at the IISD-Experimental Lakes Area (Ontario, Canada). Mass balanced accounting of DOC concentrations in precipitation, watershed runoff, and inflow and outflow streams, and integrated weekly hydrological data determined annual mass flux of DOC to and from the lake. Inputs minus outputs represented two residual terms: (1) mineralization and evasion of CO2 and (2) DOC flocculation and sediment burial. Accumulation of organic carbon in sediment cores estimated permanent storage and evasion was calculated by subtraction of burial from the annual retention over 40 yr (1971–2010). Terrestrial sources accounted for 92% ± 1% of DOC load; 37% ± 2% of which was lost via the outflow. About 40% ± 3% of DOC load accumulated in sediments and 23 ± 3% was lost as CO2. Over 40 yr, C sequestration in sediments was a more important sink than evasion or outflow. We explore the fate of DOC during decade long periods of differing precipitation patterns. Loading and loss via the outflow was higher in wet (1990–2010) compared to dry (1980–1990) years. Due to longer DOC processing times when water residence times are longer, it is possible that if drought increases in the boreal forest, the efficiency of headwater lakes to sequester C in sediments maybe greater than in wet periods.

Dissolved organic carbon (DOC) in aquatic systems plays a central role in global carbon cycling, with lakes and rivers acting as important sources and transit routes of carbon from terrestrial ecosystems to the large carbon pools in the ocean and atmosphere (Williamson et al. 1999; Algesten et al. 2003; Cole et al. 2007; Prairie 2007; Tranvik et al. 2009; Hanson et al. 2011). However, inland aquatic systems are not simply passive transport conduits of DOC. Numerous processes that occur in lakes impact not only the amount of DOC transferred to downstream systems, but also biogeochemical cycling and energy flow within lakes. These processes include carbon sequestration via burial in sediments (Molot and Dillon 1996), provision of energy for heterotrophic metabolism (Kling et al. 1991; Wetzel 2001; Smith and Prairie 2004), enhancing solubility and transport of metals while reducing metal bioavailability (e.g., Driscoll et al. 1988; Aiken et al. 2011), and the protection of biota from the effects of ultraviolet radiation (Scully and Lean 1994; Schindler et al. 1996; Molot et al. 2004). DOC can also strongly influence the temperature structure in lakes because of attenuation of light (Rasmussen et al. 1989; Fee et al. 1996; Snucins and Gunn 2000). The importance of DOC processes in lake functioning has led to the concept that inland water systems act as “active pipes” (Cole et al. 2007) and a new paradigm of “carbocentric” classification of lakes has been suggested (Williamson et al. 1999; Prairie 2007).

Carbon cycling within lakes is a complex balance between external additions and losses of carbon to and from lakes, and internal processing and storage within them. Although autotrophic fixation and other processes generate DOC in lakes, run off from forested watersheds provides the major proportion of DOC to oligotrophic aquatic systems (Wetzel 2001; Kritzberg et al. 2005; Kortelainen et al. 2006a). As a result, the type of vegetation and the wetland coverage in the catchment area determine both the amount and the chemical composition of DOC loaded to the lake (Dillon et al. 1997; Curtis and Schindler 1997; Ågren et al. 2008). Once in the lake, DOC leaves via the outflow stream or is available to be modified by internal biophysical processes. DOC is either mineralized in the water column (Cole and Caraco 2001; Bertilsson and Jones 2003) or flocculated and settled to the bottom of the lake (von
Wachenfeldt et al. 2008, 2009; von Wachenfeldt and Tranvik 2008). The labile portion of DOC is mineralized leaving the remainder for long-term burial (Sobek et al. 2009; Gudasz et al. 2012). The dissolved CO₂ produced by mineralization in the littoral and profundal sediments as well as in the water column either flows out of the lake or is degassed to the atmosphere (Dillon and Molot 1997; den Heyer and Kalff 1998; Algesten et al. 2005). Due in part to challenges associated with accurately measuring these individual processes (Raymond and Bauer 2001; Matthews et al. 2005; Battin et al. 2009; Hanson et al. 2011; Guillemette et al. 2017) and the lack of long-term holistic monitoring studies, there remains uncertainty in assessing the fate of carbon within lakes (Hanson et al. 2004; Benoy et al. 2007; Cole et al. 2007; Holgerson and Raymond 2016). Careful, long-term mass balance studies on lakes (Schindler et al. 1976), are therefore required to better understand carbon cycling and their net exchange of carbon with other ecosystems.

Though mass balances can be effective tools for understanding how DOC cycles in lakes, their interpretation over long-time periods can be complicated by seasonal and hydrological changes (Sobek et al. 2007; Diodato et al. 2016). For example, during periods of heavy rainfall and runoff in forested catchments, delivery of DOC to lakes typically increases (Solomon et al. 2015) and illustrates the close linkages between forested watersheds and waterbodies (Schiff et al. 1998; Einola et al. 2011). Greater runoff and DOC loading to lakes may result in both increased storage of DOC within the lake and higher losses to downstream aquatic systems due to shorter water residence times. On the other hand, dry periods may allow lakes to more effectively process DOC and allow increased sedimentation due to longer water residence times, but supply from the watershed can be limited during these periods (Schindler 1997; Dillon and Molot 2005). Using a combination of lake mass balance studies with long-term meteorological monitoring may provide opportunity to understand how carbon cycling in lakes responds to measurable climate shifts that are ongoing globally, especially in lake-rich northern regions (Adrian et al. 2009).

Here, we use a 40-yr historical record of annual DOC mass balances in a headwater boreal system to assess how several components of lake carbon cycles respond to substantial changes in precipitation, DOC loading, and lake water retention time (WRT). Specifically, we focus on how carbon retention changes with climate and by using estimates of long-term carbon accumulation in sediments, we estimate CO₂ evasion from allochthonous DOC inputs.

Methods

Study site and lake hydrology

Lake 239 (L239; also known as Rawson Lake) is a 55 ha headwater lake at the IISD-Experimental Lakes Area (ELA) in Canada’s western Boreal Shield ecozone (49°39'34.84"N, 93°43'39.84"W) (Brunskill and Schindler 1971). The lake has a maximum depth of 30.4 m (mean: 10.9 m) and has little shoreline development except for a small bay off of its southwest corner. A 339 ha watershed surrounds L239 consisting mostly of a 35 yr old fire regenerated jackpine (Pinus banksiana) forest, thin Brunisolic soils, and extensive areas of exposed granitic bedrock. The climate of the ELA is characterized as Continental, with moist, warm summers (DfB; Köppen, Peel et al. 2007). Mean annual air temperature (1981–2010), as measured at the Rawson Lake Meteorological Station within the watershed, ranges from 1°C to 3°C with coldest conditions in January (daily mean: −16.0°C) and warmest conditions in July (mean: +19.7°C). Mean annual total precipitation is 710 mm (range: 488–1018 mm) with 56–87% (mean: 75%) falling as rain. ~ 60% of all precipitation falls between May and September each year, typically as storm events (McCullough and Campbell 1993).

Lake 239 receives nearly all of its water and chemical inputs from three first-order streams (draining 239 ha), other unmeasured runoff (100 ha), and direct precipitation onto the lake surface (Fig. 1). The East (EIF; 170.3 ha) and Northwest (NWIF; 56.4 ha) inflows primarily drain upland soils but pass through areas of wetland before discharging to the lake. The Northeast inflow (NEIF; 12.4 ha) drains a small bog wetland before flowing into the lake. The flow from all three streams has been monitored continuously since 1971 using calibrated v-notch weirs and automatic water level recorders (Beaty and Lyng 1989). Precipitation has been measured at the meteorological station (Fig. 1) using standard and tipping-bucket rain or Nipher snow gauges and is scaled to lake area to estimate precipitation volume added directly to the lake surface. The water level of L239 has been automatically monitored at a shoreline stilling well since 1970 while, during the same period, flow exiting the lake (outflow) has been measured using a Parshall flume and an automatic water level recorder. Groundwater inputs to the lake through bedrock cracks are negligible (Beaty 1981a), which permits estimates of evaporative loss from the lake surface during open water conditions via hydrologic budgets (Beaty 1981b).

Budget calculations

Mass balance budgets are an effective method of quantifying the cycling of constituents in lakes. Subtracting measured outputs of DOC from DOC inputs in precipitation, inflows, and runoff yields the annual retention of DOC and includes a residual term of evasion following DOC mineralization (either photo-lytically or biologically) combined with storage following flocculation and sedimentation. Lake 239 was represented in the budget model by two well-mixed boxes, the epilimnion, and the volume below the epilimnion. Epilimnion depth (as defined by temperature changes > 0.25°C per 25 cm) was measured at biweekly intervals during the ice-free season, and linearly interpolated between sampling date; WRT was calculated as the lake volume divided by outflow volume. Because L239 is dimictic, the volume of the epilimnion box is equal to the lake volume during the spring and autumn mixing period when the water column is isothermal, and during the ice-covered period. However, it is well known that the whole lake does not continue to

S151
mix rapidly under the ice (Jansen and Hesslein 2004). As soon as the epilimnion is created in the spring, the volumes of the two boxes are redefined. As a result of using the two-box model, during the stratified period the inflows are only diluted into the volume of the epilimnion and the outflow only depletes the epilimnion as actually occurs in the lake. Simulations of conservative constituents Ca, Mg, Na, and K (data not shown) demonstrated that the model approach using data driven inputs and outputs matched the amounts measured in the lake very well. For simulations of conservative constituents, the use of a two-box model made only a small difference to the budget calculations, however, more labile constituents could be significantly affected. The model assumed that there was no change in water storage in the lake. While small changes in water storage may have occurred on an annual basis (to a maximum of 0.25 m [1980–2011] such changes represented only ~ 2% of the lake volume; Emmerton et al. 2018), these annual differences were negligible for the mass of water or dissolved chemicals.

**Inputs and outputs via precipitation and streams**

Annual inputs, outputs, and masses of DOC in L239 were calculated using the modeling software STELLA® (isee systems) and hydrological and chemical data collected over a period of four decades. Inflow, outflow, and precipitation data were calculated using daily time steps, from which annual averages (± SE) were calculated as described in Eq. 1.

\[
\text{Annual retention of DOC (mmol m}^{-2}\text{yr}^{-1}) = \text{Inputs} - \text{outflow} \pm \Delta \text{mass}_s,
\]

where Inputs = DOC inputs from precipitation and runoff; outflow = DOC loss via the L239 outflow; and \(\Delta \text{mass}_s\),
represents the annual change due to water storage which was negligible over the 40-yr time period.

Inputs from precipitation were calculated by multiplying DOC concentrations by precipitation volumes to the surface of L239. Daily estimates of inflows and outflows of DOC were calculated by multiplying daily flows by linearly interpolated concentrations in samples collected weekly (Beatty and Lyng 1989; Dillon and Molot 1997; Heagle et al. 2007). Daily inflows from the areas of the terrestrial watershed not drained by streams (100 ha ungauged drainage) were estimated by multiplying the area of ungauged drainage by the per unit area inflow of a 50/50 mixture of the inflows from the East and Northwest sub-basin streams, as described in Hesslein et al. (2009). Yields of DOC into and out of the lake via streams were divided by the area of L239 to present mass of DOC per unit area. Annual budgets for suspended C (Susp C), dissolved inorganic C (DIC), and total C were calculated using the same model and methods as with DOC.

**Loss to sediments and atmosphere**

The “Annual retention of DOC” term of Eq. 1 combines two components: (1) flocculation followed by net sedimentation and subsequent burial (henceforth “Burial”); and (2) pelagic and hypolimnetic mineralization followed by evasion of CO₂ and possibly CH₄ to the atmosphere (henceforth “Evasion”). Although CO₂ from DOC can be fixed by primary producers, we assume that newly fixed DOC will be highly labile and rapidly mineralized (Nalewajko and Schindler 1976; Guillemette et al. 2013). Burial was quantified using dated cores (see below) and this was subtracted from the annual retention of DOC to provide Evasion, as follows:

\[
\text{Evasion} = (\text{Inputs} - \text{Outflow} \pm \Delta \text{mass}_v) - \text{accumulation in cores.} \tag{2}
\]

**Burial**

Estimates of net sediment accumulation of C were obtained using ²¹⁰Pb dated sediment cores collected at nine depths (9.5–30.1 m) in L239 in 1980 and 1987 (Supporting Information Table S1) (Kippht 1978; Curtis 1991).Dating of cores using ²¹⁰Pb provided us with a long-term record of carbon deposition to sediments and we assume that this core data represents burial rates during the years for which we have budget data. To estimate whole-basin accumulation (Engstrom and Rose 2013), we corrected for the area of deposition in L239 by taking the proportion of area below the depositional zone of the average of all cores using Rowan et al. (1992).

**Movement of material to the hypolimnion**

Sedimentation traps, as well as the model, were used to estimate rates of C transported between the two modeled boxes (epilimnion and below epilimnion) via sedimentation. The rate of sedimentation was measured by collecting material from a number of traps placed in various locations greater than 8 m depth in the lake from May 1985 to May 1986 (Curtis 1991) and from late June 2002 to late October 2002. Material was collected weekly during the summer, biweekly during the spring and fall, and monthly during the ice-covered periods. Samples were pooled, dried, weighed, and ground with a mortar and pestle prior to analysis of C content. Sedimentation rates, calculated on a daily basis, were equal to 0.2 m d⁻¹ and were extrapolated to an annual rate by multiplying by average number of ice-free years between 1969 and 2000 (200 d). To obtain the mass of C as DOC in traps, concentrations of DOC in the water column were multiplied by the volume of water in the traps, which was then subtracted from the total weight of trap material. A single first-order rate constant for flocculation selected by iteration and a single settling velocity chosen from literature values were used to produce modeled DOC concentrations for the lake that were consistent with the 40 yr data record. Model iterations (not shown) present the total rate at which DOC flocculates within the water column of L239 as ~ 0.0008 d⁻¹ (29.2% per year). The two-box model splits this as ~ 0.0012 d⁻¹ in the epilimnion and ~ 0.0007 d⁻¹ in the hypolimnion (based on Curtis and Schindler 1997). This flocculated DOC becomes part of the Susp C pool in the lake and is then removed by settling at 0.2 m d⁻¹, consistent with data from sediment traps in L239. These rates of settling produced in model iterations were also consistent with the rates reported from other studies of lakes (Baines and Pace 1994; Effler and Brooks 1998). All of these estimates consider the contribution of autochthonous C to long-term burial to be minimal, in part because quality of autochthonous C is likely such that it is rapidly mineralized. We confirmed this in our study by calculating the contribution of algal fixation in our lake to C settling in traps. The C from biomass of algal material settling to the hypolimnion was calculated by multiplying annual estimates of algal biomass (Supporting Information Table S2) collected as described in Findlay et al. (2001) by the settling rates obtained from sedimentation traps. Finally, we used Susp C mass balance budgets (see above) to confirm that particulate C inputs from the watershed were minimal. We assumed that aerial inputs of C to the lake (aside from those in precipitation) were zero.

Generally 50–90% of suspended organic matter is lost in the process of sedimentation as evidenced by measurements of quality and decomposition rates of C in sediments vs. traps (Fallon and Brock 1980; Cole et al. 1984; Hilton 1985; Baines and Pace 1994; Cuddington and Leavitt 1999; Guillemette et al. 2017). In fact, in a similar oligotrophic lake at the ELA, Stephenson et al. (1995) found that only 10% of radioactively labeled C added to the lake ended up in the long-term sedimentary record. As a result, we adjusted our Burial values by 10% to account for algal remains in sediments.

To provide a comparison of our evasion rates with DIC available for evasion from the lake, we estimated the pool of DIC in the hypolimnion, by calculating the rate of
accumulation of DIC below 5 m. We choose 5 m because the depth of the epilimnion was never greater than 5 m. Concentrations of DIC were collected every 5 m from surface to maximum depth during the ice-free season between two and four times in 27 of 40 yr in our dataset. Concentrations were multiplied by the volume of water in each depth zone and summed to obtain the mass of C as DIC in the entire lake for each time period. The rate of change was calculated for each time period by taking the slope of a regression between mass and sample day and extrapolated to an annual rate by multiplying by 365. Finally, rates were converted to mass C (DIC m⁻² lake area yr⁻¹) by multiplying by total lake area. The accumulation of mineralized organic C as DIC in the hypolimnion represented both autochthonous (C fixation by primary producers) and allochthonous (flocculated DOC) sources.

Evasion

The loss of C to the atmosphere was calculated by subtracting the long-term rates of C burial and outputs via the stream outflow from the total inputs (mmol m⁻² yr⁻¹) as in Eq. 2 above.

Sample collection

Since 1970, surface-water samples have been collected weekly from each inflowing stream and from the lake outflow for analyses of water chemistry. Water sampling of L239’s pelagic water column occurred approximately bi-weekly over the course of the ice-free season. During each sampling effort, lake water was collected from the epilimnion using a depth-integrating bottle sampler. Discrete-depth sampling at 5 m, 10 m, 15 m, 20 m, and 25 m (using a Van Dorn sampler in the earlier decades and small pump in more recent decades) was conducted monthly during the ice-free period. Water from L239 was also collected periodically through the ice (1–2 times per year) at discrete depths starting just below the base of the ice, and then every 5 m to near the lake bottom. In all cases, water samples were collected in precleaned plastic bottles and transported to the ELA’s onsite laboratory within 1–2 h of collection.

Bulk precipitation for chemical analyses was collected at one of three locations during the monitoring history of the L239 watershed; collectors deployed on islands near lake-level within L239 and nearby Lake 240 and at the meteorological station. All samples were collected into a secured plastic bucket lined with a clean plastic bag. Large particles were removed or were prevented from entering the collector by a 1 mm nylon mesh. Samplers were typically operational between May and November each year; however, a continuous series of accumulated snow was collected periodically during the monitoring record during colder months.

Sample processing and analyses

All DOC samples were initially filtered through precombusted Whatman GF/C filters, acidified, stripped of inorganic carbon, and digested with acid persulfate by autoclaving (1971–1975), irradiating with UV (1975–1985), or heating to 102°C (1986 and after). The resulting CO₂ was measured by gas chromatography (thermal conductivity detector 1971–1979) change in specific conductance after barium stripping (1976–1985) or infrared absorbance (1986 and after). DIC was determined by acidifying sealed whole water samples and analyzing a portion of the gas in the headspace as with CO₂ from DOC digestion above. Method changes were extensively intercalibrated to ensure that all data were comparable. Protocols and methods of analyses in detail are given by Stainton et al. (1977) and Stubbins and Dittmar (2012).

Results

Water budgets

Inputs

Water inputs to L239 occurred via streamflow from the watershed and precipitation directly onto the lake surface (Supporting Information Table S3 and Fig. S1A). Typically, 20–40% of precipitation falling on the terrestrial watershed entered the lake via streamflow or as runoff from the undefined drainage area. Overall, 60–75% of water inputs to the lake were via stream inputs from the watershed, with the remainder comprising precipitation directly to the lake surface.

Throughout the record, annual precipitation ranged from 0.48 m yr⁻¹ to 1.02 m yr⁻¹ (0.71 ± 0.02 m yr⁻¹) with ~15–50% falling as snow (Supporting Information Figs. S2, S3). Long-term trends in total precipitation followed a sinusoidal pattern with a 30- to 37-yr cycle (Parker et al. 2009; Diodato et al. 2016). Underlying this pattern was an increase in long-term precipitation (12.4 ± 4.6 mm decade⁻¹), and since 1990 sustained high-annual rainfall has led to an intensive “wet” period relative to earlier portions of the data series (Emmerton et al. 2018). As a result, and as illustrated by long-term running means (Supporting Information Fig. S2), the data series can be broken into periods of intermediate (“intermediate” period; 1970–1980), low (“dry” period; 1980–1990), and high (“wet” period; 1990–2010) precipitation. These decadal trends were often punctuated by wet and dry years that were outside of the 10-yr running means (Diodato et al. 2016). Outlying years include 1977 and 1985 (wet years in an intermediate and dry period, respectively), 1976 (dry year in an intermediate period), and 2003 and 2006 (dry years in a wet period).

Annual water inputs from streams were highly correlated with total precipitation ($r² = 0.62, 0.70, and 0.74$ for EIF, NWIF, and NEIF, respectively; Supporting Information Fig. S1B). However, deviations arise because the fraction of watershed precipitation that enters the lake is dependent on antecedent moisture conditions and proportion falling as snow or rain. Water inputs via the three inflowing streams were generally similar to each other ranging from ~0.06–0.09 m yr⁻¹ in dry
years and 0.4–0.5 m yr\(^{-1}\) in wet years (Supporting Information Table S3). The fraction of total precipitation exported from each sub-basin reflected the influence of antecedent moisture and evapotranspiration and ranged from 10% to 58% (Supporting Information Fig. S1C). Prior to 1985, the decadal average snow to rain ratio was higher than in later years (45% prior to 1985 and 30–33% in all subsequent years; Supporting Information Fig. S3). As a result, runoff yields in the early study period were higher because more runoff occurred over frozen ground prior to spring thaw.

**Outputs**

Water loss from the watershed of L239 occurred via one gauged outflow stream flowing into Lake 240 (0.06–0.4 m yr\(^{-1}\)) and via evaporation from the surface of the lake (0.13–1.12 m yr\(^{-1}\); Supporting Information Table S3). Losses via evaporation were calculated as the difference between gauged outflow and the sum of inputs from precipitation and gauged inflow streams. Because evaporation was calculated by difference, as opposed to being measured directly, this term also includes error associated with the other water budget parameters.

**Water residence time**

WRT is an important parameter to consider in mass balance budgets of constituents that are transformed by in-lake processes (Hanson et al. 2011). For example, the longer DOC is held in the lake, the longer the opportunity for photodegradation of complex forms to simpler forms which may be more easily mineralized to CO\(_2\) (Vachon et al. 2017). In L239, the WRT ranged from 3.5 yr to 21.5 yr. Antecedent moisture, evaporation, and transpiration can change the fractional yield of precipitation so that the same amount of precipitation can result in different WRT in different years and therefore changes in WRT can be much more exaggerated than changes in precipitation. For example, in L239, the decadal running average WRT in the 1970s was 6 ± 1 yr and was equal to that of the 1990s and 2000s even though annual precipitation in the 1970s was lower. A seasonally later thaw of ground and higher percentage snow during the 1970s compared to later years resulted in higher water yields from the watershed during spring. In the dry period over the course of the 1980s, the mean average WRT was 13 ± 2 yr. Cooler temperatures, lower evapotranspiration, or a different forest condition due to changes over time or with fire could all contribute to different WRT because all of these parameters could change the fraction yield of precipitation from the watershed.

**DOC budgets**

**Inputs**

Measured inputs of DOC from all sources ranged between 925 mmol m\(^{-2}\) yr\(^{-1}\) and 4933 mmol m\(^{-2}\) yr\(^{-1}\), with an average of 2527 mmol m\(^{-2}\) yr\(^{-1}\) across all years. Although precipitation contributed to DOC inputs to the lake (< 2–23%; mean = 7.6% ± 0.8% total annual DOC inputs), the majority of DOC was delivered to L239 via inputs from watershed runoff, which as described above, were influenced in a positive nonlinear relationship by precipitation route (Supporting Information Table S4). The export of DOC on a per unit area basis from watersheds was highest from the EIF (172 ha) (33–54% of total DOC inputs; Fig. 2A,B), which is the largest sub-basin of the lake (Fig. 1). Ungauged watershed runoff (100 ha) was also important (21–35% of total inputs),

![Fig. 2. Forty-year record of (A) DOC yield per m\(^2\) of lake surface (mmol DOC m\(^{-2}\) yr\(^{-1}\)), (B) the proportion of total DOC inputs (percentage of total inputs) from individual streams, run off, and precipitation, and (C) the retention (Evasion + Burial) of DOC in the lake.](image-url)
followed by the two other inflow streams (9–21% and 4–9% of total inputs for NWIF [56 ha] and NEIF [14.5], respectively; Fig. 2, Table 1). Loads of Susp C and DIC (40-yr average = 176 ± 11 mmol m⁻² yr⁻¹ and 379 ± 10 mmol m⁻² yr⁻¹, respectively) in precipitation and runoff were low relative to those of DOC (40-yr average = 2527 ± 173 mmol m⁻² yr⁻¹).

Table 1. Total input and outputs of Dissolved organic carbon (DOC) per m² lake area over 40 yr.

| Year | Total inputs (I) | Retention | L239 outflow (OF) | Sedimentation | Evasion |
|------|------------------|-----------|-------------------|---------------|---------|
|      | mmol m⁻² yr⁻¹   | %         | mmol m⁻² yr⁻¹     | mmol m⁻² yr⁻¹ | mmol m⁻² yr⁻¹ |
| 1971 | 3085.57          | 51.5      | 1495.67           | 836           | 753.8   |
| 1972 | 2437.33          | 59.8      | 979.65            | 836           | 621.6   |
| 1973 | 2587.19          | 49.2      | 1314.37           | 836           | 436.7   |
| 1974 | 2801.41          | 52.0      | 1345.82           | 836           | 619.5   |
| 1975 | 2148.21          | 44.4      | 1195.20           | 836           | 116.9   |
| 1976 | 1060.42          | 47.5      | 556.25            | 836           | 5.4     |
| 1977 | 2420.44          | 60.0      | 967.33            | 836           | 25.5    |
| 1978 | 2392.28          | 58.6      | 990.17            | 836           | 23.7    |
| 1979 | 1522.10          | 58.0      | 638.62            | 836           | 3.1     |

Mean ± SE 2527 ± 173 63 ± 2 940 ± 71 37 ± 2 836 ± 0 40 ± 3 751 ± 118 23 ± 3
The fraction of total DOC inputs from precipitation were greater in the dry and intermediate periods (mean = 14% + 2% and 9% ± 1%, respectively; Fig. 2B) compared to the wet periods (mean = 4% ± 1%) because during dry period watershed inputs decreased due to more retention of precipitation by basin areas.

**Outputs**

**Outflow stream**

Loss of DOC via the lake outflow stream ranged between 225 mmol m⁻² yr⁻¹ and 1878 mmol m⁻² yr⁻¹ (mean = 940 ± 71 mmol m⁻² yr⁻¹), representing between 14% and 56% (mean = 37% ± 2%) of total annual inputs from precipitation and runoff (Table 1; Fig. 2C). The percent of total DOC input loss via the outflow was greatest in the intermediate period (mean = 45% ± 2%) compared to the wet and dry periods (36% ± 2% and 31% ± 4%, respectively).

**Burial**

Since sediment cores represent time periods of many years (typically 40 yr or more), we used an average burial rate of 1080 ± 34 mmol C m⁻² yr⁻¹ calculated from all cores (Supporting Information Table S1). This was adjusted to the area of deposition by multiplying by 0.86. Because the contribution of algal material in our lake was small (see below) and in keeping with literature values suggesting that the majority of algal contributions to sediments are rapidly mineralized, we decreased our storage values by 10% to account for autochthonous material in the cores. Therefore, the average C contributed by DOC was 836 mmol m⁻² yr⁻¹.

**Movement of material to the hypolimnion**

The settling traps gave annual values of 1498–3447 (40 yr average = 2463 ± 427) mmol m⁻² yr⁻¹ of C settled to the traps (Supporting Information Table S5). Of that material, we estimated an average of 202 ± 12 mmol m⁻² yr⁻¹ to be contributed by algal biomass (Supporting Information Table S2) and mass balance budget calculations showed that the retention of SuspC was only 99 ± 8 mmol m⁻² yr⁻¹ (Supporting Information Table S6). The accumulation of DIC in the hypolimnion ranged from 1458 mmol m⁻² yr⁻¹ to 3621 mmol m⁻² yr⁻¹, with a 40 yr annual average = 2115 ± 175 mmol m⁻² yr⁻¹ (Supporting Information Table S2).

**Evasion**

The differences in total inputs and outflow of DOC represent the annual retention of DOC, which can be lost via: (1) mineralization and subsequent evasion; and (2) flocculation and subsequent burial (Fig. 2C). When C Burial was subtracted from the annual retention of DOC (as per Eq. 2), evasion rates ranged between −332 mmol m⁻² yr⁻¹ and 2445 mmol m⁻² yr⁻¹, with a 40-yr average of 751 ± 118 mmol m⁻² yr⁻¹ (Supporting Information Table S2). In several years, the subtraction of carbon burial from the annual retention of DOC as in Eq. 2 yielded a negative evasion term. We attribute this to the use of short-term annual budget data and long-term, low-resolution burial data.

**Discussion**

Lake 239 is a typical first-order boreal lake that receives the majority of DOC as runoff from terrestrial parts of the watershed. Once in the lake, a small portion of DOC may be taken up by biota, but the majority of DOC has three fates: (1) Some DOC is flocculated and settles to the bottom of the lake. A portion of this material is mineralized leaving the remainder for long-term burial in the sediments (Ferland et al. 2014); (2) another portion of the DOC is mineralized in the water column, which then evades to the atmosphere or is used in
primary production; (3) the remaining DOC flows out of the lake and downstream. The total DOC in the lake is therefore made of “year classes” each of which, as they age, has had progressively more DOC flocked and settled, mineralized, or released via the outflow (Duffy et al. 2018). Highly labile material such as recently deposited algal material and flocculated DOC will be preferentially mineralized (Fallon and Brock 1980; Cole et al. 1984; Baines et al. 1994; Sobek et al. 2009; Gudasz et al. 2012; Koehler et al. 2012). Flocculation and mineralization works faster on this “younger” labile DOC pool (Raymond and Bauer 2001; Hanson et al. 2011; Koehler et al. 2012; Guillemette et al. 2017) such that DOC lost via the outflow over time is more recalcitrant than “younger” DOC from the inflows. In wet periods, the proportion of “younger” DOC released out the outflow would be greater than in dry years because in wet years more DOC entered the lakes via runoff, and increased outflows would be associated with shorter WRTs and reduced in-lake DOC processing. Similarly, settled DOC represented a mixture of ages and each year the new sediment layer would consist of flocc from that mixture. While the average age of this new layer likely affects the rate at which it is mineralized to CO₂, lability will decrease over time (Koehler et al. 2012). So, more precipitation and runoff would introduce more labile DOC that would increase CO₂ production, but would also increase the water outflow (i.e., reduce water residence time) and, therefore, DOC and DIC lost to downstream.

Our mass balance budget model representing these processes and tested with 40 yr of data showed that on average 92% ± 1% of the externally derived DOC came from terrestrial sources. The proportion of total DOC inputs derived from direct precipitation inputs ranged from under 5% in wet years to over 22% in dry and 8% in intermediate years (Figs. 3, 4). Over 40 yr, an average of 37% ± 2% of the total load of DOC was lost via the outflowing stream. The loss of carbon via long-term burial and evasion represent low-resolution data as compared to the retention term that was calculated using data collected at finer scales. The Burial of carbon in sediments represented an average carbon loss of 40% ± 3% and the average loss via Evasion was 23% ± 3% of total C inputs (Fig. 5A). We confirm Curtis and Schindler’s (1997) conclusion that DOC retention in L239 is correlated with WRTs (Supporting Information Fig. S4). While we acknowledge that DOC can be generated from living and decomposing biota, as well as decomposition of particulate C loaded from the watershed, we show that DOC dominates the C budget in our lake and these sources are, as such, negligible.

Evidence aside from the mass balance calculations support our conclusion that DOC is the dominant form of C that is sequestered in L239. Between 2000 mmol and 3000 mmol of C m⁻² yr⁻¹ were collected in sediment traps and includes both autochthonous and allochthonous material in varies stages of decomposition. The contribution from inputs of algal biomass and terrestrial Susp C in L239 was less than 10% and 5% of the C in the traps, respectively. Neither of these sources support the amount of C in the traps, so we assumed that the majority of the trap material must have been flocculated DOC. If we assume that of the material in the traps, 836 mmol C m⁻² yr⁻¹ was buried in sediments, the subtraction of that buried C from the sediment trap C yields 1200–2000 mmol C m⁻² yr⁻¹ available to the water column either as DIC or DOC. Of this C, we calculated that on average 751 mmol C m⁻² yr⁻¹ was evaded as CO₂, leaving between 450 mmol C m⁻² yr⁻¹ and 1250 mmol C m⁻² yr⁻¹ unaccounted for. This C could be fixed, lost to the outflow, or

![Fig. 4. (A) Average annual mass of DOC inputs and outputs (g C m⁻²) ± SE over the complete data series (1971–2010); and conceptual diagrams during (B) “wet” and (C) “dry” periods. WRT, water residence time.](image-url)
recycled back to the algal pool. The material in the traps may be an overestimate of C because the quality of autochthonous C is likely such that it is rapidly mineralized (Sobek et al. 2009; Ferland et al. 2014). Generally 50–70% of suspended organic matter is lost in the process of sedimentation as evidenced by measurements of quality and decomposition rates of C in sediments vs. traps (Fallon and Brock 1980; Cole et al. 1984; Hilton 1985; Baines and Pace 1994; Guillemette et al. 2017). As well, sediment traps collect a short-term mixture of flocculated, resuspended, and/or recycled allochthonous and autochthonous C, and therefore sediment trap data likely overestimated the amount of C transferred to sediments and buried.

We also compared the pool of DIC in the hypolimnion to evasion calculated via mass balance budget. An average of 2115 ± 175 mmol C m⁻² yr⁻¹ of DIC accumulated in the hypolimnion during the stratified periods. We assumed 202 mmol C m⁻² yr⁻¹ of DIC stored in the hypolimnion originated from settled autochthonous C, leaving between 1738 mmol C m⁻² yr⁻¹ and 2088 mmol C m⁻² yr⁻¹ DIC in the hypolimnion pool. The value of DIC in the hypolimnion was ~2.5x times greater than evasion calculated by subtracting Burial from the DOC retention term (751 mmol C m⁻² yr⁻¹), leaving between 987 mmol C m⁻² yr⁻¹ and 1337 mmol C m⁻² yr⁻¹. The DIC in the hypolimnion that was not mineralized and evaded had the potential to be taken up by fixation in subsequent seasons and thus may also be an overestimate of C available for evasion.

Comparisons between “wet” and “dry” periods

The transport and fate of DOC during different precipitation regimes is influenced by two main factors. First, changes in precipitation amounts result in different loading of DOC via watershed runoff. During dry periods, a decrease in loading due to lower terrestrial runoff means that there is less labile DOC available for in-lake processing and less DOC loss from the outflow compared to wet periods. In fact, loading and loss via L239’s outflow was higher in wet (1990–2010) compared to dry (1980–1990) years (Fig. 2). Second, rates of in-lake processing are highly dependent on WRTs, which are also influenced by precipitation and runoff amounts. Our study has confirmed original work by Curtis and Schindler (1997) showing that the degradation of organic matter in L239 depends on WRT. Recently, both Evans et al. (2017) and Catalán et al. (2016) reported significant negative correlation between decay rates and WRTs in both field and laboratory scenarios in seven different types of aquatic systems over 10 climatic regions (Catalán et al. 2016) and 82 waterbodies with WRTs ranging from 1 week to 700 yr (Evans et al. 2017). Longer WRT (> 3 yr) during dry periods allow for increased DOC processing (i.e., aging of DOC), which decreases lability resulting in increased settling and decreased mineralization (Koehler et al. 2012; Arndt et al. 2013; Catalán et al. 2016; Evans et al. 2017). In wet periods, WRTs are shorter and less in-lake processing of DOC results in more mineralization of younger, more labile DOC and increased loss of DOC via the outflow.

While our dataset contains annual DOC inputs, outputs, and estimates of sedimentation and evasion, it remains inappropriate for calculating “year-to-year” variations in sedimentation or evasion. The Burial and Evasion terms in the model are calculated by difference (see Eq. 2), and incorporate errors in inputs, outputs, and storage, which cannot be easily validated over short timescales (i.e., between individual years). Over longer time periods, the Burial term was successfully validated using carbon accrual in the sediment record, suggesting that error terms in the model were not consistently biased. A similar argument exists in comparing the fates of DOC during decadal length precipitation patterns because we used a single long-term average burial rate to estimate evasion by subtraction. However, we can speculate on differences in DOC fates in differing precipitation regimes based on the relationship between WRT and C cycling in our system.

Over the complete 40-yr data series (1971–2010), Burial (40% ± 3%) was a more important sink than Evasion (23% ± 3%) or outflow (37% ± 1%; Fig. 4). Because of the relationship between the rates of burial of DOC and WRTs, we speculate that natural variations in precipitation and DOC Inputs have the potential to strongly influence in-lake DOC processing (i.e., the partitioning of the Retention term to Evasion and Burial is not static). During a decade (1980–1990) of very low regional precipitation (i.e., “dry” period), the proportion of inputs permanently buried are likely elevated because DOC has more time to flocculate and settle. This would potentially reduce the proportion of inputs evaded to the atmosphere. Increases in precipitation through the 1990–2010 period may have led to marked decreases in DOC processing leading to a lower proportion of inputs buried and a higher proportion of inputs evaded than during dry periods (Fig. 4). The changes that occur in the fates of DOC during differing precipitation regimes may also be impacted by the fact that the character of DOC is changing with age. For example, during low-precipitation periods, both loading and lability decrease and the majority of DOC in the lake will age to a less labile composition. Flocculation and mineralization of a smaller pool due to decreased loading will be less efficient compared to fresher, more labile DOC, while simultaneously remaining in the lake longer due to long WRTs. In the event of a high precipitation year in a dry period (in our case, 1985 during the 1980s drought), there will be pulse of new, labile DOC that will be retained in the lake for longer than in wet periods because the WRT will still be representative of drought conditions. Because it is labile, a large portion of the DOC will floc and mineralize in the subsequent few years.

Comparison to other budgets

Despite the identified importance of carbon cycling in freshwater systems (e.g., Butman et al. 2016), researchers have only recently begun synthesizing decades of research on
mechanistic processes into a more comprehensive understanding of the sources and sinks of organic carbon in lakes. Recent attempts at modeling DOC in lakes have begun to present conceptual frameworks that link together processes governing DOC cycling in lakes over ecologically significant time periods. Evidence supports the assertion that lakes can be net sources of CO₂ to the atmosphere because whole lake respiration (and subsequent evasion) generally exceeds fixation by primary producers (Cole et al. 1994; Hanson et al. 2004; Algeseten et al. 2005). Other findings show that lakes simultaneously accumulate C in sediments via long-term burial, suggesting that boreal lakes are net C sinks (Benoy et al. 2007; Cole et al. 2007). The process of DOC flocculation and subsequent sedimentation and burial of flocculated DOC has been well studied (von Wachenfeldt et al. 2008, 2009; von Wachenfeld and Tranvik 2008) and the mass of C contributions to permanent burial in boreal lakes has been quantified to ~ 2–90 g C m⁻² yr⁻¹ (Gudasz et al. 2010; Ferland et al. 2014; Dietz et al. 2015; Heathcote et al. 2015) for individual lakes and 0.15 Pg C yr⁻¹ globally (Mendonça et al. 2017). A few recent studies have estimated that waterbodies < 0.001 km² release 0.57 Pg C yr⁻¹ globally (Holgerson and Raymond 2016), whereas all inland waterbodies release 2.1 Pg C yr⁻¹ globally (Raymond et al. 2013).

To compare our resulting C mass balance budget to others presented in the literature, we converted our data to g C m⁻² yr⁻¹ and, in keeping with recent conventions (Cole et al. 2007; Tranvik et al. 2009; Anas et al. 2015), present our budget as funnel diagrams (Fig. 4). There are two main considerations when comparing our results to others. First, we must consider that the specific proportions of the DOC input going to the various fates as determined by this study are, of course, specific to the characteristics of Lake 239. For any other lake, the specific portions will depend on a number of factors, including the ratio of the terrestrial drainage area to the lake area, lake volume, climate parameters, forest type, and nutrient status. For example, Ferland et al. (2012) showed that organic C burial rates in boreal systems in northern Québec were a function of lake size. However, while the surface areas of the lakes included in their work were similar to L239, they were between 2X (max depth = 15 m) and 5X (max depth = 6 m) shallower, with significantly shorter WRTs (1 month to 1.6 yr).

### Table 2. Fates of dissolved organic, total organic, or total C (DOC, TOC, TC, respectively) in recent studies. All data presented are from boreal lakes, except Tranvik et al. (2009) which includes global inland waters.

| Study | Inputs | Outflow | Evasion | Burial |
|-------|--------|---------|---------|--------|
| Current study | DOC = 30.4 ± 2.1 | 11.3 ± 0.8 (37% ± 2%) | 9.0 ± 1.4 (23% ± 3%) | 10.0 ± 0 (40% ± 1%) |
| Dillon and Molot (1997) | DOC = 4.46 | 2.23 (40%) | 1.48 (24%) | 1.2 (20%) |
| Algesten et al. (2003) | TOC = 5.34 | 2.52 (49%) | 2.25 (41%) | 0.29 (6%) |
| Sobek et al. (2006) | TOC = 7.56 | 2.76 (34%) | 3.42 (43%) | 1.5 (19%) |
| Jonsson et al. (2007) | TOC = 8.6 | (50%) | (45%) | |
| Einola et al. (2011) | TOC = 8.15 | 7.72 (74%) | 4.02 (44%) | 0.22 (2.4%) |
| Kang et al. (2016)* | DOC = 4.34 | 3.00 (70%) | 1.34 (30%) | |
| Chmiel et al. (2016)* | 17.6 t C yr⁻¹ (79%) | 13.9 t C yr⁻¹ (79%) | 3.4 t C yr⁻¹ (19%) | 0.3 t C yr⁻¹ (2%) |
| Kortelainen et al. (2006b)‡ | TC = 2.9 Pg C yr⁻¹ (31%) | 0.9 Pg C yr⁻¹ (31%) | 1.4 Pg C yr⁻¹ (48%) | 0.6 Pg C yr⁻¹ (21%) |
| Tranvik et al. (2009) | TC = 2.9 Pg C yr⁻¹ | 47–59 Tg C yr⁻¹ (21%) | 2–3 Tg C yr⁻¹ (21%) | |
| Anas et al. (2015) | TC = 66 Tg C yr⁻¹ (21–54%) | 14–36 Tg C yr⁻¹ (21–54%) | 12–21 Tg C yr⁻¹ (18–31%) | 18–31 Tg C yr⁻¹ (27–47%) |

*Kang et al. (2016) did not separate evasion from burial. The estimate presented here represents retention in lake.

†Chmiel et al. (2016) measured sediment mineralization, open water respiration, and photomineralization; evasion here presented as the sum.

‡Kortelainen et al. (2006b) measured partial pressure of CO₂ and modeled gas evasion using piston velocities as obtained via Schmidt numbers, and concentrations of CO₂ in water in each of four seasons. Accumulation to sediments was estimated using Holocene accumulation rates presented in Pajunen (2004).
than L239 (max depth = 30 m, mean WRT = 8 yr). Because overall retention of DOC is negatively correlated with WRT, which is in turn strongly correlated with precipitation (Supporting Information Fig. S4), we are reluctant to compare our study directly with theirs. Similarly in other systems, Hanson et al. (2004) showed that temperate lakes with residence times < 1 yr exported ~ 60% of the DOC, whereas lakes with residence times > 6 yr mineralized ~ 60% of the DOC. In view of the way DOC is processed in lakes, it is not surprising that other studies that have examined DOC cycling in lakes with different water residence times, different temperatures, and DOC pools that may be of different lability would arrive at different rates and proportions of DOC lost via evasion and burial. Second, other studies may present results as either DOC or total C budgets. Because C cycling in L239 is so thoroughly dominated by DOC cycling other forms of C in our lake are of little influence. As a result, comparisons with total C budgets from other lakes are applicable.

Given their importance to global carbon cycling, the transport and fate of C within boreal lakes and their watersheds has been estimated in numerous locations across North America and Scandinavia. Since C cycling within lakes are influenced by context specific factors (e.g., lake size, WRT, DOC quality of inputs, etc.), it should not be surprising that there is a wide variation in estimates for model components between studies, and in efforts to extrapolate to regional and global scales. Improvements in scaling to regional and global estimates are dependent on increasing the number of mass balance studies across different lake and watershed types, across different precipitation regimes, and, where possible, over longer timeframes. Our results show that a greater proportion of total DOC was buried rather than evaporated within a boreal headwater lake over a 40 yr record. With the exception of boreal lakes examined by Dillon and Molot (1997) and von Wachenfeldt and Tranvik (2008) (which found that sedimentation and evasion were similar to each other), most current studies estimated that evasion was considerably higher than permanent burial (Table 2). Studies scaling to boreal forest biomes contradict each other; lakes in Scandinavia contribute 21 times as much C to the atmosphere via mineralization and evasion compared to burial (Kortelainen et al. 2006b), whereas lakes in North American contribute a similar mass of C to both evasion and burial (Anas et al. 2015). Our results also differ from an estimate of rates of total C for total global inland waters reported by Tranvik et al. (2009). This global estimate suggests that almost half of total C input to lakes is evaporated as CO₂, while one-fifth is accumulated in sediments (Algesten et al. 2003; Tranvik et al. 2009; Kortelainen et al. 2013). Our study suggests that C sequestration in sediments may be underestimated in these global analyses.

Global climate change implications

Interest in identifying the role of inland lakes in C sequestration is high since it is critical to understanding biogeochemical responses to the Earth’s changing climate. Global climate change models (GCCMs) predict that both temperatures and precipitation will increase in boreal forest ecosystems (Intergovernmental Panel on Climate Change 2014). However, the uncertainty of GCCMs in predicting precipitation patterns such as drought vs. deluge is high and therefore we cannot preclude the possibility of significant droughts in the boreal forest. Given the length of our dataset and its inclusion of “wet,” “dry,” and “intermediate” periods, we were able to speculate on the changing fate of DOC under different precipitation regimes. Under higher precipitation scenarios (such as our “wet” period), DOC loading will increase and a greater proportion of that loading will be evaporated to the atmosphere or transferred to downstream systems (where a proportion of this allochthonous C will be further processed and then buried or evaporated). During these wet periods, CO₂ evasion could be greater than in periods of drought. During droughts (such as our “dry” period), the decrease in runoff will result in less DOC loading, longer WRTs, and proportionally less C lost to the downstream systems via the outflow stream. But of the DOC in lakes, proportionally more may be permanently buried with an accompanying decline in the proportion of C inputs lost to evasion. This suggests that if a changing climate impacts the hydrological regimes in the boreal forest such that drought increases, the efficiency headwater lakes to sequester C in sediments could be greater than in times of deluge.

The objective of the current study was to quantify and partition rates of DOC over a 40-yr time period using a traditional mass balanced account of high-resolution DOC inputs and outputs, and permanent burial rates from cores. However, our model also has the capability to act as a “lake carbon cycle simulator” because it allows the user to test relations between mechanistic process like flocculation and settling and burial and mineralization and to explore rates by iterative assessment in the context of L239. It would also allow for exploration of impacts of changing external forcing factors such as precipitation, temperature, wind velocity, or length of the ice-free season among others. While our results are specific to our study lake, we believe that the lake carbon simulator is robust for application to low productivity boreal lakes and could be easily modified for others. For example, the model could be adjusted to examine lakes other than first-order lakes by considering preprocessing that DOC received upstream and inputs of dissolved CO₂ from upstream. This adjustment to the model should be the topic of investigation in the near future to further elucidate the role of boreal lakes in a changing global climate.

References

Adrian, R., et al. 2009. Lakes as sentinels of climate change. Limnol. Oceanogr. 54: 2283–2297. doi:10.4319/lo.2009.54.6_part_2.2283
Ågren, A., I. Buffam, M. Berggren, K. H. Bishop, M. Jansson, and H. Laudon. 2008. Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer. J. Geophys. Res. Biogeosci. 113: G03031. doi:10.1029/2007JG000674

Aiken, G. R., H. Hsu-Kim, and J. N. Ryan. 2011. Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids. Environ. Sci. Technol. 45: 3196–3201. doi:10.1021/es103992s

Algesten, G., S. Sobek, A.-K. Bergström, A. Ågren, L. J. Tranvik, and M. Jansson. 2003. Role of lakes for organic carbon cycling in the boreal zone. Glob. Chang. Biol. 10: 141–147.

Algesten, G., S. Sobek, A.-K. Bergström, A. Jonsson, L. J. Tranvik, and M. Jansson. 2005. Contribution of sediment respiration to summer CO₂ emission from low productive boreal and subarctic lakes. Microb. Ecol. 50: 529–535. doi:10.1007/s00248-005-5007-x

Anas, M. M. U., K. A. Scott, and B. Wissel. 2015. Carbon budgets of boreal lakes: State of knowledge, challenges, and implications. Environ. Rev. 23: 275–287. doi:10.1139/er-2014-0074

Arndt, S., B. B. Jørgensen, D. E. LaRowe, J. J. Middelburg, A. K. Aufdenkampe, A. Boström, and J. Kaartokallio. 2015. Organic carbon decomposition rates controlled by water retention time across inland waters. Nat. Geosci. 9: 501–504. doi:10.1038/ngeo2720

Chmielewski, W., J. K. Kachel, and M. Schellhorn. 2016. The role of sediments in the carbon budget of a small boreal lake. Limnol. Oceanogr. 61: 1814–1825. doi:10.1002/lno.10336

Cole, J. J., G. E. Likens, and J. E. Hobbie. 1984. Decomposition of planktonic algae in an oligotrophic lake. Oikos 42: 257–266. doi:10.2307/3544393

Cole, J. J., N. F. Caraco, G. W. Kling, and T. K. Kratz. 1994. Carbon dioxide supersaturation in the surface waters of lakes. Science 265: 1568–1570. doi:10.1126/science.265.5178.1568

Cole, J., and N. F. Caraco. 2001. Carbon in catchments: Connecting terrestrial carbon losses with aquatic metabolism. Mar. Freshw. Res. 52: 101–110. doi:10.1046/j.1362-2870.2001.00084.x

Dillon, P. J., and L. A. Molot. 1997. Dissolved organic and inorganic carbon mass balances in Central Ontario lakes. Biogeochemistry 36: 29–42. doi:10.1023/A:1005731828660
Dillon, P. J., and L. A. Molot. 2005. Long-term trends in catchment export and lake retention of dissolved organic carbon, dissolved organic nitrogen, total iron, and total phosphorus: The Dorset, Ontario, study, 1978–1998. J. Geophys. Res. Biogeosci. 220: G01002. doi:10.1029/2004JG000003

Diodato, N., S. Higgins, G. Bellocci, F. Fiorillo, N. Romano, and F. M. Guadagno. 2016. Hydro-climatic forcing of dissolved organic carbon in two boreal lakes of Canada. Sci. Total Environ. 571: 50–58. doi:10.1016/j.scitotenv.2016.07.112

Driscoll, C. T., R. D. Fuller, and D. M. SImone. 1988. Longitudinal variations in trace metal concentrations in a northern forested ecosystem. J. Environ. Qual. 17: 101–107. doi:10.2134/jeq1988.00472425001700010015x

Duffy, C. J., H. A. Dugan, and P. C. Hanson. 2018. The age of water and carbon in lake-catchments: A simple dynamical model. Limnol. Oceanogr.: Lett. 3: 236–245. doi:10.1002/lo2.10070

Effler, S. W., and C. M. Brooks. 1998. Gradients and dynamics in downward flux and settling velocity in Cannonsville Reservoir. Lake Reserv. Manag. 14: 213–224. doi:10.1080/07438149809354332

Einola, E., M. Rantakari, P. Kankaala, P. Kortelainen, A. Ojala, H. Pajunen, S. Mäkelä, and L. Arvola. 2011. Carbon pools and fluxes in a chain of five boreal lakes: A dry and wet year comparison. J. Geophys. Res. Biogeosci. 116: G03009. doi:10.1029/2010JG001636

Emmerton, C. A., et al. 2018. Long-term responses of nutrient budgets to concurrent climate-related stresses in a boreal watershed. Ecosystems. doi:10.1007/s10021-018-0276-7

Engstrom, D. R., and N. L. Rose. 2013. A whole-basin, mass-balance approach to paleolimnology. J. Paleolimnol. 49: 333–347. doi:10.1007/s10933-012-9675-5

Evans, C. D., M. N. Futter, F. Moldan, S. Valinia, Z. Frogbrook, and D. N. Kothawala. 2017. Variability in organic carbon reactivity across lake residence time and trophic gradients. Nat. Geosci. 10: 832–835. doi:10.1038/ngeo3051

Fallon, R. D., and T. D. Brock. 1980. Planktonic blue-green algae: Production, sedimentation, and decomposition in Lake Mendota, Wisconsin. Limnol. Oceanogr. 25: 72–88. doi:10.1034/j.1970.2153.201501002

Fee, E. J., R. E. Hecky, S. E. M. Kasiian, and D. R. Crukshank. 1996. Effects of lake size, water clarity, and climatic variability on mixing depths in Canadian Shield lakes. Limnol. Oceanogr. 41: 912–920. doi:10.1034/j.1996.41.5.0912

Ferland, M.-E., P. A. del Giorgio, C. R. Teodoru, and Y. T. Prairie. 2012. Long-term C accumulation and total C stocks in boreal lakes in northern Québec. Global Biogeochem. Cycles 26: GB0E04. doi:10.1029/2011GB004241

Ferland, M.-E., Y. T. Prairie, C. Teodoru, and P. A. del Giorgio. 2014. Linking organic carbon sedimentation, burial efficiency, and long-term accumulation in boreal lakes. J. Geophys. Res. Biogeosci. 119: 836–847. doi:10.1002/2013JG002345

Findlay, D. L., S. E. M. Kasiian, M. P. Stainton, K. Beaty, and M. Lyng. 2001. Climatic influences on algal populations of boreal forest lakes in the Experimental Lakes Area. Limnol. Oceanogr. 46: 1784–1793. doi:10.4319/lo.2001.46.7.1784

Gudasz, C., D. Bastviken, K. Steger, K. Premke, S. Sobek, and L. J. Tranvik. 2010. Temperature-controlled organic carbon mineralization in lake sediments. Nature 466: 478–481. doi:10.1038/nature09186

Gudasz, C., D. Bastviken, K. Premke, K. Steger, and L. J. Tranvik. 2012. Constrained microbial processing of allochthonous organic carbon in boreal lake sediments. Limnol. Oceanogr. 57: 163–175. doi:10.4319/lo.2012.57.1.0163

Guillemette, F., S. L. McCallister, and P. A. del Giorgio. 2013. Differentiating the degradation dynamics of algal and terrestrial carbon within complex natural dissolved organic carbon in temperate lakes. J. Geophys. Res. Biogeosci. 118: 963–973. doi:10.1002/jgrf.20077

Guillemette, F., E. Von Wachenfeldt, D. N. Kothawala, D. Bastviken, and L. J. Tranvik. 2017. Preferential sequestration of terrestrial organic matter in boreal lake sediments. J. Geophys. Res. Biogeosci. 122: 863–874. doi:10.1002/2016JG003735

Hanson, P. C., A. I. Pollard, D. L. Bade, K. Predick, S. R. Carpenter, and J. A. Foley. 2004. A model of carbon evasion and sedimentation in temperate lakes. Glob. Chang. Biol. 10: 1285–1298. doi:10.1111/j.1529-8817.2003.00805.x

Hanson, P. C., D. P. Hamilton, E. H. Stanley, N. Preston, O. C. Langman, and E. L. Kara. 2011. Fate of allochthonous dissolved organic carbon in lakes: A quantitative approach. PLoS One 6: e21884. doi:10.1371/journal.pone.0021884

Heagle, D. J., M. Hayashi, and G. Van der Kamp. 2007. Use of sulfur mass balance to quantify geochemical processes in a prairie recharge wetland. Wetlands 27: 806–818. doi:10.1672/0277-5212(2007)27[806:UOSMBT]2.0.CO;2

Heathcote, A. J., N. J. Anderson, Y. T. Prairie, D. R. Engstrom, and P. A. del Giorgio. 2015. Large increases in carbon burial in northern lakes during the Anthropocene. Nat. Commun. 6: 10016. doi:10.1038/ncomms10016

Hesslein, R. H., M. A. Turner, D. Guss, and M. Lyng. 2009. Separating the effects on water chemistry of climate variation and experimental manipulation in the long-term acidification and recovery of lakes. Can. J. Fish. Aquat. Sci. 66: 1864–1874. doi:10.1139/F09-124

Hilton, J. 1985. A conceptual framework for predicting the occurrence of sediment focusing and sediment redistribution in small lakes. Limnol. Oceanogr. 30: 1131–1143. doi:10.4319/lo.1985.30.6.1131

Holgersen, M. A., and P. A. Raymond. 2016. Large contribution to inland water CO2 and CH4 emissions from very small ponds. Nat. Geosci. 9: 222–226. doi:10.1038/ngeo2654

Intergovernmental Panel on Climate Change. 2014. Climate change 2014: Synthesis report, p. 151. In Core Writing
Team, R. K. Pachauri, and L. A. Meyer [eds.], Contribution of working groups I, II and III to the fifth assessment report of the Intergovernmental Panel on Climate Change. 

Isee systems. 1985–2015. STELLA® Modeling & Simulation Software.

Jansen, W., and R. H. Hesslein. 2004. Potential effects of climate warming on fish habitats in temperate zone lakes with special reference to Lake 239 of the Experimental Lakes Area (ELA), North-Western Ontario. Environ. Biol. Fishes 70: 1–22. doi: 10.1023/B:EBFL.0000023035.06554.c7

Jonsson, A., G. Algesten, A.-K. Bergström, K. Bishop, S. Sobek, L. J. Tranvik, and M. Jansson. 2007. Integrating aquatic carbon fluxes in a boreal catchment carbon budget. J. Hydrol. 334: 141–150. doi: 10.1016/j.jhydrol.2006.10.003

Kang, P.-G., M. J. Mitchell, P. J. McHale, C. T. Driscoll, S. Inamdar, and J.-H. Park. 2016. Importance of within-lake processes in affecting the dynamics of dissolved organic carbon and dissolved organic and inorganic nitrogen in an Adirondack forested lake/watershed. Biogeoosciences 13: 2787–2801. doi: 10.5194/bg-13-2787-2016

Kipphut, G. 1978. An investigation of sedimentary processes in lakes. Columbia Univ.

Kling, G. W., G. W. Kipphut, and M. C. Miller. 1991. Arctic lakes and streams as gas conduits to the atmosphere: Implications for tundra carbon budgets. Science 251: 298–301. doi: 10.1126/science.251.4991.298

Koehler, B., E. von Wachenfeldt, D. Kothawala, and L. J. Tranvik. 2012. Reactivity continuum of dissolved organic carbon decomposition in lake water. J. Geophys. Res. Biogeosci. 117: G01024.

Kortelainen, P., T. Mattsson, L. Finer, M. Anttiainen, S. Saukkonen, and T. Sallantaus. 2006a. Controls on the export of C, N, O, and Fe from undisturbed boreal catchments, Finland. Aquat. Sci. 68: 453–468. doi: 10.1007/s00203-006-0833-6

Kortelainen, P., et al. 2006b. Sediment respiration and lake trophic state are important predictors of large CO2 evasion from small boreal lakes. Glob. Chang. Biol. 12: 1554–1567. doi: 10.1111/j.1365-2486.2006.01167.x

Kortelainen, P., et al. 2013. Carbon evasion/accumulation ratio in boreal lakes is linked to nitrogen. Global Biogeochem. Cycles 27: 363–374. doi: 10.1002/gbc.20036

Kritzberg, E. S., J. J. Cole, M. L. Pace, and W. Granelli. 2005. Does autochthonous primary production drive variability in bacterial metabolism and growth efficiency in lakes dominated by terrestrial C inputs? Aquat. Microb. Ecol. 38: 103–111. doi: 10.3354/ame038103

Matthews, C. J. D., E. M. Joyce, V. St. Louis, S. L. Schiff, J. J. Venkiteswaran, B. D. Hall, R. A. (Drew) Bodaly, and K. G. Beatty. 2005. Carbon dioxide (CO2) and methane (CH4) production in small reservoirs flooding upland boreal forests. Ecosystems 8: 267–285. doi: 10.1007/s10021-005-0005-x

McCullough, G. K., and P. Campbell. 1993. Lake variation and climate change study: ELA lakes, 1986-1990. II. Watershed geography and lake morphology. Can. Tech. Rep. Fish. Aquat. Sci. 1898: iv + 29.

Mendonça, R., R. A. Müller, D. W. Clow, C. Verpoorter, P. A. Raymond, L. J. Tranvik, and S. Sobek. 2017. Organic carbon burial in global lakes and reservoirs. Nat. Commun. 8: 1694. doi: 10.1038/s41467-017-01789-6

Molot, L. A., and P. J. Dillon. 1996. Storage of terrestrial carbon in boreal lake sediments and evasion to the atmosphere. Global Biogeochem. Cycles 10: 483–492. doi: 10.1029/96GB01666

Molot, L. A., et al. 2004. Risk assessment of dissolved organic matter-mediated ultraviolet B exposure in Canadian inland waters. Can. J. Fish. Aquat. Sci. 61: 2511–2521. doi: 10.1139/f04-165

Nalewajko, C., and D. W. Schindler. 1976. Primary production, extracellular release, and heterotrophy in two lakes in the ELA, Northwestern Ontario. J. Fish. Res. Board Can. 33: 219–226. doi: 10.1139/f76-033

Pajunen, H. 2004. Lake sediments as a store of dry matter and carbon. Geological Survey of Finland, p. 308.

Parker, B. R., D. W. Schindler, K. G. Beatty, M. P. Stainton, and S. E. M. Kasiyan. 2009. Long-term changes in climate, streamflow, and nutrient budgets for first-order catchments at the Experimental Lakes Area (Ontario, Canada). Can. J. Fish. Aquat. Sci. 66: 1848–1863. doi: 10.1139/f09-149

Peel, M. C., B. L. Finlayson, and T. A. McMahon. 2007. Updated world map of the Köppen-Geiger climate classification. Hydrol. Earth Syst. Sci. 11: 1633–1644. doi: 10.5194/hess-11-1633-2007

Prairie, Y. 2007. Caribocentric limnology: Looking back, looking forward. Can. J. Fish. Aquat. Sci. 65: 543–548. doi: 10.1139/f08-011

Rasmussen, J. B., L. Godbout, and M. Schallenberg. 1989. The humic content of lake water and its relationship to watershed and lake morphometry. Limnol. Oceanogr. 34: 1336–1343. doi: 10.4319/lo.1989.34.7.1336

Raymond, P. A., and J. E. Bauer. 2001. Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. Nature 409: 497–500. doi: 10.1038/35040343

Raymond, P. A., et al. 2013. Global carbon dioxide emissions from inland waters. Nature 503: 355–359. doi: 10.1038/nature12760

Rowan, D. J., J. Kalff, and J. B. Rasmussen. 1992. Estimating the mud deposition boundary depth in lakes from wave theory. Can. J. Fish. Aquat. Sci. 49: 2490–2497. doi: 10.1139/f92-275

Schiff, S., R. Aravena, E. Mewhinney, R. Elgood, B. Warner, P. Dillon, and S. Trombore. 1998. Precambrian shield wetlands: Hydrologic control of the sources and export of dissolved organic matter. Clim. Chang. 40: 167–188. doi: 10.1023/A:1005496331593

Schindler, D. W. 1997. Widespread effects of climatic warming on freshwater ecosystems in North America. Hydrol.
Schindler, D. W., R. W. Newbury, K. G. Beaty, and P. Campbell. 1976. Natural water and chemical budgets for a small Precambrian lake basin in central Canada. J. Fish. Res. Board Can. 33: 2526–2543. doi:10.1139/t76-297

Schindler, D. W., S. E. Bayley, B. R. Parker, K. G. Beaty, D. R. Cruikshank, E. J. Fee, E. U. Schindler, and M. P. Stainton. 1996. The effects of climatic warming on the properties of boreal lakes and streams at the Experimental Lakes Area, northwestern Ontario. Limnol. Oceanogr. 41: 1004–1017. doi:10.4319/lo.1996.41.5.1004

Scully, N. M., and D. R. S. Lean. 1994. The attenuation of ultraviolet radiation in temperate lakes, p. 135–144. In C. E. Williamson and H. E. Zagarese [eds.], Advances in limnology: Impact of UV-B radiation on pelagic freshwater ecosystems. Archiv fur hydrobiologie bilheft. E-Schweizer-bartsche-Verlagsbuchhandlung

Smith, E., and Y. Prairie. 2004. Bacterial metabolism and growth efficiency in lakes: The importance of phosphorus availability. Limnol. Oceanogr. 49: 134–147. doi:10.4319/lo.2004.49.1.0137

Snucins, E., and J. Gunn. 2000. Interannual variation in the thermal structure of clear and colored lakes. Limnol. Oceanogr. 45: 1639–1646. doi:10.4319/lo.2000.45.7.1639

Sobek, S., B. Söderbäck, S. Karlsson, E. Andersson, and A. K. Brunberg. 2006. A carbon budget of a small humic lake: An example of the importance of lakes for organic matter cycling in boreal catchments. Ambio 35: 469–475. doi:10.1579/0044-7447(2006)35[469:ACBOAS]2.0.CO;2

Sobek, S., L. J. Tranvik, Y. Prairie, P. Kortelainen, and J. J. Cole. 2007. Patterns and regulation of dissolved organic carbon: An analysis of 7,500 widely distributed lakes. Limnol. Oceanogr. 52: 1208–1219. doi:10.4319/lo.2007.52.3.1208

Sobek, S., E. Durisch-Kaiser, R. Zurbrügg, N. Wongfun, M. Wessels, N. Pasche, and B. Wehrli. 2009. Organic carbon burial efficiency in lake sediments controlled by oxygen exposure time and sediment source. Limnol. Oceanogr. 54: 2243–2254. doi:10.4319/lo.2009.54.6.2243

Solomon, C., et al. 2015. Ecosystem consequences of changing inputs of terrestrial dissolved organic matter to lakes: Current knowledge and future challenges. Ecosystems 18: 376–389. doi:10.1007/s10021-015-9848-y

Stainton, M. P., M. J. Capel, and F. A. J. Armstrong. 1977. The chemical analysis of fresh water, p. 166. Fish. Mar. Serv. Misc. Spec. Publ.

Stephenson, M., W. J. Schwartz, M. F. Motycka, D. J. Rowan, C. A. Kelly, and R. D. Roshon. 1995. Fate and distribution in sediments of carbon-14 added to Canadian Shield lakes of differing trophic state. Limnol. Oceanogr. 40: 779–790. doi:10.4319/lo.1995.40.4.0779

Stubbins, A., and T. Dittmar. 2012. Low volume quantification of dissolved organic carbon and dissolved nitrogen. Limnol. Oceanogr.: Methods 10: 347–352. doi:10.4319/mom.2012.10.347

Tranvik, L. J., et al. 2009. Lakes and reservoirs as regulators of carbon cycling and climate. Limnol. Oceanogr. 54: 2298–2314. doi:10.4319/lo.2009.54.6_part_2.2298

Vachon, D., Y. Prairie, F. Guillemette, and P. A. del Giorgio. 2017. Modeling allochthonous dissolved organic carbon mineralization under variable hydrologic regimes in boreal lakes. Ecosystems 20: 781–795. doi:10.1007/s10021-016-0057-0

von Wachenfeldt, E., S. Sobek, D. Bastviken, and L. J. Tranvik. 2008. Linking allochthonous dissolved organic matter and boreal lake sediment carbon sequestration: The role of light-mediated flocculation. Limnol. Oceanogr. 53: 2416–2426. doi:10.4319/lo.2008.53.6.2416

von Wachenfeldt, E., and L. J. Tranvik. 2008. Sedimentation in boreal lakes - the role of flocculation of allochthonous dissolved organic matter in the water column. Ecosystems 11: 803–814. doi:10.1007/s10021-008-9162-z

von Wachenfeldt, E., D. Bastviken, and L. J. Tranvik. 2009. Microbially induced flocculation of allochthonous dissolved organic carbon in lakes. Limnol. Oceanogr. 54: 1811–1818. doi:10.4319/lo.2009.54.5.1811

Wetzel, R. G. 2001. Limnology: Lake and river ecosystems, 3rd ed. Academic Press.

Williamson, C. E., D. P. Morris, M. L. Pace, and O. G. Olson. 1999. Dissolved organic carbon and nutrients as regulators of lake ecosystems: Resurrection of a more integrated paradigm. Limnol. Oceanogr. 44: 795–803. doi:10.4319/lo.1999.44.3_part_2.0795

Acknowledgments

We acknowledge staff and students at the Experimental Lakes Area that collected hydrological and chemical data under the supervision of K. Beaty and M. Stainton, respectively. D. Findlay collected and analyzed all algal biomass data.

Conflict of Interest

None declared.