

Controls of $\delta^{13}\text{C}$ -DIC in lakes: Geochemistry, lake metabolism, and morphometry

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Abstract

We investigated $\delta^{13}\text{C}$ -dissolved inorganic carbon (DIC) values in 72 lakes from diverse regions using literature data as well as new measurements for 32 lakes. $\delta^{13}\text{C}$ -DIC varied broadly among lakes from -31 to $+2.6\text{‰}$. This variation of surface-water $\delta^{13}\text{C}$ -DIC among lakes is greater than the seasonal variation within most lakes. Several statistical models account for a large portion of the interlake variation and indicate that geochemical (e.g., DIC, pH, alkalinity) and morphometric (area) variables are important, whereas biological (e.g., gross primary productivity [GPP], respiration [R], chlorophyll *a*) variables are generally not significant. A process-based model including gas exchange with the atmosphere, inorganic carbon speciation, and ecosystem metabolism was also constructed. The model provides a reasonable fit to the data for lakes, in which respiration exceeded GPP (heterotrophic lakes; 75% of lakes sampled). Lakes for which GPP exceeded respiration (autotrophic) were not fit well by the process-based model. The data and models indicate that metabolism creates substantial variation in $\delta^{13}\text{C}$ -DIC around the potential $\delta^{13}\text{C}$ -DIC that is set by geochemical factors of the watershed.

Stable isotope analysis of dissolved inorganic carbon (DIC) has become an important tool for understanding the movement and fate of carbon (C) in lake ecosystems. Several studies have used DIC stable isotopes to understand the carbon cycle of individual lakes by tracking change in the isotope signature through time (Quay et al. 1986; Herczeg 1987; Stiller and Nissenbaum 1999). Few studies have examined $\delta^{13}\text{C}$ -DIC for a broad range of lakes to determine the causes and importance of the variation among lakes. Early reports suggested that the possible range of $\delta^{13}\text{C}$ -DIC values could be between -21‰ and 0‰ (Degens 1969). Striegl et al. (2001) compared DIC isotope signatures of 142 lakes during ice cover and concluded that lakes with higher partial pressure of CO_2 ($p\text{CO}_2$) had lower $\delta^{13}\text{C}$ -DIC values as a result of the dominance of respiration of terrestrial organic material.

The ratio of ^{13}C to ^{12}C in DIC is influenced by several major processes that alter the input or output of either isotope. Inputs include atmospheric CO_2 , respiration of organic

matter, surface water and groundwater inflow of aqueous CO_2 and alkalinity (HCO_3^- and CO_3^{2-}), calcite dissolution, and methane oxidation. Losses that affect the isotope signature include evasion of CO_2 , calcite precipitation, photo-synthetic uptake, and water outflow.

It has long been recognized that lake metabolism plays an important role in influencing the isotope signature of DIC (Oana and Deevey 1960). Prior to our study, we hypothesized that productivity and respiration would be correlated with $\delta^{13}\text{C}$ -DIC in surface water of lakes. Increasing productivity should increase $\delta^{13}\text{C}$ -DIC, whereas increasing respiration should decrease $\delta^{13}\text{C}$ -DIC. Similarly, $\delta^{13}\text{C}$ -DIC should be related to those factors controlling productivity and respiration in lakes, such as total phosphorus (TP) and dissolved organic carbon (DOC) (Carignan et al. 2000; Prairie et al. 2002; Hanson et al. 2003).

Indeed, studies have observed summer increases in epilimnetic $\delta^{13}\text{C}$ -DIC as a result of increases in productivity (Herczeg 1987; Hollander and McKenzie 1991; Wang and Veizer 2000). Respiration is generally considered to be the reason for declining $\delta^{13}\text{C}$ -DIC in the hypolimnion during the stratified season (Quay et al. 1986; Miyajima et al. 1997). Respiration may hold $\delta^{13}\text{C}$ -DIC below atmospheric equilibrium during periods of mixis and low productivity (Wachniew and Rózański 1997). Since productivity and respiration are important for changing carbon isotope ratios in lakes, lakes with different levels of metabolism may have distinctly different isotope signatures (e.g., Schindler et al. 1997).

On the other hand, the loading of DIC from the watershed

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may ultimately determine the $\delta^{13}\text{C}$ -DIC. If watershed inputs are the dominant term in the DIC budget, then the isotope signature should approach that of the inflowing DIC. Additionally, alkalinity inputs from the watershed may influence the isotopic signature of DIC because of fractionation between inorganic carbon species at equilibrium with the atmosphere (Zhang et al. 1995).

In this study we investigate the variability in isotope values that exists in the surface water of lakes during the open water seasons. We attempt to determine the relative influence of lake metabolism versus external loading on the cycling of DIC isotopes. Herein we present original data from a comparative study of lakes in the Northern Highland region of Northern Wisconsin and the Upper Peninsula of Michigan, and we augment this information with data from the literature to investigate patterns that arise across a diversity of lakes. We consider several methods to predict isotope signatures in different lakes, including correlation and regression models as well as a process-based model. These models provide an integrated picture of the sources and processes most important for $\delta^{13}\text{C}$ -DIC in lakes.

Methods

Northern Highland lakes survey: Study sites—Thirty-two lakes in the Northern Highland Lake District of Northern Wisconsin and the Upper Peninsula of Michigan were selected based upon extant data and proximity to the University of Notre Dame Environmental Research Center and the University of Wisconsin Trout Lake Station. Using previously measured TP and DOC concentrations, we selected lakes to create a data set that would be roughly orthogonal with respect to these variables, which are known to affect lake metabolism (Hanson et al. 2003).

Limnological sampling—Each lake was sampled at the deepest point and the parameters measured at each lake were temperature, dissolved oxygen, DIC, pCO_2 , pH, TP, DOC, chlorophyll *a* (Chl *a*), and $\delta^{13}\text{C}$ -DIC. All sampling was performed at 0.5 m depth, except for temperature and dissolved oxygen profiles. The lakes were each surveyed once during the summer-stratified period of 2000, from mid-June through the end of August. One lake (Morris Lake) was sampled twice and four lakes (Allequash, Cranberry, Diamond, and Hummingbird Lakes) were sampled three times throughout the summer to observe temporal changes in $\delta^{13}\text{C}$ -DIC. Samples were collected using a peristaltic pump. Each sample bottle used for determination of gaseous species (O_2 , CO_2 , and DIC) was triple-rinsed, filled completely, and allowed to overflow for the amount of time taken to fill the bottle. For all other sample collections, the bottle was triple-rinsed and filled.

Temperature and dissolved oxygen profiles were measured using a YSI temperature/dissolved oxygen meter. DIC and pCO_2 were measured on a Shimadzu GC-8AIT gas chromatograph (GC) with a thermal conductivity detector. DIC was determined using the method of Stainton (1973). Water was collected in three 300-ml BOD bottles. An aliquot (10 ml) was drawn into a 60-ml syringe, injected with 200 μl of 2 N H_2SO_4 , and then 20 ml of He was added. The syringe

was immediately capped, shaken for 1 min, and then 5 ml of headspace gas was injected into the GC. If values from two of the BOD bottles replicated within 5%, the third bottle was not run. The partial pressure of CO_2 was determined by the headspace equilibration method of Cole et al. (1994), in which 2 liters of water is equilibrated with 60 ml of air in a polycarbonate bottle. The equilibrated headspace gas is drawn into two 20-ml syringes and taken back to the lab for analysis on the GC. Two replicate equilibrations were performed at each lake. The coefficient of variation for both procedures is less than 5%.

DIC- ^{13}C samples were collected in 1-liter amber glass bottles. One milliliter of 10 N H_2SO_4 was added to preserve the sample at a pH of <2 . The gas-tight cap was placed on the bottle, covered with Parafilm, and then taped shut with black electrical tape. The samples were stored in the dark until they were sent to the Marine Biological Laboratory (Woods Hole, Massachusetts) for isotope analysis. Precision of replicate samples is usually less than 0.2‰.

Chl *a* was determined fluorometrically (Marker et al. 1980). Chl *a* was collected on Whatman GF/F filters by filtering 200 ml of lake water. All filters were frozen for at least 24 hr and then extracted with methanol for 24 hr. Fluorescence was determined before and after acidification to correct for pheopigments. Total phosphorus was analyzed on a Lachat autoanalyzer after persulfate digestion of a whole-water sample. The pH was measured using an Orion digital pH meter with automatic temperature-compensating electrode. DOC samples were collected as the filtrate through Whatman GF/F filters. Twenty milliliters of water was preserved in glass scintillation vials by acidifying to a pH of <2 with 2 N H_2SO_4 . The samples were analyzed on a Shimadzu model 5050 high-temperature TOC analyzer. Alkalinity was calculated based on measurements of pH, DIC, and water temperature (Stumm and Morgan 1996).

Measurements of whole-ecosystem gross primary productivity (GPP) and respiration (R) were made on a subset of 25 lakes by continuous measurement of dissolved oxygen using automated recording O_2 electrodes (Cole et al. 2000). The metabolism measurements were conducted for a period of 2–4 d starting on the day of limnological sampling. The metabolism measurements in these 25 lakes are presented by Hanson et al. (2003).

Literature survey—We collected from the open literature and unpublished sources 395 measurements of $\delta^{13}\text{C}$ -DIC from 72 freshwater lakes on four continents. If the data from the literature was not in tabular form, values were extracted from graphs with the use of a caliper. Other variables of interest that were collected were DIC concentration, pCO_2 , pH, temperature, and area. Only measurements of surface water (less than 1-m depth for most lakes) during open-water seasons were collected. The sources of the data are found in Web Appendix 1 (http://www.aslo.org/lo/toc/vol49/issue_4/1160a1.pdf).

Process-based lake model—We created a process-based model to simulate $\delta^{13}\text{C}$ -DIC values in our primary study lakes. The model simultaneously accounts for total DIC and DI^{13}C . Total DIC is modeled according to Fig. 1. Respiration

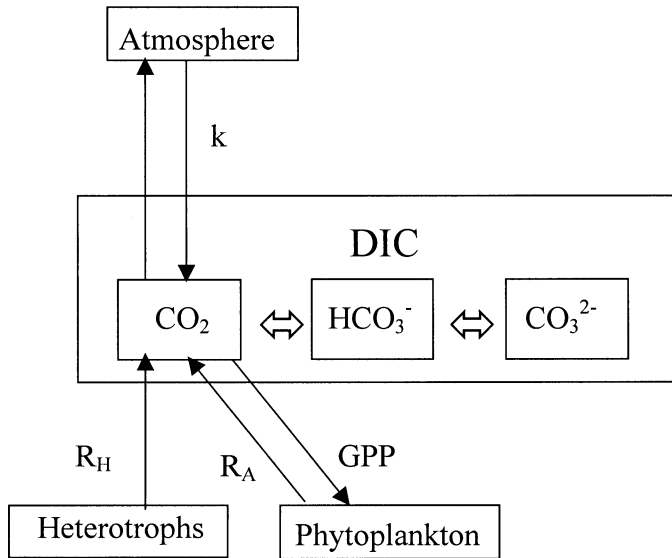


Fig. 1. Conceptual diagram of total DIC portion of isotope model.

adds CO_2 to the DIC pool and GPP removes CO_2 . For each lake, R and GPP estimates from Hanson et al. (2003) are used in the simulation. These estimates are based on O_2 dynamics and assume a 1:1 conversion (by moles) from O_2 to CO_2 . CO_2 also exchanges with the atmosphere, which is driven by the CO_2 concentration gradient between the lake and the atmosphere, and a mass transfer coefficient (k). The value of k for all simulations was set at 0.5 m d^{-1} , which is a typical value for lakes of this size (Cole and Caraco 1998; Cole et al. 2000). Temperature is set at 20°C for all lakes. Alkalinity is calculated from the measured values of DIC, pH, and temperature and remains constant throughout the model run. During the simulation, pH is calculated from DIC, alkalinity, and temperature; carbonate speciation is determined by carbonate thermodynamic equilibrium (Stumm and Morgan 1996). DIC inputs from groundwater or surface water were ignored in this model, as were other internal processes such as calcite precipitation (generally nonexistent in these softwater lakes), mixing across the thermocline (small during the stratified period; Cole and Pace 1998), and methane oxidation. The differential equation for the total DIC pool is

$$\frac{d[\text{DIC}]}{dt} = R - \text{GPP} + \frac{\{k \times (\text{CO}_{2\text{eq}} - [\text{CO}_2])\}}{Z_{\text{mix}}} \quad (1)$$

where $\text{CO}_{2\text{eq}}$ is the concentration of CO_2 in water in equilibrium with the atmosphere, $[\text{CO}_2]$ is the actual concentration of CO_2 in the water, and Z_{mix} is the mixed layer depth.

The DI^{13}C is modeled in a similar fashion but takes into account the isotopic signature of different inputs of DIC, the biological fractionation that occurs during photosynthesis, and chemical fractionation between different carbonate species. We assume that photosynthesis fractionates carbon by -20‰ relative to the isotopic signature of CO_2 . For example, if the isotope signature of CO_2 is -15‰ , then the isotope signature of autochthonously produced organic carbon would be -35‰ . We use the photosynthetic fractionation

factor of -20‰ , which is below maximum, because it is unlikely that in an assemblage of phytoplankton all are fractionating maximally because of differences in growth rate or utilization of other carbon sources, such as HCO_3^- (Laws et al. 1995). Respiration is the sum of two components; respiration of autochthonously produced carbon (R_A), with an isotope signature equal to GPP (-35‰ , from example above), and respiration of allochthonous material (R_H), with an isotope signature assumed to be -27‰ . R_A was assumed to be 90% of GPP (Cole et al. 2000; but *see* Results), and the remaining 10% of GPP is permanently removed from the system because of flushing or permanent burial in the sediments, neither of which is explicitly modeled. R_H is then calculated as the difference of R_A from R . The differential equation for the DI^{13}C pool is

$$\frac{d[\text{DI}^{13}\text{C}]}{dt} = R_{H13} - \text{NPP}_{13} + \frac{\{k \times ({}^{13}\text{CO}_{2\text{eq}} - [{}^{13}\text{CO}_2])\}}{Z_{\text{mix}}} \quad (2)$$

where R_{H13} is R_H multiplied by the proportion of terrestrial carbon (-27‰) that is ^{13}C . Net primary production (NPP_{13}) is the difference of GPP minus R_A multiplied by the proportion of autochthonous carbon that is ^{13}C (dependent upon $\delta^{13}\text{C}\text{-CO}_2$ and phytoplankton fractionation factor). ${}^{13}\text{CO}_{2\text{eq}}$ is the concentration of $^{13}\text{CO}_2$ in water in equilibrium with the atmosphere, and $[{}^{13}\text{CO}_2]$ is the actual concentration of $^{13}\text{CO}_2$ in the water. The fractionation factors between carbonate species were calculated according to Zhang et al. (1995) and were used to determine $^{13}\text{CO}_2$.

The initial conditions for the model were set to those measured at the time of the survey, and the model was run until an equilibrium $\delta^{13}\text{C}\text{-DIC}$ value was reached. Model equilibration was defined as the time when $\delta^{13}\text{C}\text{-DIC}$ did not change more than 0.001‰ between iterations.

A sensitivity analysis was conducted on the model to determine what parameters have the most influence on model predictions or whether any of the parameters gave surprising results when manipulated. The parameters that were tested included Z_{mix} , R , GPP, k , temperature, photosynthetic fractionation (phyto. fractionation), percentage of GPP respired (phyto. respiration), and alkalinity. For each lake, the parameter of interest was varied by $\pm 1\%$ and $\pm 10\%$. The new predicted $\delta^{13}\text{C}\text{-DIC}$ value was subtracted from the original prediction, and the mean of the deviation was calculated over all lakes. The lakes used in this sensitivity analysis were the 20 lakes that had negative net ecosystem production ($\text{NEP} = \text{GPP} - R$).

The model above ignores external inputs of DIC, which are often unknown. However, we were able to create a more complete budget for three lakes (Trout, Allequash, and Big Musky Lakes), in which this input can be well estimated. Inputs of water from the watershed were calculated based on estimates of water residence times for these lakes and precipitation and evaporation values for the region (Michaels 1995; Webster et al. 1996). To estimate the alkalinity of the inflowing water, we assumed a steady-state alkalinity in the lake, and acid deposition that is balanced by internal alkalinity generation. The alkalinity of inflowing water (Alk_{in}) could then be calculated simply as

$$\text{Alk}_{\text{in}} = (\text{Alk}_{\text{lake}})\text{Out}/\text{In} \quad (3)$$

where Alk_{lake} is the alkalinity observed in the lake, Out is the losses of water, excluding evaporation, and In is the surface and groundwater inflows to the lake. In these lakes, precipitation ($\sim 0.8 \text{ m yr}^{-1}$) generally exceeds evaporation ($\sim 0.5 \text{ m yr}^{-1}$), diluting incoming alkalinity. The amount of DIC entering the lake associated with this alkalinity was determined from regression analysis of well-water data from 12 wells located within the watersheds of these lakes ($\text{DIC}(\mu\text{mol L}^{-1}) = 276.3 \times \ln(\text{Alk}(\mu\text{eq L}^{-1})) - 801.1$ $R^2 = 0.47$, $n = 120$; North Temperate Lake Long Term Ecological Research Program data, J. Rusak. The isotope signature of the groundwater was set at -20% based on measurements from the watershed by Kenoyer and Bowser (1992). Outflowing water had the same DIC concentration and isotope composition as that of the lake. The model was run to an equilibrium value, as outlined in the original model above.

The relative influence of external inputs of DIC versus internal processes was determined by calculating the fractional turnover rates of DIC for each process at the equilibrium condition of the model. The fractional turnover rates (τ_i) are calculated as

$$\tau_i = J_i/[\text{DIC}] \quad (4)$$

where J_i is the particular flux of interest and $[\text{DIC}]$ is the equilibrium DIC concentration. The same calculations were done for DI^{13}C . Fractional turnover rates are additive when determining the overall turnover rate

$$\tau = \sum_{i=1}^n \tau_i \quad (5)$$

From Eq. 5 it is apparent that if a particular process has a fast turnover rate, other processes will be less significant in the cycling of DIC isotopes (Stumm and Morgan 1996). The fractional turnover rates considered for total carbon dynamics include (from Eq. 1): inputs from NEP (τ_{NEP}), external loading of DIC (τ_{IN}), atmospheric invasion and evasion of CO_2 (τ_{GASIN} , τ_{GASEV}), and outflow (τ_{OUT}). Since there was no accounting for the fate of GPP or the source of R, we did not consider the fractional turnover rates of these processes individually, but rather represent it with τ_{NEP} . On the other hand, the governing equation for ^{13}C (see Eq. 2) considers the heterotrophic respiration of allochthonous material ($\tau_{13\text{RH}}$) and the loss of NPP ($\tau_{13\text{NPP}}$). In addition are the inflow and outflows ($\tau_{13\text{IN}}$, $\tau_{13\text{OUT}}$) and CO_2 invasion and evasion ($\tau_{13\text{GASIN}}$, $\tau_{13\text{GASEV}}$).

Results

Northern Highland lake survey—The 32 lakes surveyed from the Northern Highland Lakes District of Wisconsin and Michigan ranged from clear-water, low-DOC lakes to darkly stained, high-DOC lakes (Table 1). These lakes are oligotrophic to mesotrophic in nutrient status. There was little correlation between TP and DOC ($R^2 = 0.08$, $n = 32$, $P = 0.12$), although we found no lakes with both high TP ($>50 \mu\text{g L}^{-1}$) and high DOC ($>10 \text{ mg L}^{-1}$).

The variation of $\delta^{13}\text{C}$ -DIC among lakes is much greater

than the variation observed within five of the lakes over time (Fig. 2). The DIC isotope signature of individual lakes ranges from -31.1% in West Long Lake to -2.1% in Trout Lake (Table 1). The greatest temporal change we observed within a lake was only 5%.

The isotope signature of DIC is correlated with several variables. The most significant of these were $\log(\text{DIC})$ ($R^2 = 0.73$, $n = 32$, $P < 0.01$; Fig. 3a) and $\log(\text{alkalinity})$ ($R^2 = 0.73$, $n = 32$, $P < 0.01$; Fig. 3b). pH ($R^2 = 0.35$, $n = 32$, $P < 0.01$; Fig. 3c) and $\log(\text{area})$ ($R^2 = 0.40$, $n = 32$, $P < 0.01$; Fig. 3d) also have significant positive correlations with $\delta^{13}\text{C}$ -DIC. The pH relationship has several obvious outliers. The two most obvious, Peter and Snipe, were highly productive, as indicated by the pCO_2 values below atmospheric equilibrium. When these are removed, the R^2 value approaches that of DIC and alkalinity. There is a weak but significant correlation of $\delta^{13}\text{C}$ -DIC and $\log(\text{TP})$ ($R^2 = 0.16$, $n = 32$, $P < 0.05$). Overall, the relationship with DOC and $\delta^{13}\text{C}$ -DIC is negative but weak ($R^2 = 0.14$, $n = 32$, $P < 0.05$). However, for the lakes with DIC concentrations greater than $360 \mu\text{mol L}^{-1}$, there is a strong negative correlation of DOC and $\delta^{13}\text{C}$ -DIC ($R^2 = 0.73$, $n = 16$, $P < 0.01$). For lakes with DIC concentrations below $360 \mu\text{mol L}^{-1}$, there is no significant correlation of DOC and $\delta^{13}\text{C}$ -DIC ($R^2 = 0.03$, $n = 16$, $P = 0.52$). For these lakes, all the $\delta^{13}\text{C}$ -DIC values are relatively low, as predicted by the DIC relationship. No significant correlations ($P < 0.05$) existed between $\delta^{13}\text{C}$ -DIC and Chl *a*, pCO_2 , GPP, or R.

Several linear regression models predict the isotope signatures of lakes (Table 2). The model with the highest R^2 resulting from stepwise linear regression includes $\log(\text{DIC})$ and pCO_2 as predictor variables ($R^2 = 0.86$). For all models, the coefficients for $\log(\text{DIC})$ and $\log(\text{area})$ are positive, and the coefficients for pCO_2 and DOC are negative. Parameters considered in the stepwise regression were pCO_2 , pH , $\log(\text{DIC})$, $\log(\text{alkalinity})$, $\log(\text{area})$, $\log(\text{TP})$, DOC, and $\log(\text{Chl } a)$.

Literature survey—In the literature survey, lake isotope signatures ranged from -29.6% to $+2.6\%$ (Fig. 4). For most lakes, the range of $\delta^{13}\text{C}$ -DIC values is within $\pm 5\%$ of the mean value for that lake. Only one lake, Hakanoa (New Zealand; McCabe 1985), has $\delta^{13}\text{C}$ -DIC values that span nearly the entire range of values across all lakes.

For the literature survey lakes, mean $\delta^{13}\text{C}$ -DIC was correlated with mean pH ($R^2 = 0.61$, $n = 38$, $P < 0.01$). However, between pH 5 and 7, $\delta^{13}\text{C}$ -DIC increases, and between pH 8 and 10 it decreases (Fig. 5a). Also in Fig. 5a, the line showing the $\delta^{13}\text{C}$ -DIC values at isotopic equilibrium with the atmosphere is displayed. The isotopic equilibrium is calculated according to Zhang et al. (1995) and is dependent on pH . Most lakes have $\delta^{13}\text{C}$ -DIC values below isotopic equilibrium with the atmosphere. $\log(\text{alkalinity})$ and $\log(\text{DIC})$ are also correlated with $\delta^{13}\text{C}$ -DIC ($R^2 = 0.37$, $n = 289$, $P < 0.01$ and $R^2 = 0.25$, $n = 358$, $P < 0.01$, respectively).

Lake area appears to be related to the degree to which lakes deviate from isotopic equilibrium with the atmosphere. Larger lakes are closer to isotopic equilibrium with the atmosphere than are smaller lakes (Fig. 5b). While a positive

Table 1. Limnological data from 32 Northern Highland lakes surveyed in the summer of 2000.

Lake	Day of year	Area (ha)	pCO ₂ (µatm)	pH	DIC (µmol L ⁻¹)	Alkalinity (µeq L ⁻¹)	TP (µg L ⁻¹)	DOC (mg L ⁻¹)	Total chl (µg L ⁻¹)	δ ¹³ C-DIC (‰)
Allequash	173	168.4	315	7.2	947	823	36.6	3.1	8.0	-10.6
Allequash	200	168.4	261	7.2	880	761	43.0	4.3	8.4	-8.9
Allequash	228	168.4	172	7.5	867	814	59.0	3.7	12.6	-10.0
Big Musky	230	396.3	273	6.8	429	307	9.4	4.5	4.5	-11.6
Bogpot	210	1.83	287	6.1	48	16	41.5	13.5	37.5	-30.7
Bolger	214	1.07	3,813	6.3	452	217	34.4	14.6	13.8	-19.3
Brown	196	32.9	403	7.5	1,431	1,328	55.9	9.1	13.2	-8.5
Crampton	181	25.8	442	5.9	38	10	13.2	4.0	3.5	-25.1
Cranberry	165	1.4	87	4.8	7	<1	22.7	10.5	30.5	-28.0
Cranberry	195	1.4	437	4.7	22	<1	13.1	11.6	17.0	-25.1
Cranberry	237	1.4	1,118	3.8	46	<1	20.1	12.4	20.2	-30.2
Crystal	200	36.7	143	5.8	33	7	4.4	1.6	2.7	-23.7
Diamond	174	49.4	434	6.0	47	13	8.1	2.0	1.7	-23.0
Diamond	201	49.4	303	7.5	35	33	6.1	2.0	3.1	-27.5
Diamond	229	49.4	359	6.2	39	15	7.0	1.7	2.8	-27.2
East Long	235	2.3	1,689	5.5	95	11	23.2	12.4	14.7	-29.2
Helmet	221	2.8	2,705	5.5	145	19	19.9	20.3	15.4	-26.2
Hiawatha	217	14.6	371	6.9	363	275	20.2	17.5	3.5	-16.3
Hummingbird	164	0.8	1,409	5.0	63	3	34.7	17.4	13.6	-28.0
Hummingbird	187	0.8	7,280	4.6	357	6	33.9	20.8	20.4	-26.1
Hummingbird	230	1.4	3,321	4.9	154	5	27.0	22.7	23.6	-28.3
Kickapoo	192	7.9	3,227	6.6	625	399	34.9	14.2	14.3	-14.0
Little Arbor Vitae	208	216.1	150	8.5	1,114	1,121	105.3	3.2	56.9	-7.7
Mary	220	1.2	1,273	5.9	96	25	18.6	21.7	25.1	-25.7
Morris	186	5.9	1,603	7.1	980	837	no data	13.0	7.7	-11.0
Morris	210	5.9	1,314	7.3	977	867	30.5	14.8	23.4	-11.0
Muskellunge	207	110	218	7.2	808	703	78.3	5.0	18.4	-11.0
North Gate Bog	206	0.3	4,950	4.2	226	2	15.3	24.6	2.7	-27.5
Palmer	227	257	395	7.2	1,041	914	51.1	8.2	12.2	-11.9
Paul	166	1.7	820	6.3	94	41	9.9	4.1	2.8	-15.5
Peter	236	2.7	33	9.0	46	48	21.3	6.4	30.2	-28.6
Plum	193	91.0	150	7.7	638	609	28.0	4.7	10.3	-7.5
Reddington	206	1.2	5,650	5.9	388	94	34.0	23.1	17.6	-20.9
Snipe	207	96.7	120	7.4	52	47	26.8	4.0	12.1	-30.6
Sparkling	227	64.0	237	6.8	670	492	16.8	3.1	2.3	-8.8
Tenderfoot	195	165.2	414	7.7	992	952	42.5	7.8	17.3	-9.2
Trout	202	1,090.9	229	7.4	962	870	25.2	2.2	3.0	-2.1
Trout Bog	200	1.1	929	4.6	42	1	29.3	17.0	38.8	-28.0
Tuesday	171	0.8	344	6.3	53	23	21.7	7.5	14.3	-24.0
Ward	210	2.7	948	7.2	1,658	1,438	28.1	7.0	5.8	-8.4
West Long	234	5.5	1,143	5.9	81	18	13.8	6.6	7.6	-31.1

correlation exists between lake area and pH in this data set, a similar but much weaker relationship exists between distance from equilibrium and pH.

A regression model to predict the mean values of δ¹³C-DIC was constructed from the literature survey data. The variables considered in the model were log(DIC), pH, pCO₂, and area. The best model was δ¹³C-DIC = -105.32 + 21.90(pH) - 1.25(pH)² + 1.54(log(area)) ($R^2 = 0.69$, $n = 41$, $P < 0.01$). A weak but significant correlation exists between δ¹³C-DIC and mean log(DIC) ($R^2 = 0.30$, $n = 50$, $P < 0.01$). No relationship was found with pCO₂ alone.

Process-based lake model—Model predictions of equilibrium δ¹³C-DIC compared reasonably well with actual observations for 20 lakes (Fig. 6). The model produced predictions that ranged from -25.8‰ to 0.80‰, which is close to

the observed range, but truncated at the negative end and slightly expanded at the positive. The time for the model to reach equilibrium varied from <30 d to >4 yr and was dependent upon the size of the DIC pool as well as the metabolic rates. This may not be the actual time for a lake to reach equilibrium, since the model time to equilibrium is dependent upon the initial conditions.

Model predictions and observed values of δ¹³C-DIC were plotted against the ratio of GPP:R to assess the influence of metabolism (Fig. 7a). Model predictions with low values of GPP:R had the most negative isotope values; as GPP:R approached unity, there was a nonlinear increase in isotope values toward zero. The scatter of observations around model predictions was greatest for intermediate values of GPP:R (0.5–0.8). Since the regression models showed the importance of DIC, model predictions and observed δ¹³C-DIC

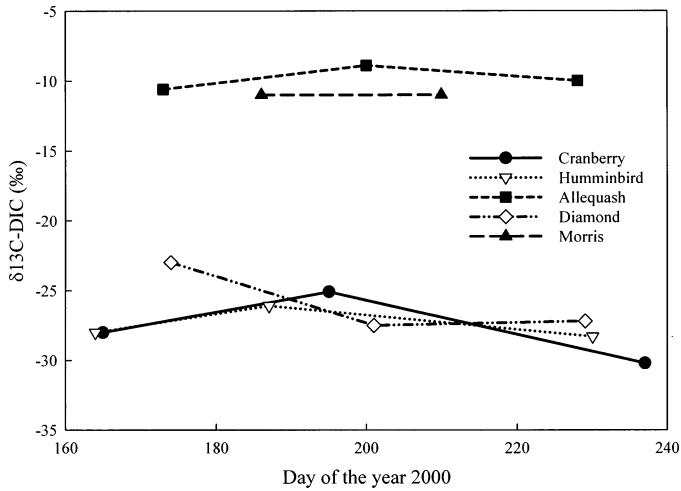


Fig. 2. Temporal variation of $\delta^{13}\text{C-DIC}$ (‰) in five lakes throughout the survey period.

were also plotted against DIC (Fig. 7b). The lakes with the lowest DIC were consistently overestimated (predictions were more positive than observed) by the model. Lakes with higher DIC concentrations showed no apparent pattern in the residuals.

Lakes that had positive NEP were excluded from Figs. 6 and 7 because they were not fit well by the model. The fit could be improved with ad hoc tuning of parameters, as follows (Table 3). The percentage of GPP respired (phyto. respiration) was reduced so that autotrophic respiration did not exceed total respiration. Theoretically the value for this parameter must exceed zero, since phytoplankton themselves must respire. The parameter could be as large as 100% if all GPP is utilized and respired back into the water column. Quay et al. (1986) summarize this value to be between 54% and 88%; however, others have used 90% in modeling exercises (Cole et al. 2000; Caraco and Cole in press). In addition, the piston velocity was increased to allow enough CO_2 influx to support the level of primary production. This is reasonable, since periods of high productivity can draw down CO_2 and increase pH, allowing chemically enhanced diffusion to increase the invasion rate (Wanninkhof and Knox 1996). The magnitudes of the adjustments in k seem implausible for some cases. Even with these parameter adjustments, the predicted values were more positive than observations (Table 3).

Sensitivity analysis of the process-based model showed that R and GPP were the most influential parameters (Fig. 8). The sensitivity analysis showed one surprising result, which was the importance of the amount of GPP that is respired (phyto. respiration; this value determines R_A and $\text{NPP}_{1,3}$). The predicted values are not affected greatly by changes in Z_{mix} , k , temperature, phytoplankton fractionation factor (phyto. fractionation), or alkalinity.

External inputs of alkalinity and the corresponding DIC have varying influence on $\delta^{13}\text{C-DIC}$ depending on their magnitude and the magnitude of metabolism in Allequash, Big Musky, and Trout Lakes (Table 4). In considering the turnover rates, we will first consider inputs of DIC (positive

values in Fig. 9a,b). In Big Musky Lake, a seepage lake, water residence times are long; therefore, τ_{IN} is small and metabolism (negative NEP) is the most influential process. Allequash Lake is a drainage lake with very short water residence time. Despite this, τ_{IN} and τ_{NEP} are nearly equal. Finally, Trout Lake has a moderate residence time but an NEP value that is close to zero. External inputs (τ_{IN}) and gas exchange (τ_{GASIN}) were the dominant processes, and τ_{NEP} was not visible on the graph. The fractional turnover rates with respect to DI^{13}C show similar results, except in Trout Lake $\tau_{13\text{IN}}$ and $\tau_{13\text{RH}}$ were nearly the same as a result of the effect of some GPP being lost to sedimentation ($\tau_{13\text{NPP}}$).

Although not shown, the difference in the isotopic signature of inflowing water had little influence on the fractional turnover rates of DI^{13}C . Fractional turnover rates of the losses may be considered, but these are generally dependent upon inputs and therefore do not exhibit direct control on the cycling of DIC. For example the large τ_{GASEV} is a result of large τ_{NEP} . An exception is in the term $\tau_{13\text{NPP}}$, which is a loss that is independent of the input terms. This term shows signs of being significant in the cycling of DI^{13}C in Trout and Allequash Lakes, which corroborates with results from the sensitivity analysis of the importance of the amount of GPP that is respired.

The process-based model was compared to the statistical models with the use of the Akaike Information Criteria (AIC), which compares different models using a likelihood adjusted for the number of fitted parameters (Burnham and Anderson 1998). The statistical models that included DIC and pCO_2 performed the best (Table 5). The process-based model performed only marginally better than the regression model containing only DIC. If the complete data set (including lakes with positive NEP) is used, the process-based model does not compare favorably with any of the regression models.

Discussion

Lakes exhibit a broad range of $\delta^{13}\text{C-DIC}$ values, and the variation among lakes is generally greater than the variation over time within a lake. Patterns observed in the Northern Highland lakes were similar to those seen in the literature survey of lakes from diverse regions. The pattern of isotope signatures among lakes can be predicted using simple regression models that include effects of geochemical (pH, DIC, or alkalinity) or morphometric (lake size) variables. Simple correlations did not strongly support the hypothesis that $\delta^{13}\text{C-DIC}$ should be strongly related to productivity and respiration in the Northern Highland lake survey. However, DOC and pCO_2 , which were not highly correlated with $\delta^{13}\text{C-DIC}$, were significant predictors in regression models, suggesting a possibly important role of respiration analogous to the results of Striegl et al. (2001).

A process-based model considering only gas exchange and lake metabolism was also able to predict the variation in isotope signatures among lakes. Thus, while simple correlations with GPP or R did not have strong predictive powers, the process-based model may better represent the complex interactions that determine the carbon isotope ratio in

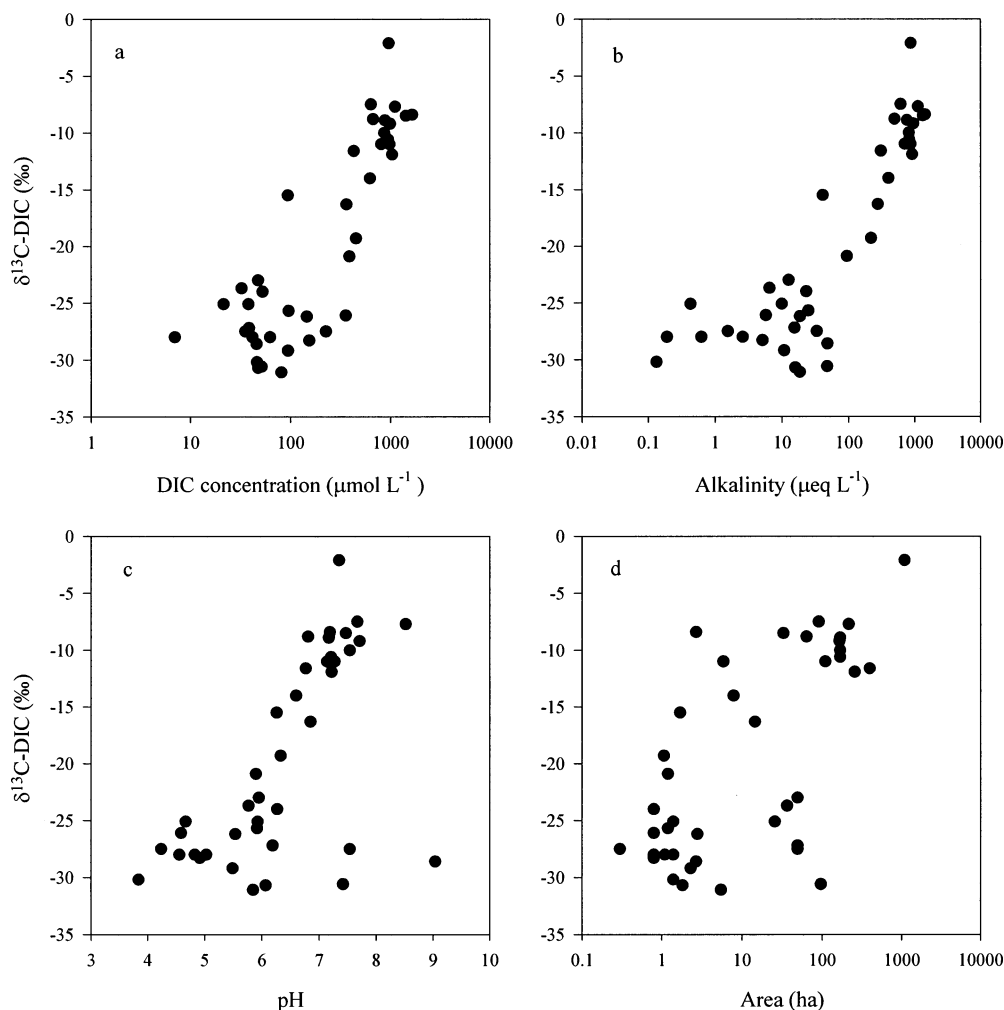


Fig. 3. Scatterplots of $\delta^{13}\text{C-DIC}$ (‰) with variables of interest: a) $\delta^{13}\text{C-DIC}$ (‰) versus DIC ($\mu\text{mol L}^{-1}$); b) $\delta^{13}\text{C-DIC}$ (‰) versus alkalinity ($\mu\text{eq L}^{-1}$); c) $\delta^{13}\text{C-DIC}$ (‰) versus pH; d) $\delta^{13}\text{C-DIC}$ (‰) versus area (ha). Note: these figures contain all data, but the statistical analyses in the text only include one data point if a lake was sampled more than once. The points included for statistical analyses for lakes sampled more than once are Allequash (day 200), Cranberry (195), Diamond (229), Morris (210), and Hummingbird (187).

lakes. Because the process-based model ignored a potential driver related to geochemical variables—terrestrial loading of alkalinity or DIC—the interaction of metabolism and geochemical variables will be considered more carefully.

Interaction of metabolism and geochemical variables—Both the literature data and our own measurement set revealed a strong effect of pH on $\delta^{13}\text{C-DIC}$. The trend of increasing isotope signatures from acidic (pH 5) to

circumneutral pH in the literature survey is similar to the trend observed in the Northern Highland lakes. Above pH values of 8 to 9, there was a trend of decreasing isotopic signature for the literature survey data. This may be due to chemically enhanced diffusion of CO_2 and its associated fractionation, as was suggested to be the case in Mohonk Lake (Herczeg and Fairbanks 1987).

Fractionation between CO_2 and carbonate species at different pH values can explain approximately 8.6% of the var-

Table 2. Linear regression models predicting $\delta^{13}\text{C-DIC}$ for Northern highland lakes.

Equation	R^2	P	n
$\delta^{13}\text{C-DIC} = 13.356 \times \log(\text{DIC}) - 0.002 \times \text{pCO}_2 - 47.999$	0.86	<0.01	32
$\delta^{13}\text{C-DIC} = 12.657 \times \log(\text{DIC}) - 0.454 \times \text{DOC} - 44.070$	0.85	<0.01	32
$\delta^{13}\text{C-DIC} = 10.652 \times \log(\text{DIC}) + 2.951 \times \log(\text{area}) - 47.060$	0.81	<0.01	32
$\delta^{13}\text{C-DIC} = 12.751 \times \log(\text{DIC}) - 48.853$	0.73	<0.01	32

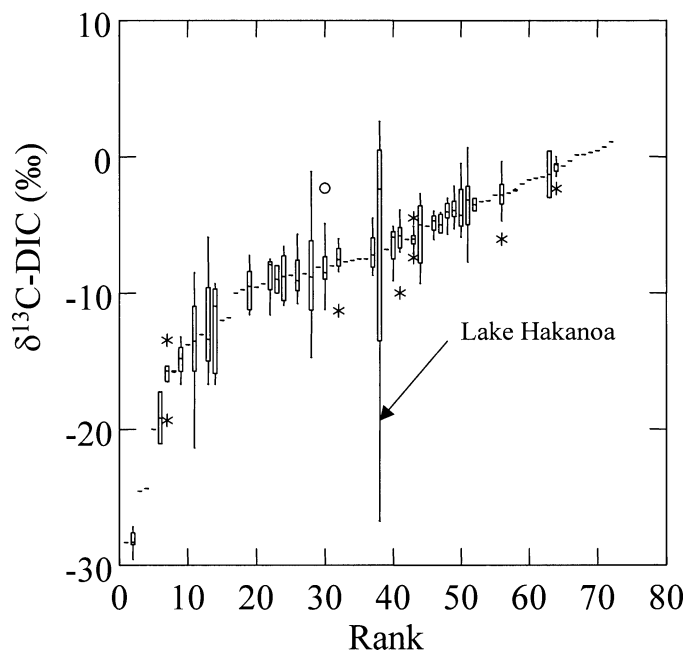


Fig. 4. Boxplot of $\delta^{13}\text{C-DIC}$ values (‰) obtained from literature and other sources versus ranked mean $\delta^{13}\text{C-DIC}$ values for each lake (i.e., the lowest mean value is given a rank of 1 and rank increases by integer steps with increasing mean isotope value). Median values are represented by a dash, and the distance between the box ends (Hspread) contain data between the first and third quartile. The whiskers show the data that fall within $1.5 \times \text{Hspread}$ from each box end. Values greater than $1.5 \times \text{Hspread}$ but less than $3 \times \text{Hspread}$ are plotted with an asterisk, and those outside of $3 \times \text{Hspread}$ are plotted with an open circle (Systat 1998). Lake Hakanoa (McCabe 1985) is noted to have variation that spans nearly the entire range observed among lakes.

iation in $\delta^{13}\text{C-DIC}$, but not the total observed variation of more than 30‰. At low pH values, with $\text{CO}_2(\text{aq})$ being the dominant carbonate species, there is only a small negative fractionation between $\text{CO}_2(\text{aq})$ and atmospheric CO_2 . As HCO_3^- becomes more dominant at higher pH values, the larger positive fractionation of this species becomes more evident in the $\delta^{13}\text{C-DIC}$ signature. Thus, at isotopic equilibrium with the atmosphere, low-pH (~ 5) lakes are depleted ($\delta^{13}\text{C-DIC} \approx -8.6\text{‰}$) in ^{13}C , compared with lakes of moderate to high pH (pH = 8, $\delta^{13}\text{C-DIC} \approx 0\text{‰}$; see line in Fig. 5a). Therefore, other factors likely covary with pH to cause the patterns observed. For example, humic lakes have a low pH because of the presence of organic acids and are generally dominated by respiration of terrestrially derived organic matter, which should decrease $\delta^{13}\text{C-DIC}$.

Through carbonate chemistry, the correlation of $\delta^{13}\text{C-DIC}$ with alkalinity and DIC concentration (in the Northern Highland lakes) is certainly not independent from the pattern observed with the pH. So perhaps the covariation could be explained by differences in external inputs of alkalinity and DIC from groundwater or surface water? Groundwater from areas dominated by carbonate dissolution may have higher DIC concentrations and a more positive isotope value than groundwater dominated by soil respiration and silicate mineral dissolution (Pawellek and Veizer 1994). Therefore, if

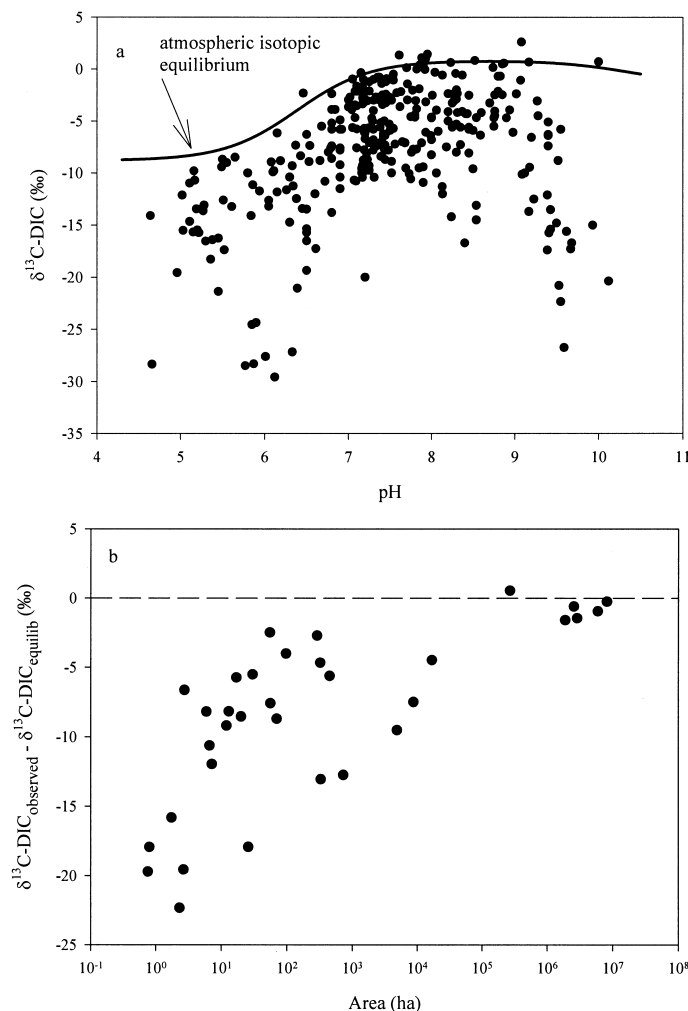


Fig. 5. $\delta^{13}\text{C-DIC}$ relationships from the literature survey and other sources. a) $\delta^{13}\text{C-DIC}$ values (‰) versus pH. The curved line represents the isotope signature of a lake that is at isotopic equilibrium with the atmosphere at a given pH (Zhang et al. 1995). b) Distance from isotopic equilibrium ($\delta^{13}\text{C-DIC}_{\text{observed}} - \delta^{13}\text{C-DIC}_{\text{equilib}}$) versus \log_{10} area (ha). $\delta^{13}\text{C-DIC}_{\text{observed}}$ is the mean $\delta^{13}\text{C-DIC}$ value for a lake and $\delta^{13}\text{C-DIC}_{\text{equilib}}$ is the atmospheric isotopic equilibrium value given the mean pH for that lake.

lakes were situated in different parent material (calcareous vs. siliceous), there could be a correlation between DIC concentration and the isotope signature. The geology of the Northern Highlands region is Precambrian bedrock overlain by sandy, noncalcareous till and outwash (Attig 1985). In this region, the role of carbonate dissolution in groundwater chemistry is minimal (Kenoyer and Bowser 1992). Therefore, within the Northern Highland Lake District, differences in external loading of alkalinity and DIC are generally related to the position of a lake within the hydrologic flowpath and not to differences in geology (Kratz et al. 1997). It is uncertain how this relationship manifests itself in terms of differences in the carbon isotope signature of incoming DIC.

The relative importance of geochemical drivers versus metabolism is difficult to discern because they may not be independent. For example, productivity and alkalinity may

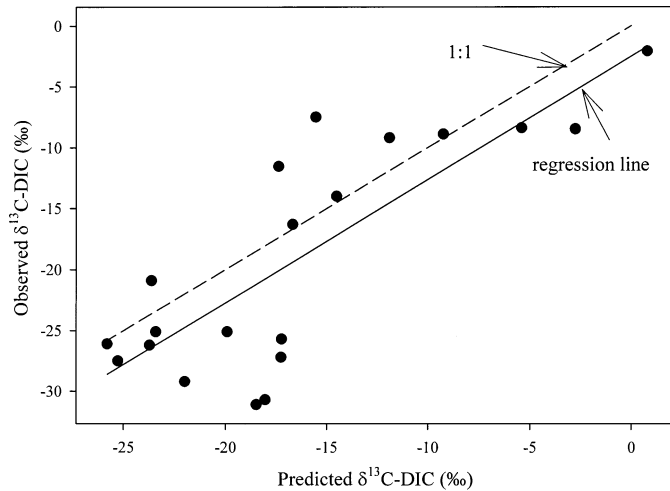


Fig. 6. Observed $\delta^{13}\text{C-DIC}$ values (‰) of Northern Highland lakes versus model predicted $\delta^{13}\text{C-DIC}$ (‰), based on measurements of GPP and R. Only lakes with negative NEP are plotted ($n = 20$). The slope and intercept of the line were indistinguishable from one (1.01 ± 0.18) and zero (-2.51 ± 3.19), respectively, and the regression was significant ($R^2 = 0.64$; $P < 0.01$).

covary through several mechanisms (Kilham 1982). In the Northern Highland lakes, there are no strong correlations between alkalinity or DIC and measures of metabolism (data not shown). However, there are no lakes with alkalinity greater than $200 \mu\text{eq L}^{-1}$ that have GPP:R ratios less than 0.5.

It was possible to consider the role of external geochemical drivers using the process-based model in three representative lakes (Table 4; Fig. 9). If external drivers were dominant, their effects should be most evident in lakes with short water residence time, such as Allequash Lake. However, this was not the case in Allequash Lake, where external inputs and NEP were of similar importance. Only in Trout Lake, where NEP was close to zero, did external inputs of DIC become the dominant process. In Big Musky Lake, where water residence time was long, NEP overshadowed external inputs. Had the fractional turnover rates of the individual process of GPP and R been considered instead of the net effect (NEP), metabolism would have been overwhelmingly dominant in all three lakes. Therefore, among the lakes sampled we find strong effects of metabolism on $\delta^{13}\text{C-DIC}$ in many lakes. Although geochemical drivers must affect $\delta^{13}\text{C-DIC}$ in all lakes, these effects may be most evident in lakes with very short water residence times or NEP values that are near zero.

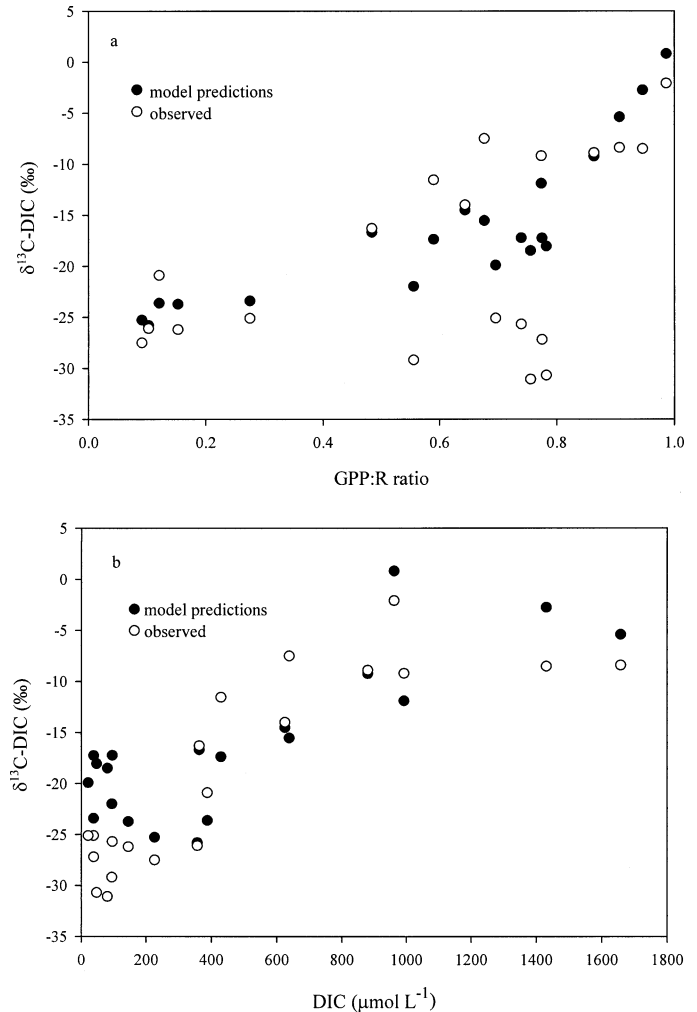


Fig. 7. Model prediction and observed $\delta^{13}\text{C-DIC}$ plotted against a) the ratio of GPP:R and b) DIC ($\mu\text{mol L}^{-1}$) for lakes with negative NEP (GPP:R < 1).

Effect of lake area—Only the largest lakes tend to be near isotopic equilibrium with the atmosphere. This may be attributed to increased wind speeds, which in turn increase gas exchange rates. To address the potential impact of wind exposure on equilibration rates, we used the following simple model. Mixed layer depth (Z_{mix}) was modeled after Fee et al. (1996) as (Fig. 10a)

$$Z_{\text{mix}}(\text{m}) = 2.92 + 0.0607 \times [\text{lake area}(\text{m}^2)]^{0.25} \quad (6)$$

This relationship was based on lakes that ranged in size from

Table 3. Parameter changes and model predictions for lakes with positive NEP.

Lake	NEP ($\text{mmols C m}^{-3} \text{ d}^{-1}$)	k (m d^{-1})	Phyto. respired	Predicted $\delta^{13}\text{C-DIC}$	Observed $\delta^{13}\text{C-DIC}$
Crystal	0.5	No change	No change	7.7	-23.7
Trout Bog	13.8	1.7	.7	15.4	-28
Muskellunge	6.3	2.1	.85	17.9	-11
Peter	14.7	4	.75	20.7	-28.6
Little Arbor Vitae	32.2	13	.75	18.6	-7.7

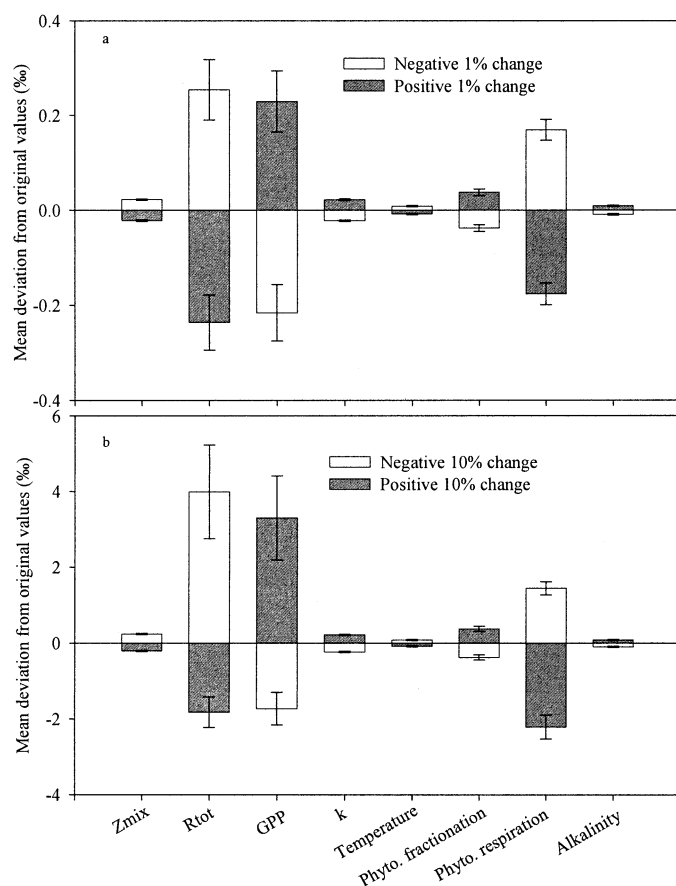


Fig. 8. Sensitivity analysis results: a) Effect of 1% change; b) Effect of 10% change. Bars indicate mean difference from the original value for the 17 lakes modeled in Fig. 6. Error bars are ± 1 standard error. Light bars represent negative change in the parameter and dark bars indicate positive change in the parameter.

3.6 ha to 34,700 ha. Above this, the relationship may not be valid and was estimated to asymptote at 20 m based on data for the Laurentian Great Lakes (Gorham and Boyce 1989). In order to calculate gas exchange rates, the effect of lake area on wind speed must be estimated. We assumed a wind speed (U_{10}) of 1 m s^{-1} for the smallest lake, based on measurements on three lakes of these sizes (Cole et al. 2000). For the largest, we assumed a wind speed of 8 m s^{-1} , based

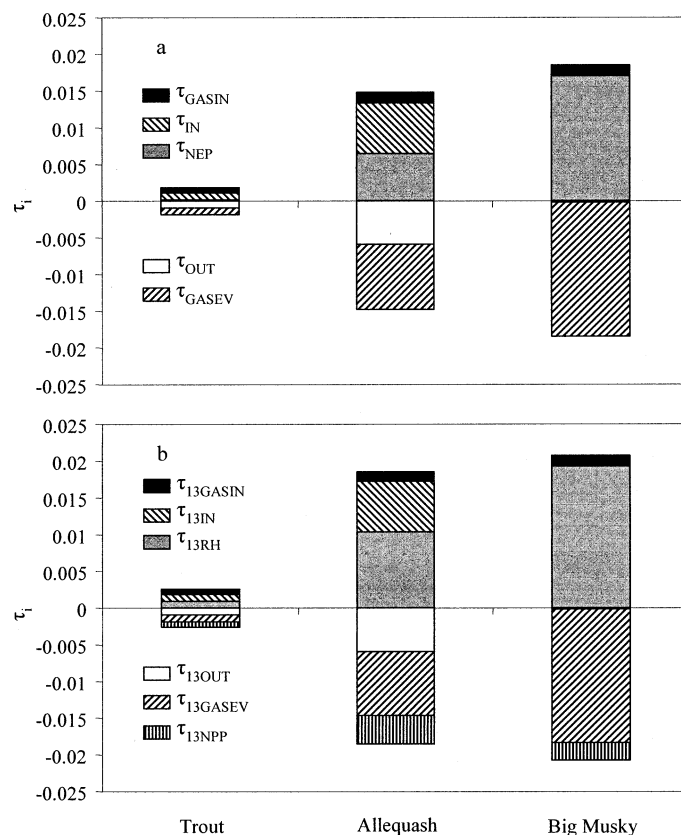


Fig. 9. Fractional turnover rates of individual processes for a) DIC and b) DI^{13}C . The summed height of the bar in the positive or negative direction is equivalent to the total turnover rate of DIC or DI^{13}C for that particular lake.

on monthly average wind speed from a moored buoy in Lake Superior (http://www.ndbc.noaa.gov/images/climplot/45001_ws.jpg). A log-linear relationship was used to estimate wind speeds for lakes between these two endpoints. The gas transfer or piston velocity (k ; m d^{-1}) was then modeled after the relationship by Cole and Caraco (1998) (Fig. 10b).

$$k = 0.497 + 0.052 \times [U_{10}]^{1.7} \quad (7)$$

A residence time (R_t ; d) of CO_2 in lake water exchanging with the atmosphere was then calculated.

Table 4. Characteristics and model results of three lakes in which external inputs of alkalinity and DIC were considered in the process-based model.

Lake	Trout	Allequash	Big Musky
NEP ($\text{mmol m}^{-3} \text{ d}^{-1}$)	-0.1	-5.4	-8.2
Water residence time (yr)	4.6	0.5	8
Inflow alkalinity conc. ($\mu\text{eq L}^{-1}$)	965	786	880
Inflow DIC conc. ($\mu\text{mol L}^{-1}$)	1,098	1,041	1,072
DIC inflow ($\text{mmol m}^{-3} \text{ d}^{-1}$)	0.89	5.87	0.07
DIC outflow ($\text{mmol m}^{-3} \text{ d}^{-1}$)	-0.79	-4.93	-0.09
Net CO_2 evasion ($\text{mmol m}^{-3} \text{ d}^{-1}$)	-0.20	-6.34	-8.18
Observed (%)	-2.1	-8.9	-11.55
Original model prediction (%)	0.80	-9.24	-17.39
Predictions with external inputs (%)	-6.87	-12.81	-17.41

Table 5. AIC values for comparison of statistical and process-based models. Data used for all model comparisons are the 20 lakes with negative NEP used in the process-based model. It is a requirement of this method that only identical data sets be compared. Lower values of AIC denote a higher likelihood that the model is correct.

Model predictor variables	AIC
DIC, pCO ₂	60.3
DIC, DOC	61.4
DIC, area	61.0
DIC	66.6
Process-based model	66.5

$$Rt = Z_{\text{mix}}/k \quad (8)$$

Based on calculation of Rt , larger lakes actually have the greatest residence time (slowest equilibration time), given similar chemical conditions of pH and DIC (Fig. 10c). However, the difference between all lakes is only a matter of days and is likely a minor difference across lakes of different sizes. Differences in the size of the DIC pool among lakes will have larger effects on the isotopic equilibration time, beyond that calculated in this exercise.

One possible explanation for decreasing $\delta^{13}\text{C}$ -DIC with decreasing lake size is the relatively high contribution of terrigenous carbon to the budget of smaller lakes. Lakes with smaller lake area to watershed area ratios (LA:WA) generally have greater inputs of organic material from the watershed than lakes with larger LA:WA values (Schindler 1971; Rasmussen et al. 1989). Also, the influence of landscape position on water chemistry may be related to lake area. Larger lakes tend to be situated lower in the hydrological landscape and therefore receive proportionally greater inputs of ion-rich groundwater (Kratz et al. 1997). Log(area) and log(DIC) are weakly correlated in this study ($R^2 = 0.19$, $n = 41$, $P < 0.01$), consistent with a relationship of lake area to groundwater input. The interaction of LA:WA ratios and landscape position may create the situation in which larger lakes have GPP:R ratios that are closer to unity, and atmospheric exchange or external inputs of DIC become the dominant factor controlling $\delta^{13}\text{C}$ -DIC.

Critique of process-based model—The main limitation of this model is the equilibrium assumption for the output values and the fact that the time to equilibrium varies among lakes and may be longer than one stratified season. In reality, lakes may or may not exist at equilibrium during the summer period. However, the narrow range of $\delta^{13}\text{C}$ -DIC within lakes indicates that lakes exist within a state of dynamic equilibrium, which is much less than the overall variability observed among lakes. Lakes with large DIC pools have the largest equilibration time and integrate variability in processes over a long time period. Therefore, they are least likely to show large variation in $\delta^{13}\text{C}$ -DIC. Lakes with small DIC pools may show more variability in $\delta^{13}\text{C}$ -DIC but still integrate processes over a good portion of the stratified season.

Lack of fit in the model occurs most notably in lakes with the most negative observed isotope values and moderate val-

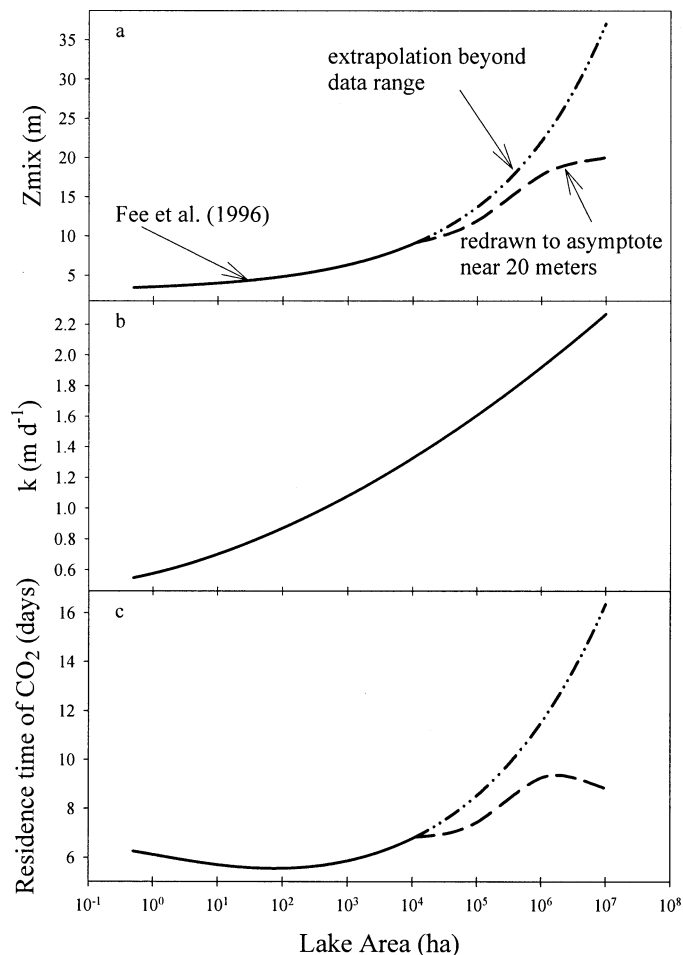


Fig. 10. Estimation of CO₂ residence time in lakes of different sizes: a) Solid line is the mixed layer depth, Z_{mix} (m) = $2.92 + 0.0607 \times [\text{Lake area (m}^2\text{)}]^{0.25}$ (Fee et al. 1996). The dotted line extrapolates this equation beyond the scope of the original data (>10,000 ha). The dashed line is estimated and hand-drawn to asymptote near 20 m for extremely large lakes (Gorham and Boyce 1989); b) Mass transfer coefficient (k ; m d⁻¹) calculated from estimated wind speeds (U_{10} ; m s⁻¹) in different size lakes (see text). c) Residence time (R_t ; d) of CO₂ versus lake area (ha). Note log scale on x axis.

ues of GPP:R (Figs. 6, 7a). $\delta^{13}\text{C}$ -DIC in these lakes tends to be overestimated by the model. The lakes overestimated by the model generally have low DIC concentrations (Fig. 7b), of which there are two types. One type is the high-DOC, slightly acidic lakes and the other is the oligotrophic lakes. Many of these lakes also tend to be smaller. These factors may help to explain areas in which the model could be improved by including or tuning parameters that would increase the inputs of isotopically light C or decrease the loss of isotopically heavy C. Two sources of light C not accounted for in the model are groundwater inputs or hypolimnetic entrainment. Groundwater inputs seem to have little influence in these softwater lakes (see Results and earlier discussion). Another possible source of light C is oxidation of methane, which is isotopically very light (−60‰; Whiticar 1999). This may be particularly important in the high-DOC,

dystrophic lakes that generally have anoxic hypolimnions and high concentrations of methane. The rates and signatures of methane oxidation presented by Bastviken et al. (2003) are within the range that could produce model predictions 5 to 10‰ more negative for the case of one dystrophic lake, East Long Lake. Alternately, in the model, a value for k that is too high would cause the lake isotope signature to approach atmospheric values too quickly. Since our sensitivity analysis and lake area analysis indicate that k and atmospheric exchange have little overall influence on $\delta^{13}\text{C}$ -DIC, we chose not to model k as a function of lake size and feel that the lack of fit is mainly due to methane oxidation.

Although the model performed well for lakes with negative NEP, the predictions for lakes with positive NEP, were unsatisfactory. There are at least two possible explanations: that the model is invalid for lakes with positive NEP or that the observations of positive NEP are transient conditions that do not represent the average state of the lake. If lakes exist in a state of positive NEP for prolonged periods, then including a new term for isotope fractionation under conditions of chemically enhanced diffusion might make the model valid and improve predictions for lakes with positive NEP. Herczeg and Fairbanks (1987) suggested that this fractionation of atmospheric CO_2 may be around -13% to -15% . Alternatively, some lakes might exhibit transient periods of positive NEP when in fact they are heterotrophic most of the time. Two examples from this study are Peter Lake, which periodically is extremely productive, but in general exists in a state of negative NEP (Cole et al. 2000), and Trout Bog, which is likely heterotrophic most of the time based on the supersaturation of pCO_2 (Table 1). We believe the latter explanation is most likely for the lakes modeled (they generally have negative NEP), especially considering the time scale considered in the model.

Despite the limitations of the process-based model, it explains much of the pattern in the data. Surprisingly, in a comparison of models using AIC, the process-based model performed nearly as well as some regression models that are fitted to minimize error. Evidence from the process-based model supports the assertion that lake metabolism should be considered important for the cycling of DIC isotopes, despite the fact that statistical models may point to the importance of geochemical variables.

For lakes in general, it seems plausible that a gradient in dominance between external inputs and metabolism may affect $\delta^{13}\text{C}$ -DIC. It could be hypothesized that isotope signatures in lakes with fast turnover times, high input DIC concentrations, or NEP values near zero should most likely be controlled by external inputs. Since streams tend to be more closely connected with groundwater inputs than lakes, especially during baseflow conditions, they present an interesting end member to consider for this hypothesis. Finlay (2003) concluded that cycling of DIC within streams and rivers by metabolism is responsible for the variation in $\delta^{13}\text{C}$ -DIC in certain systems, and therefore it appears that not only geochemical drivers, but also metabolism, are important processes influencing $\delta^{13}\text{C}$ -DIC in lakes and other aquatic ecosystems.

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