

## Impact of chemically enhanced diffusion on dissolved inorganic carbon stable isotopes in a fertilized lake

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[1] At high pH the chemical reaction of CO<sub>2</sub> with OH<sup>-</sup> can significantly increase the mass transfer of CO<sub>2</sub> between air and water. The reaction of CO<sub>2</sub> with OH<sup>-</sup> strongly fractionates carbon isotopes in comparison to simple diffusion. These processes, chemically enhanced diffusion (CED) and chemically enhanced fractionation (CEF), greatly influence the carbon budgets and carbon isotope ratios for water bodies with high pH. Using floating chambers, we estimated mass transfer coefficients for CO<sub>2</sub> and a nonreactive gas, CH<sub>4</sub>, in an experimentally eutrophied lake. The mass transfer coefficient estimated from CH<sub>4</sub> flux did not vary greatly between measurements ( $k_{600} = 1.83 \pm 0.33 \text{ cm h}^{-1}$ ; mean  $\pm 1$  SD) and agreed well with other independent estimates of mass transfer. The mass transfer coefficient of CO<sub>2</sub>, however, was chemically enhanced by 3.5- to 7.5-fold. This enhancement was related to pH and temperature but was slightly higher than predictions from an existing model. We determined the role of CEF by modifying a model of CED to include both carbon isotopes (<sup>12</sup>C and <sup>13</sup>C). A whole-lake addition of inorganic <sup>13</sup>C to Peter Lake created dynamics in  $\delta^{13}\text{C}$ -dissolved inorganic carbon (DIC) and provided a test of the new model. The value of  $\delta^{13}\text{C}$ -DIC decreased from approximately  $-9\text{‰}$  to  $-21\text{‰}$ , a result that was well predicted by the model including CEF but could not be duplicated when CEF was omitted. Thus CED and CEF influenced the mass balance of air-water CO<sub>2</sub> exchange and had isotopic consequences for DIC. Although CEF is considered inconsequential for mean oceanic conditions, this model could be applied to marine systems for inorganic carbon modeling in areas where pH is elevated or physical mass transfer is limited because of low turbulence.

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### 1. Introduction

[2] The flux of CO<sub>2</sub> between air and water is one of the most important processes in the carbon budget of aquatic ecosystems. Although many lakes are supersaturated with CO<sub>2</sub> and are a net source of CO<sub>2</sub> to the atmosphere, highly productive lakes often have algal drawdown of CO<sub>2</sub> and can be net sinks of atmospheric CO<sub>2</sub> [Cole *et al.*, 1994; Hanson *et al.*, 2004]. The flux of atmospheric CO<sub>2</sub> into a lake prevents long-term inorganic C limitation, allowing algae to fully utilize other limiting nutrients. This flux is therefore a key factor in supporting large standing stocks of algae in eutrophic lakes [Schindler *et al.*, 1972]. Under conditions of extremely high productivity, uptake of CO<sub>2</sub> by algae leads to high pH values. At high pH the flux of CO<sub>2</sub> is augmented by the reaction,  $\text{CO}_2 + \text{OH}^- = \text{HCO}_3^-$ , which maintains a steeper CO<sub>2</sub> concentration profile within the boundary layer [Schindler *et al.*, 1972; Emerson, 1975; Wanninkhof and

Knox, 1996]. At low pH this reaction becomes less prominent, and diffusive flux is rate limiting.

[3] This augmented flux, referred to as chemically enhanced diffusion (CED), has been well documented using a variety of gas transfer models and assumptions [Bolin, 1960; Hoover and Berkshire, 1969; Quinn and Otto, 1971; Broecker and Peng, 1974; Emerson, 1975; Wanninkhof and Knox, 1996]. Most measurements of CED come from wind-wave tanks or other laboratory settings, and few measurements have been conducted in natural lake settings [e.g., DeGrandpre *et al.*, 1995; Wanninkhof and Knox, 1996]. Chemically enhanced diffusion can increase the mass transfer coefficient of CO<sub>2</sub> several fold depending on conditions of pH, wind speed, and temperature. For mean oceanic conditions the enhancement is generally considered negligible [Wanninkhof and Knox, 1996], but CED can be extremely important in eutrophic lakes [e.g., Herczeg, 1987] and potentially so in highly productive areas of the ocean where pH becomes increased because of CO<sub>2</sub> uptake [e.g., Invers *et al.*, 1997].

[4] Stable carbon isotopes aid in the understanding of inorganic carbon cycling in lakes [Rau, 1978; Quay *et al.*, 1986; Herczeg, 1987; Bade *et al.*, 2004]. Carbon isotopes also help constrain estimates of CO<sub>2</sub> gas transfer in coupled atmosphere-ocean models [Quay *et al.*, 1992]. Knowledge

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of any fractionation of  $\text{CO}_2$  isotopes that occurs during transfer between air and water is extremely important for isotopic studies of dissolved inorganic carbon (DIC). Fractionation due to diffusive fluxes and carbonate speciation is well understood [Zhang *et al.*, 1995; Szaran, 1998]. The fractionation associated with the reaction of  $\text{CO}_2$  and  $\text{OH}^-$  in natural waters is less well constrained. Craig [1953] found that the reaction of  $\text{CO}_2$  with a strongly alkaline solution of  $\text{Ba}(\text{OH})_2$  resulted in dissolved inorganic carbon isotope signatures ( $\delta^{13}\text{C}$ -DIC) that were 14‰ to 15‰ more negative than atmospheric carbon. The kinetic fractionation during this chemical reaction causes the large discrimination which is much larger than the kinetic fractionation due to diffusion alone [Usdowski and Hoefs, 1986]. Several workers examined the impact of this chemically enhanced fractionation (CEF) on the overall fractionation that occurs during air-sea gas exchange and concluded that CEF did not contribute substantially to overall fractionation for mean oceanic conditions, which is similar to conclusions made for CED [Siegenthaler and Münnich, 1981; Inoue and Sugimura, 1985; Wanninkhof, 1985].

[5] Chemically enhanced fractionation is less studied in lakes, but conditions in eutrophic lakes may promote significant CEF. For example, *Herczeg and Fairbanks* [1987] observed a large flux of  $\text{CO}_2$  into Mohonk Lake (New York) that was depleted in  $^{13}\text{C}$ . Mohonk Lake is a soft water lake that experienced an intense algal bloom, creating a drawdown in  $\text{CO}_2$  and an increase in pH. The flux could not be accounted for by respiration of organic matter, and they attributed this flux to the fractionation that occurred because of conditions of CED. Studying  $\delta^{13}\text{C}$ -DIC in lakes, *Bade et al.* [2004] also observed several lakes that appeared to be influenced by CEF and noted others from the literature with high pH and depleted DIC isotope signatures.

[6] In this study we examine the role of CED and CEF in the cycling of carbon isotopes in Peter Lake (Michigan). Experimental nutrient additions created high levels of primary productivity in Peter Lake, producing conditions that should induce CED and CEF. Because few field measurements of CED exist, we compare our field measurements of CED with a model of CED to assess their reliability. We modify the model of CED to account for fractionation of  $^{13}\text{C}$  with the goal of providing a model of CEF which allows for modeling  $\delta^{13}\text{C}$ -DIC dynamics under varying physical and chemical conditions in aquatic systems. A whole-lake experimental addition of inorganic  $^{13}\text{C}$  produced  $\delta^{13}\text{C}$ -DIC dynamics which could be used to test the validity of the CEF model. Our CEF model should have wide applicability for aquatic systems with high pH.

## 2. Methods

### 2.1. Experimental Manipulation and Limnological Characterization of Peter Lake

[7] Peter Lake is a small glacial lake surrounded by noncalcareous till in the Upper Peninsula of Michigan. It has been the site of numerous whole-lake manipulations and is described extensively elsewhere [Carpenter and Kitchell, 1993; Carpenter *et al.*, 2001]. In 2002, Peter Lake received nutrient amendments to increase primary productivity. Initially, we added 1.25 L 85%  $\text{H}_3\text{PO}_4$  and 22.7 kg  $\text{NH}_4\text{NO}_3$  on 3 June and then continued with daily additions of 0.2 L

85%  $\text{H}_3\text{PO}_4$  and 3.2 kg  $\text{NH}_4\text{NO}_3$  from 10 June to 25 August. Nitrogen was added well in excess of P to ensure that P remained the limiting nutrient. Nutrients were dissolved in lake water and poured slowly over the transom of a moving boat in the central area of the lake. Peter Lake also received daily additions of 50 g  $\text{NaH}^{13}\text{CO}_3$  from 17 June to 21 July. We added the  $^{13}\text{C}$  to the epilimnion of each lake between 0600 and 0800 LT. On the lake the preweighed amount of  $\text{NaH}^{13}\text{CO}_3$  (>98%  $^{13}\text{C}$ ; Isotec) was dissolved with lake water in a 20-L carboy. We injected the solution into the epilimnion with a peristaltic pump at a depth of 1 m. The boat was rowed around the midsection of the lake while the solution was being injected to provide good coverage of the isotope and faster mixing throughout the epilimnion.

[8] Samples for DIC isotope analysis were collected in 60-mL serum vials immediately prior to the isotope addition, acidified to  $\text{pH} < 2$  with 10 N  $\text{H}_2\text{SO}_4$ , and sealed with butyl rubber septa and aluminum crimp caps. Samples were analyzed by the University of Waterloo Environmental Isotope Laboratory using a Micromass Isochrome gas chromatographic isotope ratio mass spectrometer (GC-IRMS). Particulate organic carbon (POC) was collected on precombusted 25-mm Whatman glass fiber (GF/F) filters, dried at 60°C for at least 48 hours, and fumed with HCl prior to analysis. Carbon isotopes were analyzed using a Carlo Erba elemental analyzer coupled with a Finnigan MAT ConFlo II/III interface with a Delta+ mass spectrometer by the University of Alaska Fairbanks Stable Isotope Facility.

[9] Yellow Springs Instruments (YSI)-Endeco sondes (model 600XLM), deployed in the center of the lake, recorded temperature,  $\text{O}_2$  concentration, and pH at 5-min intervals for most of the summer period. Sonde  $\text{O}_2$  (YSI model 6562) and pH (YSI model 6561) electrodes were calibrated at least weekly [see *Cole et al.*, 2000]. Diel dynamics of  $\text{O}_2$  were used to estimate ecosystem gross primary productivity (GPP) and total respiration (TR) according to *Cole et al.* [2000]. Chl *a* was determined weekly, and samples were filtered, frozen, extracted with methanol, and measured fluorometrically [Marker *et al.*, 1980]. We measured DIC concentration according to the method of *Stainton* [1973] using a Shimadzu GC-8AIT with a thermal conductivity detector (TCD). DIC samples were initially collected at weekly intervals, along with Chl *a*, at midmorning (0830–1000 LT). Starting 17 June, we collected daily samples for DIC at the time of DIC isotope sampling. These daily samples were collected in 300-mL biochemical oxygen demand bottles, acidified, and refrigerated. The daily samples of DIC were analyzed opportunistically but always within 1 week of collection. We measured pH using an Orion digital pH meter with a gel-filled automatic temperature-compensating electrode (model 9107BN). Samples for pH were analyzed immediately upon return from the lake, after a two-point calibration using pH 7 and 10 standards. We followed the pH measurement method of *Stauffer* [1990] for dilute surface water. Alkalinity was calculated on the basis of DIC, pH, and water temperature [Stumm and Morgan, 1996]. For all chemical calculations we assumed that activity coefficients were approximately 1 for the dilute waters of Peter Lake (conductivity  $\sim 30 \mu\text{mho cm}^{-1}$ ). We also calculated that the ion activity product for  $\text{CaCO}_3$  was an order of magnitude below the solubility constant, even during periods of high pH.

[10] Wind speeds were measured in Peter Lake from a height of 2 m above the water surface, beginning on 28 June and continuing through 9 September, using an R. M. Young anemometer connected to a Campbell 6250 data logger [see *Cole et al.*, 2000]. Thirty-minute averages of continuous measurements were recorded.

## 2.2. Field Measurements of Mass Transfer Coefficients

[11] Floating chambers similar to those used by *Bastviken et al.* [2004] were deployed in Peter Lake during the summer of 2002. Change in gas concentrations in the chambers was used to estimate mass transfer coefficients. The chambers were 5-L high-density polyethylene buckets that floated upside down, intercepting the air-water interface. The opening of the chamber was approximately 5 cm below the surface of the water. Each chamber was equipped with a rubber septum to allow for extraction of gas samples. During the deployment the volume of air headspace in the chamber was estimated by calibrated marks on the chamber, and corresponding surface areas for these volumes were measured.

[12] Changes in the partial pressures of CO<sub>2</sub> and CH<sub>4</sub> were measured inside separate chambers over the period of deployment. Deployments were done opportunistically throughout much of the summer. Ambient air samples were collected in gastight syringes at the beginning of chamber deployment. For CH<sub>4</sub>, chambers were generally deployed for approximately 24 hours, and for CO<sub>2</sub> the deployments were 2–4 hours. The difference in deployment times was necessary to ensure measurable increase in concentration ( $p\text{CH}_4$ ) or to ensure that the gas was not depleted beyond what could be reasonably detected ( $p\text{CO}_2$ ). At the end of the deployment, gas samples were collected with a syringe and needle through the rubber septum. In addition, we measured the surface water partial pressures of both gases before and after deployment. Surface water  $p\text{CH}_4$  was measured by a headspace equilibration technique similar to that of *Cole et al.* [1994]. Because of extremely low CO<sub>2</sub> concentration in the water, CO<sub>2</sub> approached our limit of detection. We therefore calculated  $p\text{CO}_2$  from measurements of dissolved inorganic carbon (DIC), pH, temperature, and carbonate equilibrium constants [*Dickson and Millero*, 1987; *Stumm and Morgan*, 1996]. Errors in pH measurements can cause uncertainty when calculating  $p\text{CO}_2$  in this way. However, because the  $p\text{CO}_2$  of the water was so low, it could essentially be set to zero, and errors would have little impact on subsequent calculations (e.g., equation (1)). We measured DIC, pH, barometric pressure, and surface water temperature at the beginning and end of deployment using methods described earlier. Both gasses were analyzed using gas chromatography. We analyzed CH<sub>4</sub> using a Shimadzu GC-8A with a flame ionization detector (FID), and we analyzed CO<sub>2</sub> using a Shimadzu GC-8AIT with a TCD detector.

[13] The mass transfer coefficient or piston velocity ( $k$ ; cm h<sup>-1</sup>) for each gas was calculated as follows [*Macintyre et al.*, 1995; *Wanninkhof and Knox*, 1996]:

$$k = \frac{-\ln\left(\frac{|pX^w - pX_{t1}^w|}{|pX^w - pX_{t0}^w|}\right)}{\Delta t} \left(\frac{V}{AK_H RT}\right), \quad (1)$$

where  $pX^w$  is the partial pressure ( $\mu\text{atm}$ ) of gas  $X$  in water and  $pX_{t0}^w$  and  $pX_{t1}^w$  are the partial pressures of gas  $X$  in the

chamber at the initial and final times, respectively. The time increment is  $\Delta t$  (hours),  $V$  is the volume of the chamber (cm<sup>3</sup>),  $A$  is the surface area of the air-water interface (cm<sup>2</sup>),  $K_H$  is Henry's constant (mol L<sup>-1</sup> atm<sup>-1</sup>),  $R$  is the gas constant (L atm K<sup>-1</sup> mol<sup>-1</sup>), and  $T$  is the absolute temperature (K). The values for  $pX^w$  and  $T$  were the averages of the values obtained at the beginning and end of deployment.

[14] Changes in CH<sub>4</sub> were used to estimate  $k_{\text{CH}_4}$  and from this the unenhanced mass transfer coefficient,  $k_{\text{CO}_2}$ . Mass transfer coefficients of CH<sub>4</sub> were converted to CO<sub>2</sub> by using their respective Schmidt numbers and the following formula [*Macintyre et al.*, 1995]:

$$k_{\text{CH}_4}/k_{\text{CO}_2} = (Sc_{\text{CH}_4}/Sc_{\text{CO}_2})^{-0.5}, \quad (2)$$

with Schmidt numbers determined by *Wanninkhof* [1992].

[15] Because the pH in Peter Lake for much of the summer was >9, air-water CO<sub>2</sub> flux represents a combination of diffusion and chemical reaction with OH<sup>-</sup> (section 1). The resulting mass transfer coefficient based on CO<sub>2</sub> therefore includes chemically enhanced diffusion ( $k_{\text{enh}}$ ). The chemical enhancement factor,  $\beta$ , can then be calculated as

$$\beta = k_{\text{enh}}/k_{\text{CO}_2}. \quad (3)$$

## 2.3. Modeling Chemical Enhancement

[16] Chemically enhanced diffusion was calculated according to *Wanninkhof and Knox* [1996] using the model of *Hoover and Berkshire* [1969]. The chemical enhancement factor,  $\beta$ , is defined as

$$\beta = \frac{\tau}{(\tau - 1) + \left\{ \tanh\left[\frac{\langle r \rangle \tau D^{-1}}{z}\right] / \left[\frac{\langle r \rangle \tau D^{-1}}{z}\right] \right\}}, \quad (4)$$

where  $D$  is the molecular diffusivity [*Jähne et al.*, 1987] and  $z$  is the thickness of the stagnant boundary layer [*Lewis and Whitman*, 1924]. The stagnant boundary layer thickness,  $z$ , is equal to  $D/k_{\text{CO}_2}$ , and  $\tau$  is defined as

$$\tau = \frac{[\text{H}^+]^2}{K_1 K_2 + K_1 [\text{H}^+]} + 1, \quad (5)$$

where  $[\text{H}^+]$  is the hydrogen ion activity and  $K_1$  and  $K_2$  are the dissociation constants for the reaction between CO<sub>2(aq)</sub> and HCO<sub>3</sub><sup>-</sup> and between HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, respectively, as given by *Dickson and Millero* [1987]. Finally,  $\langle r \rangle$  is the combined rate of reaction terms:

$$\langle r \rangle = r_{\text{CO}_2} + r_{\text{OH}^-} [\text{OH}^-], \quad (6)$$

where  $[\text{OH}^-]$  is the hydroxide ion activity and  $r_{\text{CO}_2}$  and  $r_{\text{OH}^-}$  are the forward rate constants for CO<sub>2</sub> reacting with H<sub>2</sub>O or OH<sup>-</sup>, respectively, given by *Johnson* [1982].

## 2.4. Modeling Atmospheric Flux of C Isotopes

[17] The flux  $F$  of total CO<sub>2</sub> across the air-water interface was modeled as

$$F = -k_{\text{CO}_2} \beta \left( [\text{CO}_2]_{\text{aq}} - \gamma p\text{CO}_2 \right), \quad (7)$$

where  $\beta$  is the chemical enhancement factor (described in equation (4)),  $[\text{CO}_2]_{aq}$  is the aqueous concentration of  $\text{CO}_2$ ,  $\gamma$  is the solubility of  $\text{CO}_2$  ( $\text{mol atm}^{-1}$ ), and  $p\text{CO}_2$  is the partial pressure of  $\text{CO}_2$  in the air. An analogous equation can be written for  $^{13}\text{CO}_2$ :

$$F^{13} = -k_{\text{CO}_2}\beta^{13}\left([\text{CO}_2]_{aq} - \gamma^{13}p^{13}\text{CO}_2\right). \quad (8)$$

The partial pressure of  $^{13}\text{CO}_2$  was calculated as  $p^{13}\text{CO}_2 = p\text{CO}_2 \times \text{propair}$ , where  $\text{propair}$  is the proportion of  $^{13}\text{C}$  in the air based on an isotopic signature of  $-7.6\text{‰}$  [Friedli *et al.*, 1986]. The solubility of  $^{13}\text{CO}_2$  was determined from

$$\gamma^{13} = \gamma\alpha_{aq-g}, \quad (9)$$

where  $\alpha_{aq-g}$  is the equilibrium fractionation factor between gaseous and aqueous  $\text{CO}_2$ . Zhang *et al.* [1995] provide estimates of  $\alpha_{aq-g}$ . The model of  $\beta^{13}$  is given below.

[18] The  $^{13}\text{CO}_2$  will experience the same chemically enhanced diffusion as  $^{12}\text{CO}_2$  described above. However, the reaction of  $\text{CO}_2$  with  $\text{OH}^-$  is selective for the lighter carbon isotope such that there is an observed equilibrium fractionation of about  $-15\text{‰}$  [Craig, 1953]. Using this information, known equilibrium and kinetic fractionation values, and equation (4), it was possible to calculate the chemical enhancement factor for  $^{13}\text{CO}_2$ . The chemical enhancement factor of  $^{13}\text{CO}_2$  can then be used to model  $^{13}\text{C}$  flux.

[19] Zhang *et al.* [1995] determined equilibrium isotopic fractionation factors as a function of temperature between gaseous  $\text{CO}_2$  and aqueous  $\text{CO}_2$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$  ( $\alpha_{aq-g}$ ,  $\alpha_{\text{HCO}_3-g}$ , and  $\alpha_{\text{CO}_3-g}$ , respectively). From this the equilibrium fractionation factors between aqueous  $\text{CO}_2$  and  $\text{HCO}_3^-$  and between  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  could be calculated as

$$\alpha_{\text{HCO}_3-aq} = \frac{\alpha_{\text{HCO}_3-g}}{\alpha_{aq-g}} \quad (10)$$

$$\alpha_{\text{CO}_3-\text{HCO}_3} = \frac{\alpha_{\text{CO}_3-g}}{\alpha_{\text{HCO}_3-g}}. \quad (11)$$

Applying these fractionation factors to their respective dissociation constants, equation (5) then becomes

$$\tau^{13} = \frac{[\text{H}^+]^2}{\alpha_{\text{HCO}_3-aq}\alpha_{\text{CO}_3-\text{HCO}_3}K_1K_2 + \alpha_{\text{HCO}_3-aq}K_1[\text{H}^+]} + 1, \quad (12)$$

with  $\tau^{13}$  representing the case for  $^{13}\text{C}$ .

[20] Kinetic isotopic considerations are applied to the reaction rates in equation (6). Siegenthaler and Münnich [1981] determined that the kinetic isotope fraction for the reaction of  $\text{CO}_2$  with  $[\text{OH}^-]$  is  $\alpha_{r,\text{OH}} \cong 0.973$ . The kinetic isotope fractionation for the hydration of  $\text{CO}_2$  with water is  $\alpha_{r,\text{CO}_2} \cong 0.9931$ , as determined by Marlier and O'Leary [1984]. These were applied to equation (6) to get

$$\langle r^{13} \rangle = \alpha_{r,\text{CO}_2}r_{\text{CO}_2} + \alpha_{\text{OH}^-}r_{\text{OH}^-}[\text{OH}^-]. \quad (13)$$

Equations (12) and (13) were substituted back into equation (4). Substitutions were also made for the differential isotopic

diffusion of  $\text{CO}_2$ ,  $\alpha_D = D^{13}/D = 0.9991$  [Siegenthaler and Münnich, 1981], and the boundary layer thickness for  $^{13}\text{CO}_2$ , corresponding to  $z^{13} = \alpha_D D/k_{\text{CO}_2}$ . Thus  $\beta^{13}$  was calculated for input into equation (8).

## 2.5. Dynamic DIC Isotope Model

[21] We constructed a model of DIC isotope dynamics that analyzes both total C and  $^{13}\text{C}$  simultaneously to predict  $\delta^{13}\text{C}$ -DIC. The differential equation for total DIC is

$$\frac{d[\text{DIC}]}{dt} = \text{TR} - \text{GPP} + F/z_{\text{mix}}, \quad (14)$$

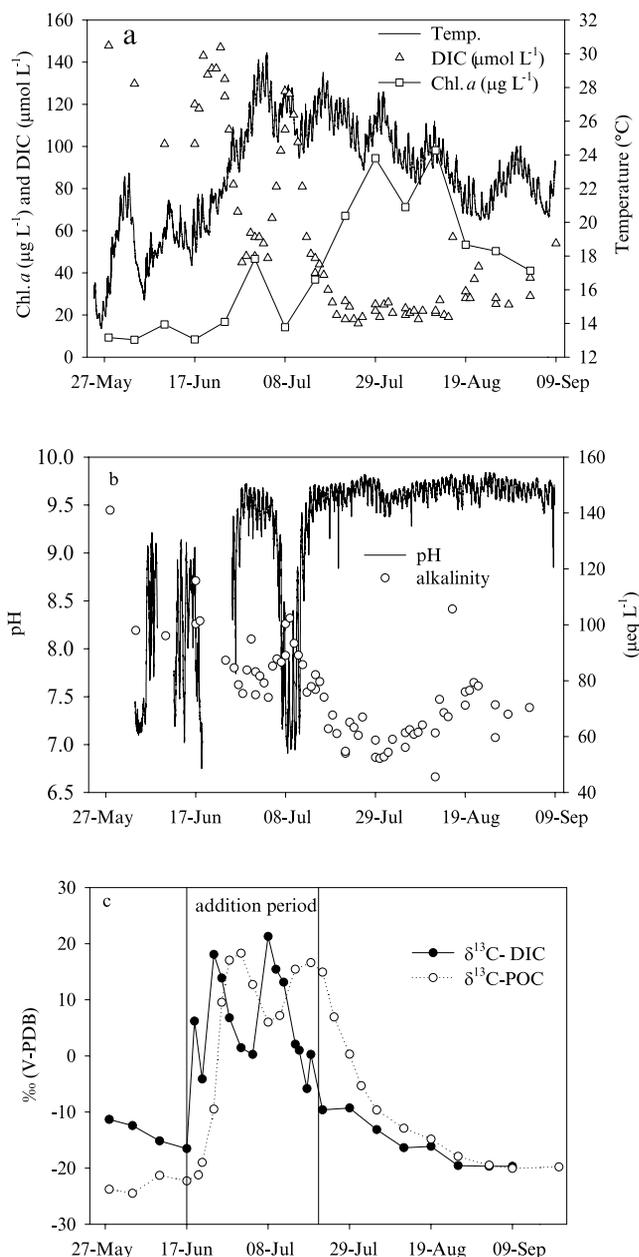
and for  $\text{DI}^{13}\text{C}$  the equation is

$$\frac{d[\text{DI}^{13}\text{C}]}{dt} = R_{\text{terr}}^{13} + R_{\text{POC}}^{13} - \text{GPP}^{13} + F^{13}/z_{\text{mix}}, \quad (15)$$

where  $F$  and  $F^{13}$  are the atmospheric flux ( $\text{mmol C m}^{-2}$ ) of total  $\text{CO}_2$  and  $^{13}\text{CO}_2$  as described in equations (7) and (8), respectively, and  $z_{\text{mix}}$  is the mixed layer depth (m). TR and GPP are total respiration and gross primary productivity ( $\text{mmol C m}^{-3}$ ).  $\text{GPP}^{13}$  is the amount of  $^{13}\text{C}$  taken up by gross primary production.  $\text{GPP}^{13}$  was determined by the isotopic signature of the organic carbon produced by the algae, such that  $\text{GPP}^{13} = \text{GPP} \times \text{propnp}$ , where  $\text{propnp}$  is the proportion of  $^{13}\text{C}$  in new algal production. Because of isotopic differences, TR was split into the respiration of terrestrial material ( $R_{\text{terr}}$ ) and respiration of POC ( $R_{\text{POC}}$ ), and  $\text{TR} = R_{\text{terr}} + R_{\text{POC}}$ . With respect to  $^{13}\text{C}$ ,  $R_{\text{terr}}^{13} = R_{\text{terr}} \times \text{propterr}$ , and  $R_{\text{POC}}^{13} = R_{\text{POC}} \times \text{propPOC}$ , where  $\text{propterr}$  and  $\text{propPOC}$  are the proportions of  $^{13}\text{C}$  in terrestrial material and POC, respectively. POC consisted mainly of algal material. The proportion of C that is  $^{13}\text{C}$  follows proportion equal to  $q/(1+q)$ , where  $q$  is the ratio of  $^{13}\text{C}$  to  $^{12}\text{C}$  determined from isotopic signatures by

$$q = 0.0112372[1 + (\delta^{13}\text{C} 1000)]$$

[22] For Peter Lake we chose to model the period of time beginning on 22 July and continuing until 21 September. This time period was characterized by relatively stable limnological conditions that enabled us to focus on the process of interest, CEF. After 22 July,  $^{13}\text{C}$  additions had ended, productivity and pH were high and not extremely variable, DIC was low and fairly stable, and mixed layer depth did not change substantially from 2 m. Initial conditions of temperature, DIC, pH, and calculated alkalinity in the model were set to those observed on 22 July, and alkalinity and temperature are assumed to remain constant over the model period. YSI sonde estimates of GPP and TR averaged 111 and 68  $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , respectively, for the period. These values were converted to volumetric C rates by applying a productivity and respiration quotient of 0.7  $\text{mmol CO}_2/\text{mmol O}_2$  [DeGrandpre *et al.*, 1997; Cimbleiris and Kalff, 1998; M. Van de Bogert, unpublished data for lakes in the region including Peter Lake, 2001] and dividing by the mixed layer depth of 2 m. Since the model uses hourly rates, daily TR was divided by 24. Daily GPP was assumed to take place over a 14-hour daylight period, with account taken for slightly decreased productivity



**Figure 1.** Time series for (a) DIC, Chl *a*, and temperature, (b) pH and alkalinity, and (c)  $\delta^{13}\text{C}$ -DIC and  $\delta^{13}\text{C}$ -POC in Peter Lake, 2002. Temperature and pH are measured at 5-min intervals using a YSI sonde (see text). DIC was measured at weekly intervals for the entire summer and at daily intervals for the later portion of the summer. Alkalinity was calculated on the basis of DIC, pH, and temperature. In Figure 1c the solid vertical lines demarcate the beginning and end of the isotope addition period.

during the several hours immediately after sunrise and before sunset.

[23] The initial  $\text{DI}^{13}\text{C}$  was set on the basis of the total DIC concentration and the  $\delta^{13}\text{C}$ -DIC value of 22 July. Algal fractionation of  $^{13}\text{C}$  appeared to be extremely reduced in the low- $\text{CO}_2$  environment [Bade, 2004]. We chose a photosynthetic fractionation value of  $-3\text{‰}$  with respect to  $\delta^{13}\text{C}$ -DIC to calculate propnp. The measured isotopic signatures of

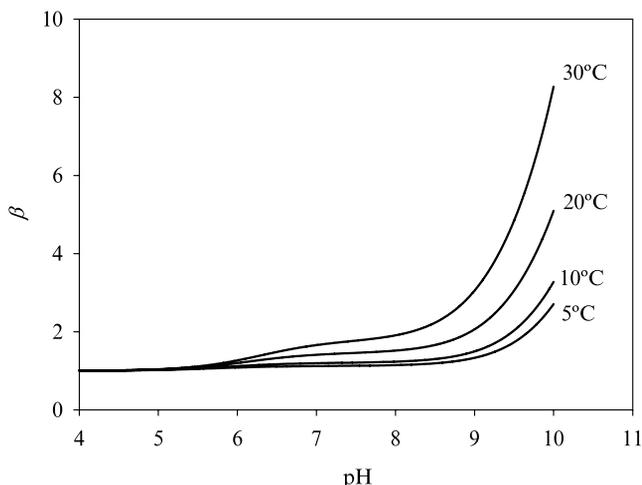
POC were splined to create daily values and used as input for propPOC, and propterr was based on the isotopic signature of  $-27\text{‰}$ , representative of C3 terrestrial vegetation [Lajtha and Michener, 1994]. The value of  $R_{\text{terr}}$  was set at  $2 \text{ mmol C m}^{-2} \text{ d}^{-1}$  [Bade, 2004].

[24] At the beginning of each time step, pH and  $\text{CO}_2$  were calculated on the basis of DIC and alkalinity;  $\beta$  and  $\beta^{13}$  were calculated on the basis of pH. The  $^{13}\text{CO}_2$  was calculated from DIC,  $\text{DI}^{13}\text{C}$ , pH, and the carbonate fractionation factors of Zhang *et al.* [1995]. The differential equations were integrated using an ordinary differential equation solver in Matlab.

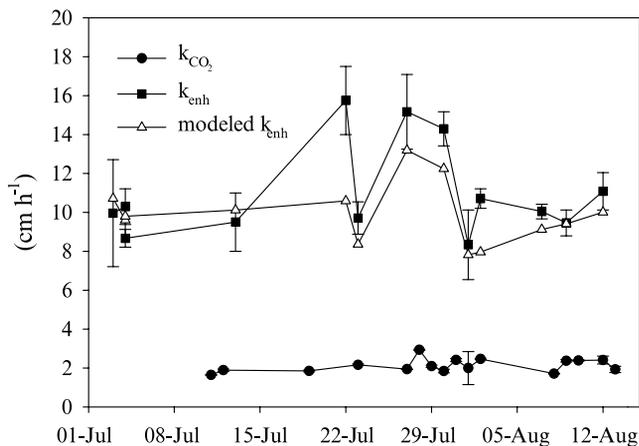
### 3. Results

[25] Nutrient additions in Peter Lake caused increases in Chl *a* (Figure 1a) and GPP and TR (data not shown), and oxygen was supersaturated for most of the summer (mean of 116%  $\text{O}_2$  saturation). This led to a decrease in total DIC and an increase in pH (Figures 1a and 1b). For much of the summer the pH exceeded 9.5. Alkalinity decreased during the first part of the summer, until late July when it began to increase (Figure 1b). During the periods of low DIC concentration and high pH,  $\text{OH}^-$  was a large component of the calculated alkalinity. The isotope addition created large shifts in  $\delta^{13}\text{C}$ -DIC and  $\delta^{13}\text{C}$ -POC (Figure 1c). Surface temperatures in Peter Lake in 2002 were typical (Figure 1a).

[26] Given the pH and low wind conditions in Peter Lake, chemically enhanced diffusion of  $\text{CO}_2$  should be an important factor in the flux of atmospheric  $\text{CO}_2$  into the lake. Figure 2 displays the calculated chemical enhancement factor ( $\beta$ ) for different temperatures over the range of pH typically observed in freshwater lakes. In Peter Lake,  $k_{\text{CO}_2}$  determined from changes in  $p\text{CH}_4$  ranged from 1.63 to  $2.92 \text{ cm h}^{-1}$  (Figure 3). After normalizing  $k_{\text{CO}_2}$  values to a Schmidt number of 600 the average value of  $k_{600}$  was  $1.83 \pm 0.33 \text{ cm h}^{-1}$  (mean  $\pm 1 \text{ SD}$ ). The lack of large variation in  $k_{600}$  is consistent with the consistently low wind speeds observed at Peter Lake. Chamber estimates of  $k_{\text{enh}}$ , based on change in  $p\text{CO}_2$ , were 3.5- to 7.5-fold



**Figure 2.** Model predictions of  $\beta$  for typical pH and temperature in freshwater lakes. It should be noted that the level of diffusive flux also influences these predictions. In this example,  $k_{600} = 1.83 \text{ cm h}^{-1}$ .

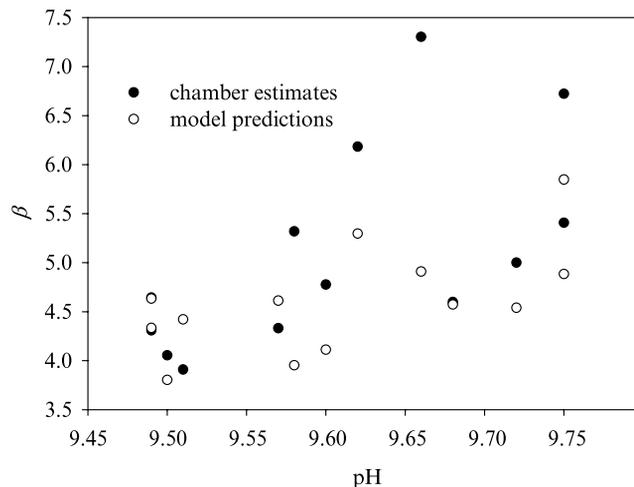


**Figure 3.** Chamber estimates of  $k_{\text{CO}_2}$  and  $k_{\text{enh}}$  and model estimates of  $k_{\text{enh}}$ . Measurements of  $k_{\text{CO}_2}$  are based on  $k_{\text{CH}_4}$  determined from changes in  $p\text{CH}_4$  and Schmidt number conversion, and measurements of  $k_{\text{enh}}$  are determined directly from changes in  $p\text{CO}_2$ . Model estimates of  $k_{\text{enh}}$  are calculated on the basis of pH, temperature, and mean  $k_{600} = 1.83 \text{ cm h}^{-1}$ . Error bars are 1 SD, usually based on three chambers. The large deviations in the one measurement of  $k_{\text{CO}_2}$  were caused by a heavy rain event during that deployment.

higher than  $k_{\text{CO}_2}$  (Figure 3). Using the average value of  $k_{600}$  obtained from chambers, pH, temperature, and the model for chemical enhancement,  $k_{\text{enh}}$  was calculated for each interval of chamber deployment. In many cases the observed CED was larger than predicted by the theoretical model (Figure 3).

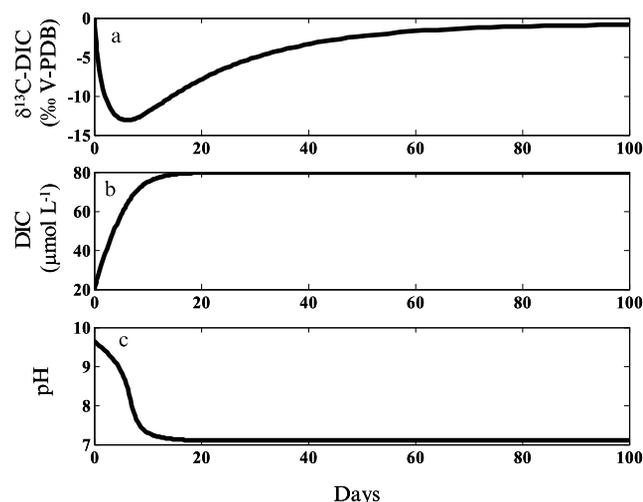
[27] Figure 4 compares the response of model predictions of  $\beta$  with the chamber estimates (calculate from equation (3)) for the observed pH and temperature corresponding with the chamber deployments. The variability in modeled  $\beta$  as a function of pH is due to variation in temperature for a given deployment. The observed values of  $\beta$  follow the expected positive trend with pH. Except for two cases (at pH 9.66 and 9.8), model estimates of  $\beta$  can be made to fit chamber estimates by a change in pH of less than 0.15 units or a change in temperature of less than  $2^\circ\text{C}$ . The pH change over the 2–4 hour period of chamber deployments was similar in magnitude to that required to fit the estimates. A linear regression of observed versus predicted  $\beta$  has a slope of  $1.3 \pm 0.4$  ( $\pm 1$  SE) and intercept of  $-0.9 \pm 1.9$  ( $R^2 = 0.47$ ;  $p < 0.01$ ;  $n = 13$ ). Despite the observation (see Figure 3) that chamber estimates of  $\beta$  are higher than model predictions, the slope and intercept are not significantly different from 1 and 0, respectively.

[28] The condition of chemically enhanced diffusion observed in Peter Lake should have an influence on  $\delta^{13}\text{C-DIC}$ . Figure 5 presents the results from a modeling simulation with starting chemical conditions similar to Peter Lake near 22 July but with  $\delta^{13}\text{C-DIC}$  starting at 0‰ and only gas exchange occurring. The influx of  $\text{CO}_2$  increases DIC and decreases pH until equilibrium values are reached. The  $\delta^{13}\text{C-DIC}$  originally decreases because of the kinetic isotope fractionation caused by chemically enhanced diffusion. As pH decreases, CED becomes less important, and  $\delta^{13}\text{C-DIC}$  gradually approaches an equilibrium value near 0‰, which is expected for pH near 7. A similar modeling

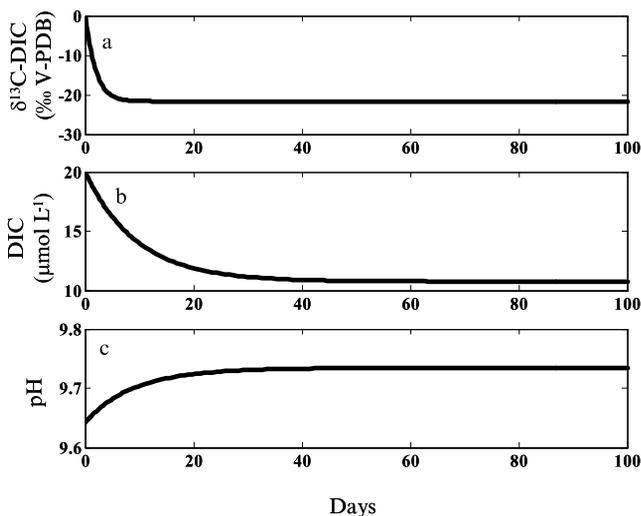


**Figure 4.** Chamber estimates and model predictions of  $\beta$  related to pH. Chamber estimates of  $\beta$  are  $\beta = k_{\text{enh}}/k_{\text{CO}_2}$ , where  $k_{\text{CO}_2}$  was based on the average  $k_{600} = 1.83 \text{ cm h}^{-1}$  and temperature. Model predictions are determined from the average  $k_{600}$ , pH, and temperature for the period of chamber deployment.

exercise was conducted, but this time  $\text{CO}_2$  was continuously removed at a rate of  $11 \text{ mmol C m}^{-3} \text{ d}^{-1}$  to represent nonequilibrium conditions. There was no fractionation of DIC due to the removal of  $\text{CO}_2$ , so that the only mechanism causing changes in the  $\delta^{13}\text{C-DIC}$  is the flux of  $\text{CO}_2$  from atmospheric exchange. This resulted in a  $\delta^{13}\text{C-DIC}$  value of  $-21.7\text{‰}$ , which is  $14.1\text{‰}$  below the atmospheric  $\text{CO}_2$  signature (Figure 6a). DIC concentrations decreased, and pH increased, over this time period (Figures 6b and 6c). In the latter exercise, if  $\beta^{13}$  is set equal to  $\beta$  (i.e., if there is no fractionation during chemically enhanced diffusion),  $\delta^{13}\text{C-DIC}$  asymptotically approaches the value of aqueous  $\text{CO}_2$  at equilibrium with the atmosphere ( $-8.8\text{‰}$ ; data not shown).



**Figure 5.** Model results of (a)  $\delta^{13}\text{C-DIC}$ , (b) DIC concentration, and (c) pH for a hypothetical scenario. Most initial conditions used represent typical values for Peter Lake:  $\text{DIC} = 20 \mu\text{mol L}^{-1}$ , alkalinity is  $67 \mu\text{eq L}^{-1}$ , temperature is  $20^\circ\text{C}$ ,  $k_{600} = 1.83 \text{ cm h}^{-1}$ , and  $\delta^{13}\text{C-DIC} = 0\text{‰}$ . There are no sources or losses of carbon except atmospheric flux.



**Figure 6.** Same as Figure 5 but including a nonfractionating loss of  $\text{CO}_2$  to maintain high levels of pH.

[29] The model of fractionation during CED was tested using  $\delta^{13}\text{C}$ -DIC data from Peter Lake for the period of 22 July to 21 September. Model predictions matched closely with observed  $\delta^{13}\text{C}$ -DIC (Figure 7a). There was considerable daily variation in  $\delta^{13}\text{C}$ -DIC due to GPP only occurring during the day, and there was variation in the ratios of chemical enhancement factors ( $\beta^{13}/\beta$ ) due to diel changes in pH. Samples for  $\delta^{13}\text{C}$ -DIC were collected in the early morning when, according to the model,  $\delta^{13}\text{C}$ -DIC values should have been near their nadir. Measured  $\delta^{13}\text{C}$ -DIC values asymptotically approach a value of  $-19.7\text{‰}$ , very near the value reached in the hypothetical exercise (see Figure 6a) and in the more realistic model.

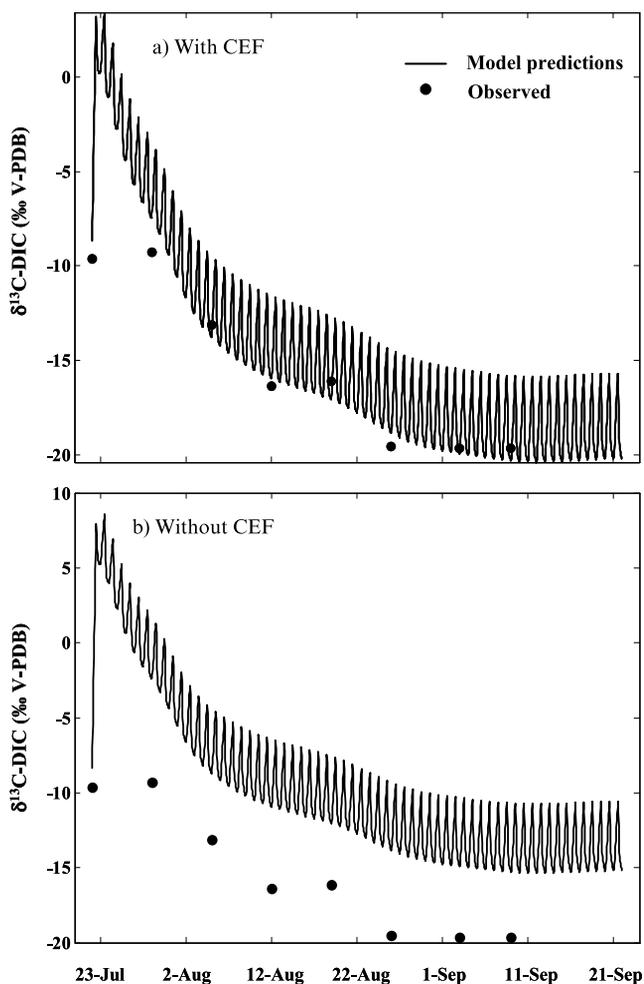
[30] Considering the null hypothesis that CEF is not a factor in  $\text{CO}_2$  gas flux (setting  $\beta^{13} = \beta$ ), the model fit was much worse (Figure 7b). We explored the plausibility of the null hypothesis further by examining other parameters that could influence  $\delta^{13}\text{C}$ -DIC. Two important parameters that contain uncertainty and exert influence on predictions are the amount of respired terrestrial material and the extent of photosynthetic fractionation. Attempting to fit these two parameters in the model not including CEF, we could not improve the fit to levels comparable when CEF was included. Even if all the respiration was attributed to terrestrial material at an isotopic value of  $-27\text{‰}$ , the model without CEF could not reproduce the  $\delta^{13}\text{C}$ -DIC values near  $-20\text{‰}$  because the large atmospheric  $\text{CO}_2$  flux keeps  $\delta^{13}\text{C}$ -DIC nearer to atmospheric values (see results related to modeling exercises in Figures 5 and 6).

[31] Modeled diel dynamics of pH and DIC were similar to those observed, giving us additional confidence that the model simulated the lake conditions, especially CED, well. Modeled DIC ranged from approximately  $20 \mu\text{mol L}^{-1}$  in the morning to  $3 \mu\text{mol L}^{-1}$  at the end of the day, and pH ranged from 9.64 to 9.81 over the same time period. No measurements were made to explicitly test the diurnal variation in DIC, but some DIC measurements made late in the afternoon for chamber deployments had concentrations down to  $7 \mu\text{mol L}^{-1}$ . The routine measurements of DIC, made in the early morning, were near  $20 \mu\text{mol L}^{-1}$  for much of the model period (Figure 1a). The diel range of

observed pH (Figure 1b) was similar to the range in modeled pH on many dates. The value of net ecosystem production ( $\text{NEP} = \text{GPP} - \text{TR}$ ) used in the model appears to have been the maximum possible for the conditions that existed in Peter Lake. If we simulated a small increase in GPP, DIC became negative, and the model was no longer realistic. In addition, a small decrease in GPP caused large increase in DIC and decrease in pH, such that the model no longer matched conditions in the lake.

#### 4. Discussion

[32] The nutrient addition in Peter Lake created conditions of increased productivity, with  $p\text{CO}_2$  well below atmospheric equilibrium and with elevated pH, conditions



**Figure 7.** Model simulation and observations of  $\delta^{13}\text{C}$ -DIC in Peter Lake. (Note that this model does not contain the entire time period presented in other figures but begins on 22 July and ends on 21 September.) In Figure 7a the model includes the term for CEF, while in Figure 7b, CED is modeled, but there is no associated fractionation. Daily variations in  $\delta^{13}\text{C}$ -DIC can be observed in the model results. The model predictions extend past the  $\delta^{13}\text{C}$ -DIC observations because data inputs for the model were available for the extended period. The extended period was included to illustrate that the  $\delta^{13}\text{C}$ -DIC may plateau near  $-20\text{‰}$  for some time, similar to the example in Figure 6.

ideal for CED. We used the conditions in Peter Lake to test our knowledge about CED and CEF and confirmed their importance to carbon and carbon isotope budgets.

[33] The total flux of CO<sub>2</sub> was measured using floating chambers. Estimates of  $\beta$  based on chamber estimates were between 3.5 and 7.5, and therefore the flux of CO<sub>2</sub> for the same time period should be increased by this factor over nonenhanced conditions. There appears to be some bias between model estimates and chamber estimates. *Wanninkhof and Knox* [1996] also noted that chamber estimates are often higher than model estimates. A number of explanations are possible. Floating chambers are often thought to introduce bias into estimates of gas exchange [*Matthews et al.*, 2003]. However, in our application of estimating  $\beta$ , bias is possibly reduced or canceled, as any artifact affecting estimates of  $k_{\text{CO}_2}$  (from  $k_{\text{CH}_4}$ ) should also affect  $k_{\text{enh}}$ , unless it affects the chemical and not the physical aspect of CO<sub>2</sub> diffusion. Therefore any changes in the turbulence of the air-water interface caused by the chambers should not affect the estimates of  $\beta$ .

[34] Our chamber estimates of  $k_{600}$  are in close agreement with values determined by additional chamber estimates in 10 nearby lakes on 22 dates in 2001 ( $k_{600} = 1.79 \pm 0.42 \text{ cm h}^{-1}$ ; mean  $\pm 1$  SD,  $n = 158$  (D. Bastviken, personal communication, 2004)). The means of wind-based estimates of  $k_{600}$  using formulas from *Wanninkhof* [1992] and *Cole and Caraco* [1998] ranged from 1.54 to 2.83 cm h<sup>-1</sup>, respectively, and results from a whole-lake SF<sub>6</sub> addition in Peter Lake in 2003 estimated  $k_{600} = 2.04 \text{ cm h}^{-1}$  (J. J. Cole, unpublished data, 2004). Inaccuracies in temperature or barometric pressure estimates (due to 24-hour deployment) or the Schmidt number exponent have very minor impacts on chamber estimates of  $k_{600}$ . Therefore we feel the estimates of  $k_{600}$  contain little bias.

[35] Since several lines of evidence support our estimate of  $k_{600}$ , bias may have entered into the estimate of  $k_{\text{enh}}$ . Errors in calculating  $p\text{CO}_2$  in water based on pH, DIC, and temperature should not affect the estimates of  $k_{\text{enh}}$ . At the pH observed, the  $p\text{CO}_2$  in water is 2–3 orders of magnitude lower than the  $p\text{CO}_2$  in the chambers and can essentially be ignored in equation (1). Decreased  $p\text{CO}_2$  inside the chamber could potentially create higher levels of enhancement, as high  $p\text{CO}_2$  can lead to OH<sup>-</sup> depletion at the air-water interface, reducing enhancement. However, this is usually considered negligible for atmospheric CO<sub>2</sub> concentrations and typical values of gas exchange [*Siegenthaler and Münnich*, 1981]. If the chambers artificially warmed the surface water inside the chambers, the reaction rates could be increased, helping to explain the higher chamber estimates of  $\beta$ .

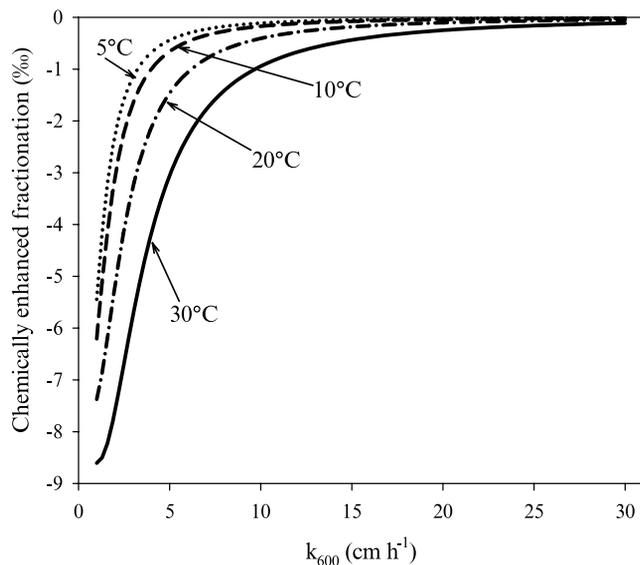
[36] The model predictions of  $\beta$  are highly sensitive to pH and temperature (Figures 2 and 4), and therefore any failure to accurately measure these parameters in the boundary layer could lead to error. It appears that the variability in pH over the time required in using chambers to estimate gas exchange could fully explain the discrepancies between model and chamber estimates of  $\beta$ . Therefore we feel that considering the uncertainty in pH, the model reasonably represents CED.

[37] For lakes, *Herczeg and Fairbanks* [1987] were perhaps the first to observe and describe an influx of CO<sub>2</sub> depleted in <sup>13</sup>C that could not be attributed to respired

organic matter and must have come from the fractionation that occurs when CO<sub>2</sub> reacts with OH<sup>-</sup>. Their approach was a mass balance of carbon isotopes, and the period of CED was relatively short-lived compared with the situation in Peter Lake. The prolonged period of high pH in Peter Lake allowed for a more detailed examination of carbon isotope flux under conditions of CED. Isotopic dynamics of DIC could not have been understood well without the inclusion of CEF. *Bade et al.* [2004] noted several lakes where GPP exceeded TR, and models that did not include CEF produced poor predictions of  $\delta^{13}\text{C-DIC}$  in those lakes. Therefore inclusion of CEF should be considered in studies of  $\delta^{13}\text{C-DIC}$ , especially in productive lakes. Most documented examples of chemically enhanced diffusion come from lakes with low-carbonate alkalinity (e.g., this study, Lake Mohonk [*Herczeg and Fairbanks*, 1987], and Lake 227 [*Emerson*, 1975]). However, eutrophic lakes with high alkalinity also experience periods of elevated pH (e.g., Lake Mendota [*Brock*, 1985] and Wintergreen Lake [*Wetzel*, 2001]) and thus should be conducive to conditions of CED similar to other alkaline lakes [*Wanninkhof and Knox*, 1996]. Chemically enhanced fractionation likely occurs in any lakes that experience CED caused by high pH, whether high pH is due to intense productivity or to the geochemistry of the lake.

[38] Chemically enhanced fractionation of atmospheric CO<sub>2</sub> has been considered unimportant for isotope dynamics in the ocean; however, these studies generally only consider mean ocean conditions of moderately high wind speeds [*Siegenthaler and Münnich*, 1981; *Inoue and Sugimura*, 1985; *Wanninkhof*, 1985]. At high wind speeds, diffusion is the rate-controlling step, and although the rate reaction with OH<sup>-</sup> remains unchanged, it is comparatively small. However, significant portions of the ocean experience low wind speeds for significant periods of time, and CED can increase the flux of CO<sub>2</sub> [*Wanninkhof*, 1992]. Figure 8 shows the extent of chemically enhanced fractionation as a function of piston velocity, given oceanic carbonate chemistry. For a mean oceanic pH the isotope fractionation is not as large as observed in Peter Lake. However, as piston velocity decreases or temperature increases in the ocean, the fractionation becomes more significant. The overall impact of this process on  $\delta^{13}\text{C-DIC}$  dynamics over the entire ocean is beyond the scope of this work, but results here strongly suggest a possibility that some areas of the ocean may have markedly different flux of carbon isotopes compared with mean conditions. In addition, areas of high productivity and low wind with elevated pH and low piston velocity could lead to even further CEF. For example, above seagrass beds, diel pH amplitudes of 0.5 units [*Invers et al.*, 1997] suggest that CEF could be increasingly important in certain areas. We suggest that spatial distribution of CEF might be an important factor to include when using isotopes to understand global flux of CO<sub>2</sub> between the atmosphere and ocean.

[39] The process of chemically enhanced diffusion is well recognized as an important factor in the carbon budget of lakes. Here we provided field-based estimates of the degree of chemical enhancement in a highly productive soft water lake. Additionally, we formulated a simple means of estimating the amount of isotopic fractionation that occurs during the process of CED. Including CEF in the model



**Figure 8.** Estimates of CEF ( $CEF = [(\beta^{13}/\beta) - 1]1000$ ), given oceanic conditions versus mass transfer coefficient for a range of temperatures. The assumed oceanic conditions were pH of 8.3 and salinity of 35‰.

of inorganic carbon for Peter Lake provided good agreement with observed  $\delta^{13}\text{C}$ -DIC. This formulation allows for dynamic modeling of isotopes in aquatic systems that are not in isotopic equilibrium with the atmosphere.

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## References

- Bade, D. L. (2004), Ecosystem carbon cycles: Whole-lake fluxes estimated with multiple isotopes, Ph.D. dissertation, Univ. of Wis.-Madison, Madison.
- Bade, D. L., S. R. Carpenter, J. J. Cole, P. C. Hanson, and R. H. Hesslein (2004), Controls of  $\delta^{13}\text{C}$ -DIC in lakes: Geochemistry, lake metabolism, and morphometry, *Limnol. Oceanogr.*, *49*, 1160–1172.
- Bastviken, D., J. Cole, M. Pace, and L. Tranvik (2004), Methane emissions from lakes: Dependence of lake characteristics, two regional assessments, and a global estimate, *Global Biogeochem. Cycles*, *18*, GB4009, doi:10.1029/2004GB002238.
- Bolin, B. (1960), On the exchange of carbon dioxide between the atmosphere and the sea, *Tellus*, *12*, 274–281.
- Brock, T. D. (1985), *A Eutrophic Lake: Lake Mendota, Wisconsin*, Springer, New York.
- Broecker, W. S., and T. H. Peng (1974), Gas exchange rates between air and sea, *Tellus*, *26*, 21–35.
- Carpenter, S. R., and J. F. Kitchell (1993), *The Trophic Cascade in Lakes*, Cambridge Univ. Press, New York.
- Carpenter, S. R., J. J. Cole, J. R. Hodgson, J. F. Kitchell, M. L. Pace, D. Bade, K. L. Cottingham, T. E. Essington, J. N. Houser, and D. E. Schindler (2001), Trophic cascades, nutrients, and lake productivity: Whole-lake experiments, *Ecol. Monogr.*, *71*, 163–186.
- Cimblaris, A. C. P., and J. Kalfj (1998), Planktonic bacterial respiration as a function of C:N:P ratios across temperate lakes, *Hydrobiologia*, *384*, 89–100.

- Cole, J. J., and N. F. Caraco (1998), Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of  $\text{SF}_6$ , *Limnol. Oceanogr.*, *43*, 647–656.
- 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.
- Cole, J. J., M. L. Pace, S. R. Carpenter, and J. F. Kitchell (2000), Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations, *Limnol. Oceanogr.*, *45*, 1718–1730.
- Craig, H. (1953), The geochemistry of the stable carbon isotopes, *Geochim. Cosmochim. Acta*, *3*, 53–92.
- DeGrandpre, M. D., W. R. McGillis, N. M. Frew, and E. J. Bock (1995), Laboratory measurements of seawater  $\text{CO}_2$  gas fluxes, in *Air-Water Gas Transfer*, edited by B. Jähne and E. C. Monahan, pp. 375–383, Aeon, Hanau, Germany.
- DeGrandpre, M. D., T. R. Hammar, D. W. R. Wallace, and C. D. Wirick (1997), Simultaneous mooring-based measurements of seawater  $\text{CO}_2$  and  $\text{O}_2$  off Cape Hatteras, North Carolina, *Limnol. Oceanogr.*, *42*, 21–28.
- Dickson, A. G., and F. J. Millero (1987), A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep Sea Res., Part A*, *34*, 1733–1743.
- Emerson, S. (1975), Chemically enhanced  $\text{CO}_2$  gas exchange in a eutrophic lake: A general model, *Limnol. Oceanogr.*, *20*, 743–753.
- Friedli, H., H. Moor, H. Oeschger, U. Siegenthaler, and B. Stauffer (1986),  $^{13}\text{C}/^{12}\text{C}$  ratios in  $\text{CO}_2$  extracted from Antarctic ice, *Geophys. Res. Lett.*, *11*, 1145–1148.
- 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, *Global Change Biol.*, *10*, 1285–1298.
- Herczeg, A. L. (1987), A stable carbon isotope study of dissolved inorganic carbon cycling in a softwater lake, *Biogeochemistry*, *4*, 231–263.
- Herczeg, A. L., and R. G. Fairbanks (1987), Anomalous carbon isotope fractionation between atmospheric  $\text{CO}_2$  and dissolved inorganic carbon induced by intense photosynthesis, *Geochim. Cosmochim. Acta*, *51*, 895–899.
- Hoover, T. E., and D. C. Berkshire (1969), Effects of hydration in carbon dioxide exchange across an air-water interface, *J. Geophys. Res.*, *74*, 456–464.
- Inoue, H., and Y. Sugimura (1985), Carbon isotopic fractionation during the  $\text{CO}_2$  exchange process between air and sea water under equilibrium and kinetic conditions, *Geochim. Cosmochim. Acta*, *49*, 2453–2460.
- Invers, O., J. Romero, and M. Perez (1997), Effects of pH on seagrass photosynthesis: A laboratory and field assessment, *Aquat. Bot.*, *59*, 185–194.
- Jähne, B., G. Heinz, and W. Dietrich (1987), Measurement of the diffusion coefficients of sparingly soluble gases in water, *J. Geophys. Res.*, *92*, 10,767–10,776.
- Johnson, K. S. (1982), Carbon dioxide hydration and dehydration kinetics in seawater, *Limnol. Oceanogr.*, *27*, 849–855.
- Lajtha, K., and R. H. Michener (1994), Sources and variations in the stable isotopic composition of plants, in *Stable Isotopes in Ecology and Environmental Science*, edited by K. Lajtha and R. H. Michener, pp. 1–21, Blackwell, Malden, Mass.
- Lewis, W. K., and W. G. Whitman (1924), Principles of gas absorption, *Ind. Eng. Chem. Res.*, *16*, 1215–1220.
- Macintyre, S., R. Wanninkhof, and J. P. Chanton (1995), Trace gas exchange across the air-water interface in freshwater and coastal marine environments, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P. Matson and R. Harriss, pp. 52–97, Blackwell, Malden, Mass.
- Marker, A. F. H., C. A. Crowther, and R. J. M. Gunn (1980), Methanol and acetone as solvents for estimating chlorophyll and pheopigments by spectrophotometry, *Ergeb. Limnol.*, *14*, 52–69.
- Marlier, J. F., and M. H. O’Leary (1984), Carbon kinetic isotope effects on the hydration of carbon dioxide and the dehydration of bicarbonate ion, *J. Am. Chem. Soc.*, *106*, 5054–5057.
- Matthews, C. J. D., V. L. St Louis, and R. H. Hesslein (2003), Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces, *Environ. Sci. Technol.*, *37*, 772–780.
- Quay, P. D., S. R. Emerson, B. M. Quay, and A. H. Devol (1986), The carbon cycle for Lake Washington—A stable isotope study, *Limnol. Oceanogr.*, *31*, 596–611.
- Quay, P. D., B. Tilbrook, and C. S. Wong (1992), Oceanic uptake of fossil fuel  $\text{CO}_2$ : Carbon-13 evidence, *Science*, *256*, 74–79.
- Quinn, J. A., and N. C. Otto (1971), Carbon dioxide exchange at the air-sea interface: Flux augmentation by chemical reaction, *J. Geophys. Res.*, *76*, 1539–1549.
- Rau, G. (1978), Carbon-13 depletion in a subalpine lake: Carbon flow implications, *Science*, *201*, 901–902.

- Schindler, D. W., G. J. Brunskill, S. Emerson, W. S. Broecker, and T. H. Peng (1972), Atmospheric carbon dioxide: Its role in maintaining phytoplankton standing crops, *Science*, *177*, 1192–1194.
- Siegenthaler, U., and K. O. Münnich (1981),  $^{13}\text{C}/^{12}\text{C}$  fractionation during  $\text{CO}_2$  transfer from air to sea, in *Carbon Cycle Modeling*, edited by B. Bolin, pp. 249–257, John Wiley, Hoboken, N. J.
- Stainton, M. P. (1973), A syringe gas-stripping procedure for gas-chromatographic determination of dissolved inorganic and organic carbon in freshwater and carbonates in sediments, *J. Fish. Res. Board Can.*, *30*, 1441–1445.
- Stauffer, R. E. (1990), Electrode pH error, seasonal epilimnetic  $\text{pCO}_2$ , and the recent acidification of the Maine lakes, *Water Air Soil Pollut.*, *50*, 123–148.
- Stumm, W., and J. J. Morgan (1996), *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed. John Wiley, Hoboken, N. J.
- Szaran, J. (1998), Carbon isotope fractionation between dissolved and gaseous carbon dioxide, *Chem. Geol.*, *150*, 331–337.
- Usdowski, E., and J. Hoefs (1986),  $^{13}\text{C}/^{12}\text{C}$  partitioning and kinetics of  $\text{CO}_2$  absorption by hydroxide buffer solutions, *Earth Planet. Sci. Lett.*, *80*, 130–134.
- Wanninkhof, R. (1985), Kinetic fractionation of the carbon isotopes  $^{13}\text{C}$  and  $^{12}\text{C}$  during transfer of  $\text{CO}_2$  from air to seawater, *Tellus, Ser. B*, *37*, 128–135.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373–7382.
- Wanninkhof, R., and M. Knox (1996), Chemical enhancement of  $\text{CO}_2$  exchange in natural waters, *Limnol. Oceanogr.*, *41*, 689–697.
- Wetzel, R. G. (2001), *Limnology: Lake and River Systems*, 3rd ed., Elsevier, New York.
- Zhang, J., P. D. Quay, and D. O. Wilbur (1995), Carbon isotope fractionation during gas-water exchange and dissolution of  $\text{CO}_2$ , *Geochim. Cosmochim. Acta*, *59*, 107–114.

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