



Biogeochemical influence on carbon isotope signature in boreal lake sediments

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Abstract

The sources of dissolved inorganic carbon (DIC) were determined in Lake 658 at the Experimental Lakes Area in northwest Ontario, Canada. The study covered a period from June to October 2001 in five different locations in the lake. The pore water chemistry (concentration of DIC and dissolved organic carbon (DOC), pH, total alkalinity (TA), and isotopic composition of DIC ($\delta^{13}\text{C}_{\text{DIC}}$) were determined on a monthly basis. Additionally, isotopic composition of the sedimentary organic carbon ($\delta^{13}\text{C}_{\text{org}}$) was measured. The carbon dynamics in the sediment was simulated by a diagenetic model, which accounts for basic processes controlling the concentration of DIC, while the model to describe the isotope data must include other processes such as oxidation of methane within the sediments. In the sediment pore water the concentration of DIC represents approx. 20% of the total carbon and its isotopic composition reflects the combination of organic carbon degradation using various electron acceptors and methanogenesis. The production of methane, which forms via acetate fermentation and is partially oxidized in the upper layer of the sediment, was especially pronounced in the shallow littoral zones of the lake.

Introduction

Lake nutrient budgets are influenced by tight coupling between benthic and overlying water processes and greatly depend on sedimentary degradation and dissolution. Degradation of sedimentary organic matter results in the consumption of dissolved oxidants such as oxygen, nitrate and sulphate and solid-phase oxidants such as manganese and iron (hydr)oxides. Exchange between pore water and overlying water means that the oxidation of organic carbon in sediments can have an important effect on the amount of O_2 in overlying water, as well as the total amount of nutrients available for photosynthesis. In freshwater (low sulfate) environments, methanogenesis proceeds uninhibited once anaerobic conditions are established. Competition by sulfate reducing bacteria is essentially absent so that the short-chained volatile fatty acids pool is available and provides, in addition to acetate fermentation or methylated amines, important substrate for production of methane which is characterized by significant depletion in ^{13}C (Marty, 1992; Whiticar, 1999). Con-

sequently, anoxic conditions can also impart isotopic control on the DIC reservoir. The distribution of dissolved species can be described by appropriate mathematical models derived from the general diagenetic equation which enables us to determine the fluxes of dissolved species at the sediment-water interface and the rate of organic matter degradation (Berner, 1980; Herczeg, 1988; Furrer & Wehrli, 1996).

The pore waters investigated in this study are enclosed within non-carbonate sediments and have a relatively high organic carbon content. Therefore, it represents an ideal environment to study the distribution and isotopic control of carbon cycling processes during early diagenesis.

Materials and methods

Site description

The research was carried out at Lake 658 at the ELA (Experimental Lakes Area – 49° 40' N, 93° 44' W) in

northwest Ontario, Canada. Lake 658 is a small, oligotrophic, headwater lake on the Canadian Shield with an area of 0.0083 km² and a mean depth of 7.5 m. Water inflow is by surface runoff and two small streams, in the western basin, while the water outflow is joined to Lake Winnage by a small channel. The hydrologic residence time in the lake is 3 years. Thermal stratification starts in May, and turnover of the water-column is generally completed by the end of October. The anoxic hypolimnion is usually established by late summer. Reoxygenation of the entire water column occurs rapidly during turnover. Porosity in the top 10 cm is >0.8 indicating that the sediment is largely composed by clayey silt. Organic carbon contents exceed 10% of total sediment by dry weight.

Sampling and analyses

Sediment samples were collected at five different locations in Lake 658. In the epilimnion at the stations G2 (2 m) and G3 (3 m), at G4 (7 m) in the hypolimnion and at the station W Basin, the deepest part of the lake (13 m), where the environment becomes anoxic during the summer (Fig. 1). Undisturbed 15 cm deep sediment cores were taken in June, July, August and September 2001 by SCUBA diving, inserting a Plexiglas tube (5 cm i.d.) directly into the sediment. The cores were transported immediately to the laboratory and sectioned into 2 cm intervals in an anaerobic glove box. The sediment was placed in polycarbonate centrifuge tubes and centrifuged for 10 min at 10 000 rpm in a refrigerated centrifuge. The pore water was extracted into glass syringes and stored in a refrigerator at ~4 °C. A subsample of the solid phase was oven-dried (65 °C) and ground to a fine powder for analyses of total and organic C and corresponding isotopic composition, $\delta^{13}\text{C}_{\text{org}}$.

Pore water pH and total alkalinity (TA) were determined immediately. The pH was measured with a UniFET microelectrode. TA was determined by the Gran titration method. Dissolved inorganic carbon (DIC) concentrations were determined using a Shimadzu TOC-5000 analyzer after acidification with 1 M HCl. Concentrations of H₂CO₃* were calculated from DIC and pH using apparent dissociation constants according to Stumm & Morgan (1981). The precision of the measurement was: ± 0.01 for pH, $\pm 1\%$ for TA, and $\pm 2\%$ for directly measured DIC.

Samples for $\delta^{13}\text{C}_{\text{DIC}}$ were introduced into evacuated septum vial containing 100% phosphoric acid. The isotopic ratio of CO₂ produced was measured

on a Europa 20-20 ANCA-TG mass spectrometer. Sediment samples for the determination of the stable isotopic composition of organic C were treated first with 1 M HCl and then ignited to CO₂ at 1800 °C in a recirculating stream of oxygen. The stable isotopic composition of the CO₂ produced was determined with an Europa 20-20 ANCA-SL mass spectrometer. Stable isotopic results are reported with δ -values as deviations in ‰ from the V-PDB standard. Analyses of organic C and total N in sediment samples were performed using a Carlo Erba elemental analyzer (mod. EA 1108). Organic C content was determined after acidification of samples with 1 M HCl (Hedges & Stern, 1984).

The precision of the analyses, based on replicate measurements, was $\pm 0.2\text{‰}$ for $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{org}}$. The precision for organic C and total N analyses in sediments was $\pm 3\%$. The water temperature and concentration of dissolved oxygen in the water column were measured regularly, biweekly as a part of the monitoring program during the sampling period. The Department of Fisheries and Oceans (DFO), Freshwater Institute, Winnipeg, Canada provided the data.

Results and discussion

The concentration of sedimentary organic carbon, its corresponding isotopic composition, $\delta^{13}\text{C}_{\text{org}}$, as well as C/N ratios depend on the sampling location. Observed concentrations of C_{org} and N_{tot} in the surface sediments were high, ranging from 10 to 36% dw (dry weight sediment) of C_{org} and 0.7 to 1.9% dw of N_{tot}. The highest concentrations were determined at location G2 in the shallow part of the lake near the wetland stream. Irregular changes in the concentrations of C_{org} and N_{tot} with depth, were more pronounced in the epilimnetic than in hypolimnetic sediments. However, sediments at the top 12 cm displayed roughly constant $\delta^{13}\text{C}_{\text{org}}$ values with depth at all five locations. The depth averaged $\delta^{13}\text{C}_{\text{org}}$ values were $-25.6 \pm 0.8\text{‰}$ at location G1, $-26.9 \pm 0.3\text{‰}$ at G2, $-25.8 \pm 0.9\text{‰}$ at G3, $-28.2 \pm 0.4\text{‰}$ at G4 and $-30.1 \pm 0.7\text{‰}$ at the W Basin. These data indicate that water plants and terrigenous organic detritus from the surroundings were the main sources of organic carbon in the shallow areas of the lake, while in the hypolimnion at 13 m the influence of methanotrophic bacteria was evident (Freeman et al., 1990). The calculated C/N ratios of these sediments vary between 10 and 26, which is

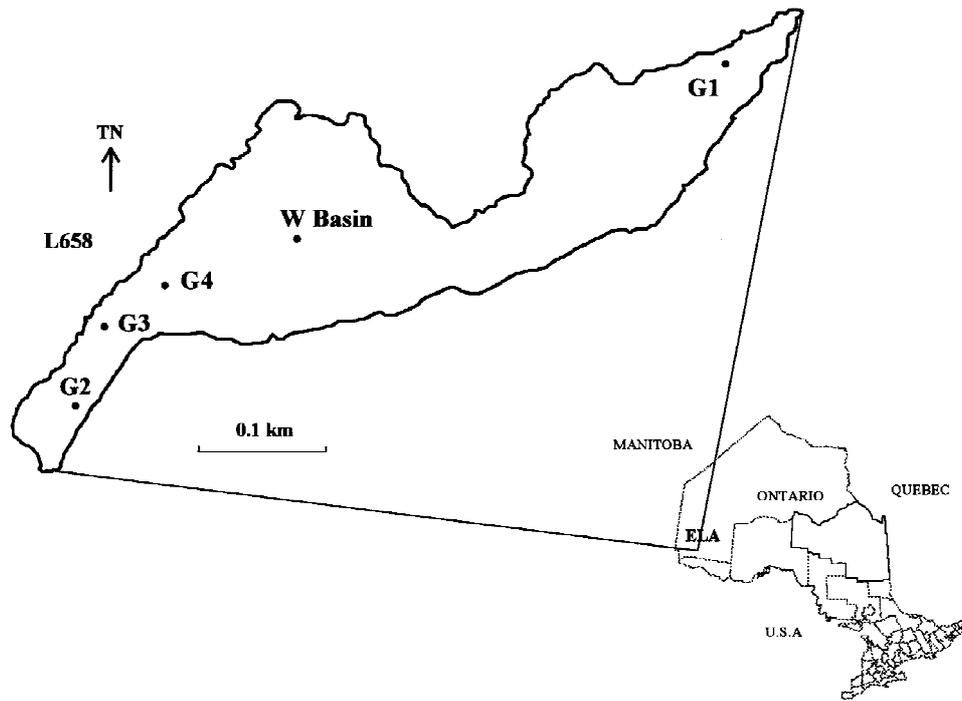


Figure 1. Study area with the sampling locations G1, G2, G3, G4 and W Basin in boreal Lake 658 at the ELA, northwest Ontario, Canada.

Table 1. The bottom water temperature, the % of DIC derived from methanogenesis within the pore water and diffusive fluxes of DIC, J_{DIC} , together with the corresponding isotopic composition, $\delta^{13}C_{J-DIC}$ during the sampling period. Also listed are the best-fit parameters obtained by fitting diagenetic equation to DIC profile and the best-fit value for β ($\delta^{13}C_{DIC}$) obtained by fitting the model to $\delta^{13}C_{DIC}$ profile

Location	Period	T [°C]	DIC methanogenesis [%]	Rc(z)			J_{DIC} [mmol m ⁻² d ⁻¹]	$\delta^{13}C_{J-DIC}$ [‰]
				R_0 [mmol dm ⁻³ s ⁻¹]	β (DIC) [cm ⁻¹]	β ($\delta^{13}C_{DIC}$) [cm ⁻¹]		
W Basin	June	4.6	67	$9.76 \cdot 10^{-7}$	0.46	0.11	1.65	4.7
G4	June	6.2	38	$2.23 \cdot 10^{-8}$	0.13		0.19	-12.5
	July	6.5	37	$1.16 \cdot 10^{-7}$	0.15	0.14	0.60	-14.1
	August	6.2	43	$4.70 \cdot 10^{-7}$	0.07	0.07	0.52	17.1
	September	6.8	47	$3.33 \cdot 10^{-8}$	0.06	0.07	0.43	34.6
G1	June	16.2	12	$2.19 \cdot 10^{-7}$	0.13		0.86	
	July	18.3	34	$5.73 \cdot 10^{-7}$	0.57	0.50	0.78	9.8
	August	20.8	29	$1.93 \cdot 10^{-8}$	0.12	0.35	0.13	-6.5
	September	17.9	75	$-1.47 \cdot 10^{-7}$	0.14	0.32	-0.5	-6.9
G2	June	17.6	8	$7.74 \cdot 10^{-7}$	0.13		0.47	
	July	22.9	20	$3.02 \cdot 10^{-7}$	0.41	0.24	0.58	13.9
	August	21.2	58	$9.10 \cdot 10^{-7}$	0.58	0.25	1.22	11.4
	September	17.9	64	$4.97 \cdot 10^{-7}$	0.29	0.32	0.81	23.0
G3	July	18.5	65	$2.31 \cdot 10^{-8}$	0.14	0.64	0.13	0.4
	August	20.8	42	$3.42 \cdot 10^{-7}$	0.34	0.36	0.78	7.9
	September	17.7	78	$5.08 \cdot 10^{-7}$	0.23	0.28	1.71	11.3

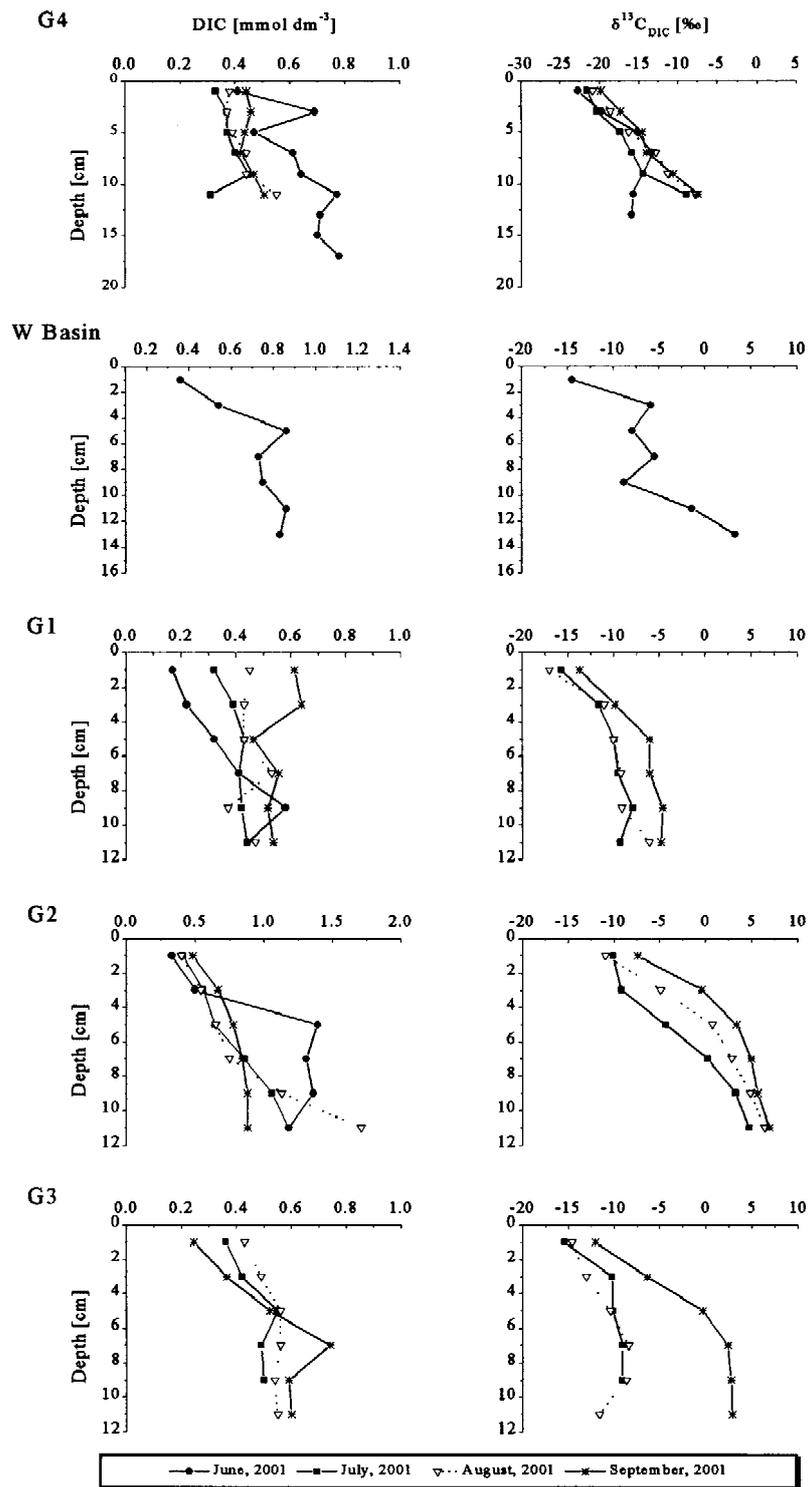


Figure 2. Depth profiles of DIC and its isotopic composition $\delta^{13}\text{C}_{\text{DIC}}$ at all sampling locations during the sampling period June–September, 2001.

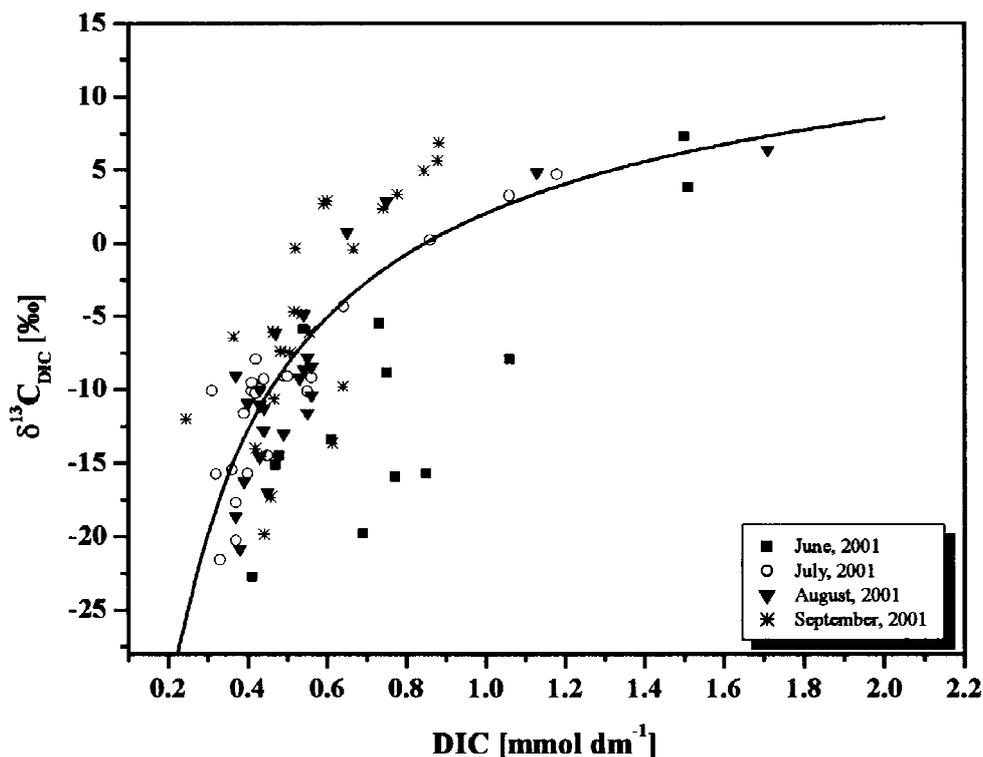


Figure 3. Relationship between $\delta^{13}\text{C}_{\text{DIC}}$ values and DIC concentrations in pore waters at sampling locations in Lake 658. The curve shown is the resulting best-fit according to the model proposed by LaZerte (1981): $\delta^{13}\text{C}_{\text{DIC}} = 20.5 - 17.9 * [\text{DIC}]^{-0.64}$.

characteristic for vascular land-plant debris (Meyers, 1994).

Concentrations of DIC and its corresponding isotopic composition, $\delta^{13}\text{C}_{\text{DIC}}$, in pore water increased with depth at all five locations. The influence of decomposition of organic matter is reflected at the top few cm of the sediment, while the importance of methanogenesis may be seen by the large positive gradient in $\delta^{13}\text{C}_{\text{DIC}}$, which is more pronounced in the littoral sediments (Fig. 2). In order to estimate the rate of the decomposition of organic matter in the sediments, the observed variations in the concentrations of DIC, were described by a diffusive-reaction model (Berner, 1980; Ogrinc et al., 2002):

$$\frac{\partial[\text{DIC}]}{\partial t} = D_{\text{HCO}_3^-} \frac{\partial^2[\text{DIC}]}{\partial z^2} + \text{Rc}(z), \quad (1)$$

where t is time [s], z is depth [cm], $\text{Rc}(z)$ is the CO_2 -production rate [$\text{mmol dm}^{-3} \text{s}^{-1}$] and $D_{\text{HCO}_3^-}$ [$\text{cm}^2 \text{s}^{-1}$] is the sediment diffusion coefficient for HCO_3^- corrected for temperature from the diffusion coefficient of Li & Gregory (1974) and average porosity (Lerman, 1979). This equation assumes that the poros-

ity and diffusion coefficient of dissolved species do not change significantly with depth and the influence of bioirrigation is negligible (Berner, 1980; Herczeg, 1988). Indeed, the results of Sweerts et al. (1991) show that in most freshwater sediments the sediment diffusion coefficient can be predicted reliably from the molecular diffusion coefficient at *in situ* temperature. The empirical model describes the overall rate of organic carbon decomposition as a first-order kinetic process (Berner, 1980), thus $\text{Rc}(z)$ is assumed to decrease exponentially with depth:

$$\text{Rc}(z) = \text{R}_0 \exp(-\beta z), \quad (2)$$

where β is the empirical constant called the depth attenuation coefficient and R_0 is the CO_2 -production rate at the depth $z=0$ (i.e. the water-sediment interface). Equation (1) was solved considering special boundary conditions for the steady-state (Ogrinc et al., 2002). Values for parameters R_0 and β were obtained by fitting the diagenetic model including Equation (2) to pore water profiles of DIC. The best-fit values summarized in Table 1 were obtained by searching for the minimum in the sum of squares of differences (ssq)

between calculated and experimental values. Results show that the degradation rate of organic matter in the hypolimnium at the station G4 was slightly decreasing in correlation with decreasing O₂ content. At the deepest location of the lake (W Basin) the degradation rate was four times higher in June 2001 than those determined at the station G4, probably caused by highly reactive fraction of organic matter derived from settling phytoplankton. This is in agreement with other studies showing that summer and fall are the most important periods for particulate loss from the water column (Kelly & Chynoweth, 1981). Seasonal changes in the CO₂-production rate at the sediment–water interface was also observed in the littoral zones of the lake, the highest being observed at stations G2 and G3 near the wetland stream inflow. These changes could be explained by the quality of sedimentary organic matter, the temperature cycle during the sampling period and the higher sedimentation rate in this part of the lake. There was a lower CO₂-production rate observed at the station G1 during the sampling period with the DIC influx determined in late summer. This station is located near the lake outflow into the Lake Winnage, which might influence the production of DIC at this location as well sediment structure.

The same model was used to describe the profile of ¹³C isotopic composition of DIC, $\delta^{13}\text{C}_{\text{DIC}}$. The model estimates for β values are listed in Table 1. It was not possible to describe the DIC and $\delta^{13}\text{C}_{\text{DIC}}$ data with the same values of β in all situations. However, the DIC concentration and corresponding isotopic composition in pore water was reasonably well described using the same β values in the model at the station G4 and in September profiles at all sampling locations. The apparent β value that best fits the $\delta^{13}\text{C}$ data in the deepest part and at the station G2 of the lake was lower than the calculated decomposition rate estimated from the DIC model fits. These findings lead us to suppose that not all the processes affecting DIC in pore waters are taken into account. A modified model may include an additional component of ¹³C-poor DIC generated by oxidation of methane in the pore waters.

The diffusive fluxes of DIC, J_{DIC} , across the sediment–water interface were estimated using Fick's first law of diffusion. Applying Equations (1) and (2) to calculate the concentration gradient of DIC in pore water, the flux is approximated by:

$$J_{\text{DIC}} = \frac{\phi R_0}{\beta}, \quad (3)$$

where ϕ is the porosity. The apparent diffusive fluxes of DIC are collected in Table 1. In addition, the isotopic composition of the DIC flux at the sediment/water interface was calculated according to Sayles & Curry (1988). The calculated values collected in Table 1, show a high enrichment in ¹³C indicating an influence of methane formation. Although there are no data for methane concentration in Lake 658 sediment pore waters, the increase in the H₂CO₃* concentration can be used as an approximation for methane production in the sediments (Rudd & Hamilton, 1978; Herczeg, 1988). The DIC produced from methanogenesis was estimated from the slope of the plot of H₂CO₃* concentration vs. concentration of DIC (r^2 of the regression ranged between 0.70 and 0.96). The calculated values are presented in Table 1. In the hypolimnetic pore water at 7 m (station G4) the production of DIC by methanogenesis remains almost constant (average 42%) during the sampling period, when the temperature was fairly constant. Higher proportions of regenerated DIC derived from methanogenesis were determined in the deepest part (W-basin: 67%) and in the shallow areas of the lake, ranging from 30 to 78% during the summer. This indicates that DIC production from methanogenesis was probably sensitive to temperature and organic carbon input.

The prevailing methane formation pathway was estimated mathematically, following the procedure proposed by LaZerte (1981) describing the relationship between the DIC concentration and corresponding isotopic composition in aquatic sediments. The methanogenic pathway was determined by fitting the model to the $\delta^{13}\text{C}_{\text{DIC}}$ vs. [DIC] data. The parameters needed were $\delta^{13}\text{C}_{\text{DIC}}$ at depths 0 and ∞ , $\delta^{13}\text{C}_{\text{org}}$, and the isotope fractionation factor between C_{org} and CH₄ determined from $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{CH}_4}$. Since there were no data available on the isotopic composition of methane, the methane was assigned a $\delta^{13}\text{C}$ value of -60‰ ($\pm 15\text{‰}$; Whiticar, 1999) in this calculation. It was estimated from the resulting best-fit equation shown in Figure 3 that about 85% of methane was produced by acetate fermentation.

Conclusions

Pore water profiles of DIC in the hypolimnetic and littoral sediments of a soft-water lake show steep gradients in the upper 12 cm of the sediments column. Seasonal changes in the CO₂-production rate and con-

sequently the DIC fluxes at the sediment-water interface observed in these sediments were limited by the supply of O₂, and directly linked to the quality and quantity of sedimentary organic matter, and the temperature cycle. $\delta^{13}\text{C}$ profiles show strong positive enrichments over the bottom-water interface due to methanogenesis proceeding predominantly (85%) by acetate fermentation. The amount of organic carbon regenerated by methane fermentation was estimated to be between 8 and 78% depending on the temperature and organic carbon input. Modeled profiles of the $\delta^{13}\text{C}_{\text{DIC}}$ in the deepest part of the lake and the littoral zone at the station G2 during the summer did not agree with the concentration data. This indicates that a diagenetic model for the isotope data must include other processes such as oxidation of methane within the sediments, which release relatively ¹³C-poor DIC into the pore waters.

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