

Extreme ^{13}C enrichments in a shallow hypereutrophic lake: Implications for carbon cycling

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Abstract

An analysis of stable carbon isotope ($\delta^{13}\text{C}$) ratios in Lake Apopka, Florida, reveals extreme ^{13}C enrichments of dissolved inorganic carbon (DIC) pools in the water column and sediment pore water of this shallow polymictic and hypereutrophic lake. The sediment pore water had high average $\delta^{13}\text{C}$ of DIC (26.4‰), DIC (8.37 mmol L⁻¹), and methane (CH₄) concentrations (1.23 mmol L⁻¹). The extreme ^{13}C enrichment in the sediment pore-water DIC pool is attributed to methanogenesis, which produces ^{13}C -rich carbon dioxide (CO₂) and ^{13}C -poor CH₄ during the bacterial fermentation of organic matter. The $\delta^{13}\text{C}$ in the water-column DIC pool ranged from 5‰ to 13‰ with an average of 9.0‰. The flux-weighted $\delta^{13}\text{C}$ from the DIC due to external loading and sediment respiration was estimated as -12‰, whereas the $\delta^{13}\text{C}$ from particulate organic carbon (POC) due to water-column production was -13‰. The ^{13}C enrichment in the water column is attributed directly to the diffusion and advection of isotopically heavy DIC from the sediment and to the isotopic fractionation by phytoplankton photosynthesis and is attributed indirectly to the removal of isotopically light CH₄ by ebullition and organic matter by sedimentation and outflow. Atmospheric invasion and sedimentation were the most important source and sink, respectively, in the carbon mass balance. CH₄ oxidation, atmospheric invasion, anaerobic respiration, and sedimentation are the important flux terms affecting the isotopic mass balance. A combination of shallow water depth, frequent wind mixing, anoxic sediments with high rates of methanogenesis, high phytoplankton productivity, and lack of external loading dominated by terrestrial carbon led to the ^{13}C enrichment of the water-column DIC pool in Lake Apopka.

Dissolved inorganic carbon (DIC) in aquatic ecosystems is often the major carbon source for photosynthesis and is maintained by several mechanisms that include, but are not limited to, atmospheric invasion, terrestrial runoff, stream and underground inputs, and oxidation of organic matter from the water column and sediments. Anaerobic decomposition of sedimentary organic matter via methanogenesis also can play an important role in the carbon cycle of eutrophic lakes. This process produces two gaseous forms of carbon compounds, methane (CH₄) and carbon dioxide (CO₂). CH₄ released from the sediments can be oxidized to form CO₂ under aerobic conditions and provides a significant in-

put of DIC to the water column during thermal stratification (Rudd and Hamilton 1978). Recently, Bastviken et al. (2003) reported that methanotrophic bacteria can be an important food source for zooplankton in several small Swedish lakes. However, the fate of CO₂ derived from methanogenesis in lacustrine systems has received less attention.

Stable carbon isotope ($\delta^{13}\text{C}$) analysis is a powerful tool for the study of sources and sinks of inorganic and organic carbon in aquatic ecosystems (Peterson and Fry 1987). The average $\delta^{13}\text{C}$ of atmospheric CO₂ is -8‰, whereas the $\delta^{13}\text{C}$ from C-3 plants is approximately -28‰ due to isotopic fractionation. The oxidation of organic matter shows little isotopic fractionation, and the $\delta^{13}\text{C}$ in DIC resembles the isotopic composition of its source. However, lacustrine systems often receive DIC inputs from more than one source, and the resulting isotope ratios typically reflect the "weighted average" of these sources. Phytoplankton fractionate against ^{13}C during carbon fixation, resulting in light isotopes in photosynthetic products and heavy isotopes in the DIC pool. Sedimentation of isotopically light organic matter may lead to ^{13}C enrichment in the water column (Schelske and Hodell 1991). $\delta^{13}\text{C}$ enrichment in the DIC pool is especially apparent when carbon demand is high and pool size is limited. Oren et al. (1995) reported that the $\delta^{13}\text{C}$ in DIC in the Dead Sea was as high as 5.1‰ during a *Dunaliella* bloom compared to -3.4‰ prior to the bloom. However, the highest carbon isotopic fractionation is associated with the anaerobic respiration (i.e., methanogenesis) of organic matter. The CH₄ and CO₂ produced during this process are depleted

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and enriched, respectively, with ^{13}C (Games and Hayes 1976). Extreme ^{13}C enrichment in pore-water DIC values as high as 17‰ from a marine sediment (Nissenbaum et al. 1972) and 14‰ from a freshwater lake (Stiller and Magaritz 1974) were reported. Both enrichments were attributed to the anaerobic decomposition of sedimentary organic matter.

We report a stable isotope study of Lake Apopka, the goal of which is to understand the mechanisms that led to ^{13}C enrichments of the DIC pools. We evaluate major biological, geochemical, and physical processes to explain the extreme ^{13}C enrichment in the water-column DIC pool and construct isotopic and mass balance models to identify dominant carbon sources and sinks in this shallow hypereutrophic lake.

Methods

Site description—Lake Apopka is a large (124 km²), shallow (mean depth = 1.7 m) freshwater lake located ~25 km northwest of Orlando in central Florida. There are no surface tributaries to the lake, which is fed by a spring (Apopka Spring); however, it is affected by groundwater seepage, precipitation, and drainage water from adjacent vegetable farms (muck farms). The water budget is balanced by discharge through an outlet (Beauclair Canal) and evaporation. Prior to 1947, Lake Apopka was a clear-water and macrophyte-dominated system that supported a large recreational fishery (Schelske and Brezonik 1992). This lake has since become plankton dominated as a result of increased nutrient loading from citrus farming and sewage discharge and, after the 1940s, as a result of muck farm agriculture on former wetlands along the north shore (Schelske et al. 2000). Lake Apopka is hypereutrophic with high total phosphorus (TP = 192 $\mu\text{g L}^{-1}$) and chlorophyll *a* concentration (96 $\mu\text{g L}^{-1}$). The lake water is alkaline with both high pH (9.0) and alkalinity (110 mg $\text{CaCO}_3 \text{ L}^{-1}$). There are large pools of DIC (2.13 mmol L^{-1}), dissolved organic carbon (DOC = 2.08 mmol L^{-1}), and particulate organic carbon (POC = 2.35 mmol L^{-1}) in the lake's water column. Thick deposits of unconsolidated flocculent sediments that average >60% organic matter are present on the lake bottom (Gale and Reddy 1994; Schelske et al. 2000). Frequent resuspension of sediments due to wind mixing occurs in this polymictic lake (Carrick et al. 1993).

Field sampling—Water samples were collected for analyses of DIC, CH_4 , and carbon isotopic ratios of DIC and POC ($\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$). Surface-water samples (0.3 m below the lake surface) on 15 September 1994 were obtained from 30 evenly spaced stations on six transects in the lake and from Apopka Spring, a second-order spring, in the southwest part of the lake. Depth series sampling was performed from a central lake station on 20 April 1995. An underwater pump was used to collect water samples in 30-ml Qorpack bottles for analyses of DIC and $\delta^{13}\text{C}_{\text{DIC}}$ and in 60-ml serum vials for CH_4 analysis after several overflows. Each bottle was injected with 1 ml of saturated HgCl_2 solution for preservation and capped with a rubber stopper.

On 20 April 1995, a sediment core (approximately 80 cm long) was retrieved from a central lake station (28°38'02"N, 81°35'23"W) with a piston corer equipped with a 4-cm-di-

ameter, clear plastic core barrel (Fisher et al. 1992). Pore water for the determination of $\delta^{13}\text{C}_{\text{DIC}}$ and DIC concentrations was obtained with 3-ml syringes screwed into the core tube at 5-cm intervals. The pore water was drawn into the syringes through preloaded filters. Each syringe filled with the pore water was capped and placed in an ice cooler. Sediment samples for the determination of CH_4 concentrations were obtained from the same series of depths using deheaded 3-ml syringes and were injected into 60-ml serum vials containing 1 ml of saturated HgCl_2 solution. The core was subsequently sectioned at 5-cm intervals, and samples were stored in sealed plastic cups for transport to the laboratory for the determination of $\delta^{13}\text{C}$ in sediment organic carbon ($\delta^{13}\text{C}_{\text{SOC}}$), total carbon (TC), total nitrogen (TN), and TP. After sectioning, three samples of approximately 20 g were placed in clear glass jars (0.5 liter) sealed with septum caps for analysis by Global Geochemistry of the $\delta^{13}\text{C}$ ratio in CH_4 ($\delta^{13}\text{C}_{\text{CH}_4}$). The top 5 cm of the sediment cores obtained from four other lake locations on 25 May 1995 was collected for the analysis of $\delta^{13}\text{C}_{\text{DIC}}$, pH, and DIC concentration.

Laboratory analyses—In the laboratory, sediment subsamples were dried in an oven at 70°C for 24 h and ground with a mortar and pestle. Sediments were acidified with diluted HCl and washed with copious amounts of deionized water. Samples for $\delta^{13}\text{C}$ analysis (ca. 0.5 mg of dry material) were loaded into tin capsules that were then placed in a Carlo Erba NA 1500 CNS analyzer and combusted at 1,240°C in a combustion tube containing chromium oxide and silvered cobaltous cobaltic oxide. Combustion gases were passed through a reduction column and a gas chromatograph by a stream of He gas, where CO_2 was separated from the other gases. The CO_2 then entered a VG PRISM II series mass spectrometer, where CO_2 was concentrated in a cryogenic triple trap and analyzed for a $^{13}\text{C}:^{12}\text{C}$ ratio against an internal reference gas (Carrara Marble-University of Florida Reference Gas).

Extraction of DIC for isotopic determination was conducted using a technique similar to that of Socki et al. (1992). Twenty-milliliter Vacutainers loaded with 20 μg of concentrated phosphoric acid (H_3PO_4) were evacuated by a vacuum line and then injected with 2- to 5-ml water samples. The Vacutainers were then immersed in a hot-water bath and shaken at 50°C for 30 min. After incubation, the Vacutainers were connected to a vacuum line; CO_2 from the headspace was cryogenically separated from other gases and water vapor and then loaded into the VG PRISM II series mass spectrometer for $^{13}\text{C}:^{12}\text{C}$ determinations. For every batch of samples, two external standards of potassium bicarbonate (KHCO_3) dissolved in CO_2 -free deionized water were also analyzed. All isotope values are reported relative to the Vienna PeeDee belemnite standard (V-PDB).

CH_4 concentrations from the water column and sediments were determined using a Shimadzu Mini-2 flame ionization detection gas chromatograph with a 3.175-mm \times 1-m molecular sieve 5a, a 60/80 mesh size column, a carrier gas of ultrapure N_2 at a flow rate of 33 ml min^{-1} , and a column temperature of 70°C.

Concentrations of DIC were determined using a model 5011 Carbon Coulometer (UIC Coulometrics) or were cal-

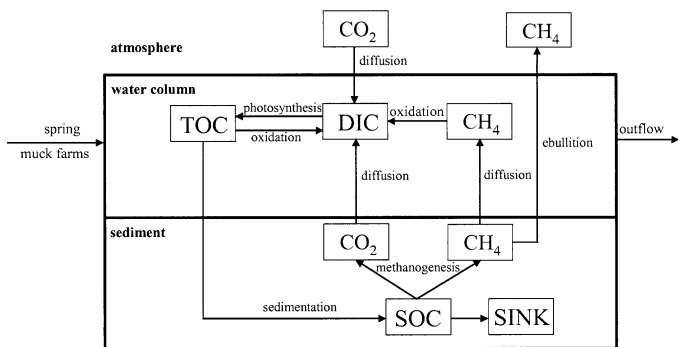


Fig. 1. Schematic diagram of major carbon cycling pathways in Lake Apopka.

culated from alkalinity, pH, and water temperature provided by the St. Johns River Water Management District (SJRWMD). Carbon and nitrogen contents of sediment organic matter were determined using a Carlo Erba NA 1500 CNS analyzer. TP was measured as an orthophosphate using an autoanalyzer, after persulfate digestion of sediments.

Isotope mass balance—We constructed an isotope mass balance to demonstrate the importance of each DIC flux to the isotopic composition of the water column. Figure 1 illustrates the major carbon cycling pathways in Lake Apopka. The input terms include DIC from atmospheric invasion, methanogenesis, CH_4 oxidation, and DIC and total organic C (TOC) from the muck farms; the output terms include sedimentation and outflow DIC, POC, and DOC. The isotope mass balance can be expressed by the following equation:

$$[\text{input}] \times \delta^{13}\text{C}_{\text{input}} - [\text{output}] \times \delta^{13}\text{C}_{\text{output}} = 0 \quad (1)$$

where [input], [output], $\delta^{13}\text{C}_{\text{input}}$, and $\delta^{13}\text{C}_{\text{output}}$ are the flux ($\text{mol m}^{-2} \text{yr}^{-1}$) and isotopic composition of each input and output term described above.

CO_2 flux between the atmosphere and lake water was estimated using the following equation:

$$\text{flux} = (Kh \times P_{\text{CO}_2} - [\text{CO}_{2(\text{aq})}]) \times D/z \times f \quad (2)$$

where Kh is a dissolution constant of CO_2 ($\text{mol cm}^{-3} \text{atm}^{-1}$), and P_{CO_2} is the partial pressure of CO_2 (atm). $[\text{CO}_{2(\text{aq})}]$ is the concentration (mol cm^{-3}) of dissolved free CO_2 in water; D is a dissolution velocity of CO_2 ($\text{cm}^{-2} \text{s}^{-1}$); and z is the thickness of stagnant boundary layer (cm) and was estimated from Kling et al. (1992). The letter “ f ” is a chemical enhancement factor that increases with pH, stagnant layer thickness, and productivity (Emerson 1975). The commonly used value for productive waters with a high pH is 3 (Schindler et al. 1972).

The input of DIC from Apopka Spring and the output of DIC, POC, and DOC from Beauclair Canal were calculated by multiplying concentrations of each component and annual flow (SJRWMD). Similarly, the input of DIC and TOC from the back pumping of the muck farms was calculated from the concentrations and average annual loading of drainage water from the muck farms (SJRWMD). The flux of DIC and CH_4 from sediments was estimated from Gale and Reddy (1994) and modified for sediment distribution.

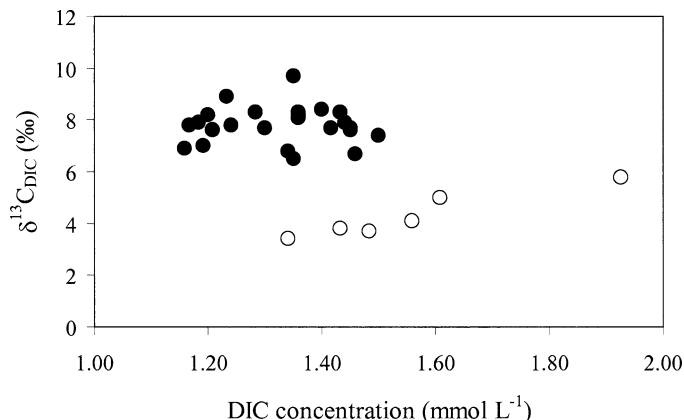


Fig. 2. Concentrations and value for $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) at 30 surface stations. Open circles denote samples taken at near-shore stations.

Results

Water column—Water samples were highly enriched in ^{13}C . The $\delta^{13}\text{C}_{\text{DIC}}$ for the surface samples from 30 lake stations mostly ranged from 6‰ to 8‰, but at six near-shore stations, these values ranged from <4‰ to 6‰ (Fig. 2). A vertical profile of $\delta^{13}\text{C}_{\text{DIC}}$ from a central lake station shows highly enriched $\delta^{13}\text{C}_{\text{DIC}}$ ranging from 9.1‰ to 10.5‰ (Table 1). Vertical profiles on six different dates also provide evidence for a highly enriched $\delta^{13}\text{C}_{\text{DIC}}$ ranging from 6‰ to 13‰ with an average of 9.0‰ (Gu and Schelske 1996). Water-column DIC concentrations averaged 2.15 mmol L^{-1} , and CH_4 concentrations were $<1.0 \mu\text{mol L}^{-1}$, except for $5.0 \mu\text{mol L}^{-1}$ at 1.8 m, the deepest depth sampled. No vertical structure was apparent in either $\delta^{13}\text{C}_{\text{POC}}$ or pH (Table 1). Gu and Schelske (1996) reported an average of $\delta^{13}\text{C}_{\text{POC}}$ of $-13.0‰$ from the central lake station.

Sediment pore water—A sediment core taken from the central lake station had higher $\delta^{13}\text{C}_{\text{DIC}}$ values (20.6–28.7‰) than the water column (Table 2). The most enriched values were found below 25 cm. The $\delta^{13}\text{C}_{\text{DIC}}$ decreased from 28.7‰ at 25 cm to 24.8‰ at 10 cm and then decreased to 20.6‰ in the top 5 cm. Sediment pore water in the upper 5 cm at four other sampling sites also showed high $\delta^{13}\text{C}_{\text{DIC}}$ values

Table 1. Vertical profiles of $\delta^{13}\text{C}$ of POC and DIC, concentrations of DIC and CH_4 , and pH and dissolved oxygen (DO) in the water column. Samples were taken on 20 April 1995.

Depth (m)	$\delta^{13}\text{C}_{\text{POC}}$ (‰)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	[DIC] (mmol L^{-1})	[CH_4] ($\mu\text{mol L}^{-1}$)	pH	DO ($\mu\text{mol L}^{-1}$)
0.0	-13.2	10.2	2.13	0.2	8.8	489
0.3	-13.9	10.5	2.13	0.2	8.9	488
0.6	-14.0	10.2	2.15	0.2	8.8	493
0.9	-14.2	10.4	2.18	0.3	8.8	459
1.2	-14.0	10.3	2.15	0.3	8.8	460
1.5	-13.8	9.9	2.14	0.3	8.8	465
1.8	-13.8	9.1	2.17	5.0	8.7	435

Table 2. Stable isotopes of sediment organic carbon (SOC), DIC, and CH_4 ; concentrations of DIC and CH_4 ; and pH, TC, TN, and TP from a sediment core collected on 20 April 1995.

Depth (cm)	$\delta^{13}\text{C}_{\text{SOC}}$ (‰)	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	[DIC] (mmol L $^{-1}$)	[CH $_4$] (mmol L $^{-1}$)	pH	TC (%)	TN (%)	TP (mg g $^{-1}$)
5	-17.9	20.6		6.43	0.13	7.4	33.3	3.3	1.3
10	-18.0	24.8		8.73	1.14	7.4	32.7	3.2	1.4
15	-18.6	25.2	-30.5	10.18	1.24	7.5	31.8	2.9	1.1
20	-20.2	25.3		9.38	1.24	7.5	33.2	3.4	1.3
25	-21.9	28.7		8.54	1.28	7.5	33.6	2.9	0.9
30	-21.4	27.5		9.51	1.29	7.5	33.2	2.9	0.9
35	-23.7	28.3		8.97	1.29	7.5	37.9	3.1	0.6
40	-24.4	24.3		9.40	1.28	7.5	40.0	3.2	0.5
45	-24.2	26.9	-43.8	9.07	1.27	7.5	42.1	3.3	0.5
50	-24.3	27.9		8.13	1.57	7.5	41.2	3.2	0.6
55	-24.4	27.6		8.13	1.27	7.5	42.3	3.3	0.5
60	-24.6	27.2		7.28	1.55	7.5	42.6	3.3	0.5
65	-24.6	27.6		7.61	0.97	7.5	40.2	3.2	0.5
70	-24.5	26.2	-51.7	7.90	1.56	7.5	36.0	2.8	0.5
75	-24.7	27.1		7.06	1.28	7.5	33.6	2.4	0.5
80	-24.6	27.0		7.62	1.28	7.5	14.5	1.3	0.5

ranging from 20.5‰ to 21.9‰ (Table 3). Concentrations of DIC and CH_4 in sediment pore water also were greater than in the water column (Table 2). The pore-water CH_4 concentration was generally >1.0 mmol L $^{-1}$, except for a concentration of only 0.1 mmol L $^{-1}$ in the top sample. The DIC concentration in pore water varied from 6.43 to 10.18 mmol L $^{-1}$, with the lowest concentration in the top sample (Table 2).

In the sediment core, both $\delta^{13}\text{C}_{\text{SOC}}$ and $\delta^{13}\text{C}_{\text{CH}_4}$ were enriched near the surface, whereas the pattern was the opposite for $\delta^{13}\text{C}_{\text{DIC}}$ (Table 2). The upcore enrichment in $\delta^{13}\text{C}_{\text{CH}_4}$ was 21.2‰ compared to only 6.7‰ in $\delta^{13}\text{C}_{\text{SOC}}$ for the three depths from which both variables were measured. Phytoplankton-derived sediments were identified by the low C:N ratios in the upper 20 cm (Fig. 3). Macrophyte-derived sediments extend from 40 to 80 cm in this sediment core. Samples from 25 to 35 cm appear to be transitional sediments. Schelske et al. (2000) used the C:N proxy to differentiate the algal layer from the macrophyte layer in the Lake Apopka sediments. An upcore increase in $\delta^{13}\text{C}_{\text{SOC}}$ beginning at 35 cm corresponds to the time when the composition of the primary producer community began to shift from macrophyte to phytoplankton dominance. This shift can be inferred from the decrease in the TC:TN ratio (Fig. 3) and is asso-

Table 3. $\delta^{13}\text{C}_{\text{DIC}}$, [DIC], and pH measured in the pore water from surface sediments (top 5 cm) of four lake sites on 25 May 1995.

Variables	Sample site			
	1*	2†	3‡	4§
$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	21.1	20.5	21.9	20.7
pH	7.5	7.5	7.6	—
[DIC] (mmol L $^{-1}$)	8.20	5.10	9.35	—

* Site 1: latitude = 28°37'40"N; longitude = 81°37'58"W.

† Site 2: latitude = 28°37'36"N; longitude = 81°37'00"W.

‡ Site 3: latitude = 28°39'30"N; longitude = 81°36'52"W.

§ Site 4: latitude = 28°35'46"N; longitude = 81°37'13"W.

ciated with an increase in TP concentration (Table 2). After the shift, $\delta^{13}\text{C}_{\text{SOC}}$ increased from -22‰ to -18‰ (Fig. 3).

Isotopic mass balance—Estimation of the CO_2 flux using Eq. 2 is based on the dissolution constant ($K_h = 3.4 \times 10^{-5}$ mol cm $^{-3}$ atm $^{-1}$), the dissolution velocity ($D = 1.9 \times 10^{-5}$ cm 2 s $^{-1}$), the atmospheric P_{CO_2} (3.6×10^{-8} atm), and an average stagnant layer thickness ($z = 0.023$ cm). The dissolved free CO_2 concentration was calculated from 24 monthly samples of alkalinity, pH, and water temperature (SJRWMD). This yielded a dissolved free CO_2 concentration of 4.88×10^{-10} mol cm $^{-3}$. Based on the above information, the average CO_2 flux to the lake water was estimated as 9.07 mol m $^{-2}$ yr $^{-1}$ between 1994 and 1995.

Gale and Reddy (1994) estimated that anaerobic respira-

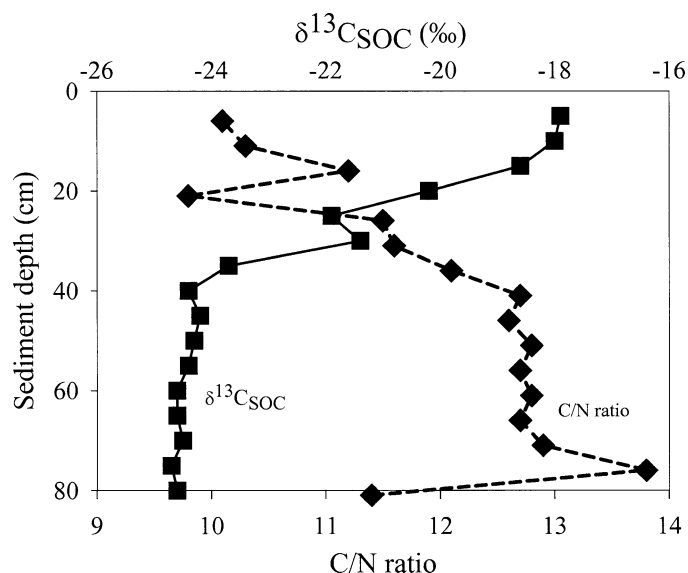


Fig. 3. Distribution of $\delta^{13}\text{C}$ and molar TC:TN ratios of sediment organic carbon (SOC) in a sediment core.

Table 4. Mass balance input and output terms and values. Unit of flux is mol C m⁻² yr⁻¹. Percent (%) is the proportion of each flux term relative to the total input or output. Product is calculated by using the numerical value of a mass flux term multiplied by its $\delta^{13}\text{C}$.

Term	Input				Term	Output			
	Flux	%	$\delta^{13}\text{C}$ (‰)	Product		Flux	%	$\delta^{13}\text{C}$ (‰)	Product
Atmospheric invasion	9.07	42	-11	-100	Net sedimentation	8.33	38	-13	-108
Anaerobic respiration	4.54	21	20	91	Gross-net sedimentation*	9.87	45	-13	-128
Muck farm DIC	3.13	15	-27	-85	DIC	1.14	5	9	10
Muck farm TOC	1.92	9	-27	-52	POC	1.17	5	-13	-15
Methane oxidation†	2.66	12	-42	-112	DOC	1.27	6	-13	-17
Apopka Spring	0.16	1	-9	-1					
Total‡	21.48	100	-12	-258	Total‡	21.78	100	-12	-258

* This is the portion of sediment organic carbon remineralized during methanogenesis and is equal to the sum of anaerobic respiration and methane oxidation in the input.

† It is assumed that methane ebullition has the same mass flux and isotopic value and hence the same product as methane oxidation. See text for additional explanation.

‡ The $\delta^{13}\text{C}$ values in the Totals are weighted averages for the input and output.

tion remineralized sediment organic matter at a rate of 196 g C m⁻² yr⁻¹ with a CO₂ and CH₄ production ratio of 1 : 1.2. We normalized this flux to sediment deposition that occurs on only 60% of the lake bottom (Schelske unpubl. data) and obtained a production rate of 4.54 mol m⁻² yr⁻¹ of CO₂ and 5.33 mol m⁻² yr⁻¹ of CH₄. Transfer mechanisms for CO₂ and CH₄ in water are very different. For CO₂, only a small fraction leaves the sediment as bubbles because CO₂ is more soluble in water than is CH₄ (Chanton et al. 1989). Thus, CO₂ transfer out of sediment is mostly diffusive. For CH₄, Chanton and Martens (1988) investigated two organic-rich freshwater sediments and found that CH₄ transfer was 50% via ebullition and 50% via diffusion. We do not have data for the CH₄ oxidation rate in Lake Apopka from previous and current studies. Assuming that the ebullitive fraction escapes to atmosphere (Martens and Klump 1980) and that the CH₄ that diffuses to the water column gets totally oxidized, the CH₄ oxidation rate in Lake Apopka would be 50% of the CH₄ production or 2.66 mol m⁻² yr⁻¹. Other studies reported various CH₄ oxidation rates in shallow productive waters ranging from 36% in Lake 227 (Rudd and Hamilton 1978) to 62% in Lake Kasumigaura of Japan (Nakamura et al. 1999).

Input of DIC from Apopka Spring was calculated from an average concentration (14 mmol L⁻¹) of three samples from the spring measured on 24 June 1994 and an inflow of 2.6×10^7 m³ yr⁻¹ (SJRWMD). This yields a DIC flux of 0.25 mol m⁻² yr⁻¹, which is small compared to other input terms. The loading of DIC and TOC from the muck farms was calculated from average concentrations of 6.25 and 3.83 mmol L⁻¹ ($n = 143$ and 84 samples), respectively, and an annual pumping amount of 6.2×10^7 m³. This yields DIC and TOC input of 3.13 and 1.91 mol m⁻² yr⁻¹. The total loading to the water column is 21.48 mol m⁻² yr⁻¹.

Losses of DIC from the water column include sedimentation of organic carbon produced by phytoplankton and outflow. Schelske et al. (2000) reported a net sedimentation rate of 8.33 mol m⁻² yr⁻¹ for Lake Apopka. Since DIC and CH₄ production (9.87 mol m⁻² yr⁻¹ in total) is derived from sediment decomposition, this amount is added to the net sedi-

mentation rate, resulting in a gross sedimentation of 18.20 mol m⁻² yr⁻¹. The loss of DIC from Beauclair Canal was calculated as 1.14 mol m⁻² yr⁻¹ from an average concentration of 2.08 mmol L⁻¹ taken from eight monthly measurements at the central lake station and an average outflow of 6.8×10^7 m³ yr⁻¹ (SJRWMD). The loss of POC and DOC from Beauclair Canal was calculated as 1.17 and 1.27 mol m⁻² yr⁻¹, respectively, taken from the average water-column POC and DOC concentrations (2.35 and 2.54 mmol L⁻¹) and the annual outflow. The total output (21.78 mol m⁻² yr⁻¹) is in good balance with the input (Table 4).

The isotopic composition for each input and output term was measured directly, was estimated, or was taken from literature (Table 4). The depletion of $\delta^{13}\text{C}$ for atmospheric CO₂ dissolved in the lake water is estimated as -11‰ on the basis of a relationship between stagnant layer thickness and pH (Herczeg and Fairbanks 1987). The values of $\delta^{13}\text{C}$ of 20‰ and -42‰ from the sediment core are used to represent the isotopic compositions as the result of the methanogenesis of CO₂ and CH₄, respectively. The average $\delta^{13}\text{C}_{\text{POC}}$ of -13‰ determined from samples collected at the central lake station (Gu and Schelske 1996) is used to represent the $\delta^{13}\text{C}$ of outflow POC and SOC. This value is also used to represent the $\delta^{13}\text{C}_{\text{DOC}}$ that was not measured during this study and is typically similar to that of its dominant source (Quay et al. 1986; Gu et al. 1994). The $\delta^{13}\text{C}_{\text{DIC}}$ from Apopka Spring determined from three samples on 24 June 1994 was -9‰. The $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{TOC}}$ from the drainage water due to muck farm pumping are assumed to be -27‰, a value resembling the isotopic composition of terrestrial carbon (Gu et al. 1996). The weighted-average $\delta^{13}\text{C}_{\text{DIC}}$ from all the inputs to the water column and the $\delta^{13}\text{C}_{\text{POC}}$ from all the outputs are estimated as -12‰ and -13‰, respectively.

Discussion

Extreme ¹³C enrichments have been found in sediment pore water from several freshwater systems (Oana and Deevy 1960; Stiller and Magaritz 1974). However, evidence for

corresponding ^{13}C enrichments was either not collected or not found from the water column of these lakes. For example, a high $\delta^{13}\text{C}_{\text{DIC}}$ (10–17.8‰) was recorded for the pore water of Lake Kinneret, Israel, but the $\delta^{13}\text{C}_{\text{DIC}}$ from the water column was depleted, ranging from –9‰ to –4‰ (Zohary et al. 1994). The only ^{13}C enrichment comparable to the water column in Lake Apopka is for evaporating brines from the Dead Sea (7.9–16.5‰), which is attributed to the preferential loss of $^{12}\text{CO}_2$ to the atmosphere during evaporation at low pH (Stiller et al. 1985).

Two mechanisms have directly contributed to the extreme ^{13}C enrichment in Lake Apopka. The first is isotopic fractionation from methanogenesis in the sediments that provides a supply of isotopically heavy DIC to the water column. This form of anaerobic respiration produces ^{13}C -rich CO_2 and ^{13}C -poor CH_4 . The second is isotopic fractionation from phytoplankton photosynthesis. During carbon fixation, phytoplankton preferentially assimilate ^{12}C , leaving the DIC pool enriched with ^{13}C (Quay et al. 1986; Hollander and McKenzie 1991). Because of isotopic fractionation, both processes produce compounds that are isotopically depleted in ^{13}C . Key to the production of ^{13}C -enriched DIC in the lake water column is that the ^{13}C -depleted carbon is lost from the lake water column by CH_4 ebullition and the burial of ^{13}C -depleted organic matter in the sediments.

Several lines of evidence indicate that ^{13}C -rich pore-water DIC produced by methanogenesis contributes to the ^{13}C enrichment of the water column. The decrease in DIC concentration in the upper 5 cm of sediments provides a concentration gradient for the DIC released into the water column, where concentrations were appreciably lower (Table 2). A gradient in $\delta^{13}\text{C}_{\text{DIC}}$ at the sediment–water-column interface was also apparent. Based on the results from Gale and Reddy (1994), we estimated a flux of $4.54 \text{ mol m}^{-2} \text{ yr}^{-1}$ of CO_2 with a $\delta^{13}\text{C}$ of approximately 20‰ to the overlying water. This accounts for 21% of the DIC loading to the water column (Table 4). Since the lake has low CO_2 partial pressure, high pH, and strong buffering capacity, the isotopically heavy CO_2 from the sediments must have been incorporated into the water-column DIC pool. Although the weighted $\delta^{13}\text{C}_{\text{DIC}}$ from external loading and sediment respiration is negative, the DIC pool would have been considerably more depleted in ^{13}C had the system not received isotopically heavy carbon from methanogenesis. Wachniew and Rózański (1997) suggested that an increased supply of methanogenesis-derived CO_2 ($\delta^{13}\text{C} = \sim 15\text{‰}$) was responsible for the elevated epilimnetic $\delta^{13}\text{C}_{\text{DIC}}$ in a Polish lake.

Another direct mechanism for the observed ^{13}C enrichment is photosynthetic isotope fractionation by phytoplankton. The $\delta^{13}\text{C}_{\text{POC}}$ (–13‰) is more negative than the weighted $\delta^{13}\text{C}_{\text{DIC}}$ (–12‰) to the water column. Schelske et al. (2003) reported an average areal net production of 0.9 g or $0.07 \text{ mol C m}^{-2} \text{ d}^{-1}$ for Lake Apopka in 1990 and 1991. The removal of lighter isotopes from the DIC pool at high rates and the sedimentation of isotopically light organic matter lead to significant ^{13}C enrichment. Carbon isotopic enrichment in the water-column DIC pool is also supported by another study in Lake Apopka (Gu and Schelske 1996) and studies in other aquatic systems (Fogel et al. 1992; Oren et al. 1995). The removal of water-column photosynthetic pro-

duction contributes indirectly to the ^{13}C enrichment of the water-column DIC pool. This is accomplished mainly in two ways, i.e., sedimentation and outflow. The gross sedimentation rate ($18.20 \text{ mol C m}^{-2} \text{ yr}^{-1}$) in Lake Apopka represents 84% of the DIC removal from the water column. Although more than half of the sediment organic carbon is recycled back to the water column as DIC and CH_4 , a significant portion ($8.33 \text{ mol C m}^{-2} \text{ yr}^{-1}$) of this flux has been buried in the sediments (Schelske et al. 2000). The upper layer of sediment represents the recent deposition of water-column production since the lake shifted from macrophyte to phytoplankton dominance in the late 1940s. The removal of organic carbon (both POC and DOC) by outflow, although less significant than sedimentation, accounts for 10% of the output.

Because Lake Apopka is shallow and polymictic, the CH_4 and CO_2 released during methanogenesis may be affected by wind-induced resuspension of sediments that occurs on temporal scales of days or weeks (Carrick et al. 1993). Smith and Lewis (1992) found that CH_4 evasion rather than oxidation accounted for most of dissolved CH_4 loss from a shallow lake during spring turnover. Chanton et al. (1989) indicated that tide-induced ebullition from an estuary sediment was as important as molecular diffusion in CH_4 emission. Ebullition of isotopically light CH_4 from Lake Apopka, therefore, is likely an important pathway leading indirectly to high ^{13}C enrichment in the DIC pool. Based on Gale and Reddy's work (1994), we estimated a CH_4 flux of $5.33 \text{ mol m}^{-2} \text{ yr}^{-1}$ out of the sediments and assumed that approximately 50% ($2.66 \text{ mol m}^{-2} \text{ yr}^{-1}$) of the CH_4 escaped to the atmosphere due to the low CH_4 solubility in water and frequent wind mixing of the water column in this shallow lake. In an isotopic study of a Polish lake, Wachniew and Rózański (1997) indicated that CH_4 evasion was partially responsible for the enriched $\delta^{13}\text{C}_{\text{DIC}}$ in the epilimnion relative to external sources.

Limited input of isotopically light carbon from terrestrial sources may also contribute to the water-column ^{13}C enrichment. The loading of DIC to the Lake Apopka water column is dominated by atmospheric invasion, which is estimated at 42%, followed by the muck farms and anaerobic respiration (Table 4). The flux-weighted $\delta^{13}\text{C}_{\text{DIC}}$ (approximately –12‰) from the inputs is considerably less negative than those from other lacustrine systems dominated by terrestrial carbon. For example, Rau (1978) reported extreme ^{13}C depletion (approximately –45‰) in planktonic organic matter in an alpine lake. Using an isotopic fractionation of –20‰ for carbon fixation, the $\delta^{13}\text{C}_{\text{DIC}}$ in this lake could be as low as –25‰, which is very close to the average $\delta^{13}\text{C}$ of terrestrial plants. Gu et al. (1999) reported an average $\delta^{13}\text{C}$ of DIC and a zooplankton species of approximately –16‰ and –38‰, respectively, for a subarctic lake. The DIC pools in both lakes were overwhelmingly dominated by the isotopically light carbon from forested watersheds.

Our mass balance indicates that approximately $21 \text{ mol m}^{-2} \text{ yr}^{-1}$ of DIC enters and leaves the lake's water column (Table 4). Atmospheric invasion and sedimentation are the most important DIC source and sink, contributing 42% and 38% to the total input and output, respectively, in Lake Apopka. The weighted average of $\delta^{13}\text{C}$ for the total input

and output is also in balance. The relative importance of each input and output term to the water-column $\delta^{13}\text{C}_{\text{DIC}}$ may be evaluated by the product of each term defined as a mass flux multiplied by its $\delta^{13}\text{C}$ value (Table 4). The product reflects the weight of each flux term in the isotopic balance of all the inputs and outputs. Among the input terms, CH_4 oxidation has the largest negative product and hence is the most influencing factor in the isotopic composition of the DIC pool, followed by atmospheric invasion and anaerobic respiration. Among the output terms, sedimentation is the most important factor. Although the ^{13}C enrichment in the water column is not affected directly by CH_4 ebullition, the escape of CH_4 to the atmosphere can prevent a significant portion of the CH_4 extremely depleted in ^{13}C from recycling back to the water-column DIC pool, which should have a profound effect on the isotopic balance of the lake. Finally, we need to point out that our model is very sensitive to small changes in the isotopic values or flux. There are several sources of errors associated with major input and output terms, particularly the isotopic and flux values for atmospheric CO_2 and the recycled carbon from CH_4 oxidation, which are either estimated or taken from literature. Nevertheless, this model successfully identifies the critical processes controlling the mass and isotopic balances in this lake.

In summary, the combination of several lake characteristics, including low terrestrial loading, shallow water depth, high sedimentation, and intensive methanogenesis in organic-rich sediments followed by ebullition and frequent wind mixing of the water column, leads to the observed ^{13}C enrichment in the water-column DIC pool. The weighted carbon isotopic composition from external inputs indicates the lack of contribution dominated by terrestrial carbon. Production of isotopically heavy CO_2 by methanogenesis and its transfer to the water column and isotopic fractionation of the water-column DIC pool by photosynthesis are processes that provide enriched $\delta^{13}\text{C}$ values. Removal of CH_4 by ebullition and organic matter by sedimentation and outflow are the key in-lake processes associated indirectly with isotopic enrichment.

References

- BASTVIKEN, D., J. EJLERTSSON, I. SUNDH, AND L. TRANVIK. 2003. Methane as a source of carbon and energy for lake pelagic food web. *Ecology* **84**: 969–981.
- CARRICK, H., F. J. ALDRIDGE, AND C. L. SCHELSKE. 1993. Wind influences phytoplankton biomass and composition in a shallow, productive lake. *Limnol. Oceanogr.* **38**: 1179–1192.
- CHANTON, J. P., AND C. S. MARTENS. 1988. Seasonal variations in ebullitive flux and carbon isotopic composition of methane in a tidal freshwater estuary. *Global Biogeochem. Cycles* **2**: 289–298.
- , AND C. A. KELLEY. 1989. Gas transport from methane-saturated, tidal freshwater and wetland sediments. *Limnol. Oceanogr.* **34**: 807–819.
- EMERSON, S. 1975. Chemically enhanced CO_2 gas exchange in a eutrophic lake: A general model. *Limnol. Oceanogr.* **20**: 743–753.
- FISHER, M. M., M. BRENNER, AND K. R. REDDY. 1992. A simple, inexpensive piston corer for collecting undisturbed sediment/water interface profiles. *J. Paleolimnol.* **7**: 157–161.
- FOGEL, M. L., L. A. CIFUENTES, D. J. VELINSKY, AND J. H. SHARP. 1992. Relationship of carbon availability in estuarine phytoplankton to isotopic composition. *Mar. Ecol. Prog. Ser.* **82**: 291–300.
- GALE, P. M., AND K. R. REDDY. 1994. Carbon flux between sediment and water column of a shallow, subtropical, hypereutrophic lake. *J. Environ. Qual.* **23**: 965–972.
- GAMES, L. M., AND J. M. HAYES. 1976. On the mechanisms of CO_2 and CH_4 production in natural anaerobic environments, p. 51–73. *In* J. O. Nriagu [ed.], *Environmental biogeochemistry*. Science.
- GU, B., V. ALEXANDER, AND D. M. SCHELL. 1999. Seasonal and interannual variability of plankton carbon isotope ratios in a subarctic lake. *Freshwater Biol.* **42**: 417–426.
- , D. M. SCHELL, AND V. ALEXANDER. 1994. Stable isotopic analysis of the plankton food web in a subarctic lake. *Can. J. Fish. Aquat. Sci.* **51**: 1338–1344.
- , AND C. L. SCHELSKE. 1996. Temporal and spatial variations in phytoplankton carbon isotopes in a polymictic subtropical lake. *J. Plankton Res.* **18**: 2081–2092.
- , ———, AND M. V. HOYER. 1996. Stable isotopes of carbon and nitrogen as indicators of diet and trophic structure of fish in a shallow hypereutrophic lake. *J. Fish Biol.* **49**: 1233–1243.
- HERCZEG, A. L., AND R. G. FAIRBANKS. 1987. Anomalous carbon isotope fractionation between atmospheric CO_2 and dissolved inorganic carbon induced by intensive photosynthesis. *Geochim. Cosmochim. Acta* **51**: 895–899.
- HOLLANDER, D. J., AND J. A. MCKENZIE. 1991. CO_2 control on carbon-isotope fractionation during aqueous photosynthesis: A paleo- pCO_2 barometer. *Geology* **19**: 929–932.
- KLING, G. W., G. W. KIPPHUT, AND M. C. MILLER. 1992. The flux of CO_2 and CH_4 from lakes and rivers in arctic Alaska. *Hydrobiologia* **240**: 23–36.
- MARTENS, C. S., AND J. V. KLUMP. 1980. Sediment–water chemical exchange in the coastal zone traced by in situ Radon-222 flux measurements. *Science* **208**: 285–288.
- NAKAMURA, T., Y. NOJIRI, M. UTSUMI, T. NOZAWA, AND A. OTSUKI. 1999. Methane emission to the atmosphere and cycling in a shallow eutrophic lake. *Arch. Hydrobiol.* **144**: 383–407.
- NISSENBAUM, A., B. J. PRESLEY, AND I. R. KAPLAN. 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia. I. Chemical and isotopic changes in major components of interstitial water. *Geochim. Cosmochim. Acta* **36**: 1007–1027.
- OANA, S., AND E. S. DEEVEY. 1960. Carbon-13 in lake waters and its possible bearing on paleolimnology. *Am. J. Sci.* **258A**: 253–272.
- OREN, A., P. GUREVICH, D. A. ANATI, E. BARKAN, AND B. LUZ. 1995. A bloom of *Dunaliella parva* in the Dead Sea in 1992: Biological and biogeochemical aspects. *Hydrobiologia* **297**: 173–185.
- PETERSON, B. J., AND B. FRY. 1987. Stable isotopes in ecosystem studies. *Annu. Rev. Ecol. Syst.* **18**: 293–320.
- 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.
- RAU, G. 1978. Carbon-13 depletion in a subalpine lake: Carbon flow implications. *Science* **201**: 901–902.
- RUDD, J. W. M., AND R. D. HAMILTON. 1978. Methane cycling in a eutrophic shield lake and its effects on whole lake metabolism. *Limnol. Oceanogr.* **23**: 337–348.
- SCHELSKE, C. L., F. J. ALDRIDGE, H. J. CARRICK, AND M. V. COVENEY. 2003. Phytoplankton community photosynthesis and primary production in a hypereutrophic lake, Lake Apopka, Florida. *Arch. Hydrobiol.* **157**: 145–172.
- , AND P. BREZONIK. 1992. Can Lake Apopka be restored?,

- p. 393–398. *In* Restoration of aquatic ecosystems: Science, technology, and public policy. National Academy Press.
- , M. F. COVENEY, F. J. ALDRIDGE, W. F. KENNEY, AND J. E. CABLE. 2000. Wind or nutrients: Historic development of hypereutrophy in Lake Apopka, Florida. *Arch. Hydrobiol. Spec. Issue Adv. Limnol.* **55**: 543–563.
- , AND D. A. HODELL. 1991. Recent changes in productivity and climate in Lake Ontario detected by isotopic analysis of sediments. *Limnol. Oceanogr.* **36**: 961–975.
- SCHINDLER, D. W., G. J. BRUNSKILL, S. EMERSON, S. BROECKER, AND T. H. PENG. 1972. Atmospheric carbon dioxide, its role in maintaining phytoplankton standing crop. *Science* **177**: 1192–1194.
- SMITH, L. K., AND W. M. LEWIS, JR. 1992. Seasonality of methane emissions from five lakes and associated wetlands of the Colorado Rockies. *Global Biogeochem. Cycles* **6**: 323–338.
- SOCKI, R. A., H. R. KARLSSON, AND E. K. GIBSON. 1992. Extraction technique for the determination of oxygen-18 in water using preevacuated glass vials. *Anal. Chem.* **64**: 829–831.
- STILLER, M., AND M. MAGARITZ. 1974. Carbon-13 enriched carbonate in interstitial waters of Lake Kinneret sediments. *Limnol. Oceanogr.* **19**: 849–853.
- , J. S. ROUNICK, AND S. SHASHA. 1985. Extreme carbon-isotope enrichments in evaporating brines. *Nature* **316**: 434–443.
- WACHNIEW, P., AND K. RÓŻAŃSKI. 1997. Carbon budget of a mid-latitude, groundwater-controlled lake: Isotopic evidence for the importance of dissolved inorganic carbon recycling. *Geochim. Cosmochim. Acta* **61**: 2453–2465.
- ZOHARY, T., J. EREZ, M. GOPHEN, I. BERMAN-FRANK, AND M. STILLER. 1994. Seasonality of stable carbon isotopes within the pelagic food web of Lake Kinneret. *Limnol. Oceanogr.* **39**: 1030–1043.

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