Biogeochemistry 4: 231–263 (1987)

A stable carbon isotope study of dissolved inorganic carbon cycling in a softwater lake

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Key words: Lake carbon cycle, stable carbon isotopes, dissolved inorganic carbon, gas exchange, net photosynthesis

Abstract. The dissolved inorganic carbon (DIC) cycle in a softwater lake was studied using natural variations of the stable isotopes of carbon, ^{12}C and ^{13}C. During summer stratification there was a progressive decrease in epilimnion DIC concentration with a concomitant increase in $\delta^{13}C_{DIC}$ due to preferential uptake of ^{12}C by phytoplankton and a change in the dominant CO_2 source from inflow and *in situ* oxidation to invasion from the atmosphere. There was an increase in hypolimnion DIC concentration throughout summer with a concomitant general decrease in $\delta^{13}C_{DIC}$ from oxidation of the isotopically light particulate organic carbon that sank down through the thermocline from the epilimnion.

Mass balance calculations of $DI^{12}C$ and $DI^{13}C$ in the epilimnion for the summer (June 23–September 25) yield a mean rate of net conversion of DIC to organic carbon (C_{org}) of 430 ± 150 moles d^{-1} (6.5 ± 1.8 mmoles $m^{-2} d^{-1}$. Net CO_2 invasion from the atmosphere was 420 ± 120 moles d^{-1} (6.2 ± 1.8 m moles $m^{-2} d^{-1}$) with an exchange coefficient of 0.6 ± 0.3 m d^{-1}. These results imply that at least for the summer months the phytoplankton obtained about 90% of their carbon from atmosphere CO_2. About 50% of CO_2 invasion and conversion to C_{org} for the summer occurred during a two week interval in mid-summer.

DIC concentration increased in the hypolimnion at a rate of 350 ± 70 moles DIC d^{-1} during summer stratification. The amount of DIC added to the hypolimnion was equivalent to $75 \pm 20\%$ of net conversion of DIC to C_{org} in the euphotic zone over spring and summer implying rapid degradation of POC in the hypolimnion. The $\delta^{13}C$ of DIC added to the deep water (−22‰) was too heavy to have been derived from oxidation of particulate organic carbon alone. About 20% of the added DIC must have diffused from hypolimnetic sediments where relatively heavy CO_2 (−7‰) was produced by a combination of POC oxidation and as a by-product of methanogenesis.

Introduction

The biogeochemical cycle of carbon in freshwater lakes involves interactions between the atmosphere, dissolved CO_2, biota and sediments; net import or export of carbon occurs via gas exchange, input and output via streams plus runoff and permanent burial of organic carbon in the sediments. Dissolved

Table 1. Carbon isotope fractionation in natural waters. The value of ε is defined as $\varepsilon = (\alpha - 1)\cdot 1000$ where α is the fractionation factor for the given reaction or process. (e.g. $\alpha(CO_2(aq) - CO_2(g)) = (^{13}C/^{12}C)_{CO_{2(g)}}/(^{13}C/^{12}C)_{CO_{2(aq)}})$.

	ε(‰)	ref.
$CO_2(aq) - CO_2(g)$	$+1.1$	1
$CO_2(aq) - HCO_3^-$	$+9$ to $+12$ (25 to 0°C)	2
$CO_2(aq) + OH^- = HCO_3^-$	~ -15	3
$CO_2(aq) \rightarrow C_{org}$	0 to > -20‰ $P_{CO_2} < 10^{-5}$ atm to $P_{CO_2} > 10^{-3.5}$ atm	4
$C_{org} \rightarrow CO_2(aq)$	~ 0	5
$2CH_2O \rightarrow CH_4 + CO_2$ $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-15 to -100	6
$CH_4 + O_2 \rightarrow CO_2$	-5 to -30	7

1. $\varepsilon_{CO_2}(aq)$–$CO_2(g) = -0.373\cdot 10^3/T + 0.19$‰ (Mook et al. 1974)
2. $\varepsilon_{CO_2}(aq)$–$HCO_3^- = -9.866\cdot 10^3/T + 24.12$‰ (Mook et al. 1974)
3. Baertschi (1952); Craig (1953)
4. Photosynthetic fixation by plankton or blue-green bacteria — Craig (1953); Deuser et al. (1968); Degens et al. (1968); Calder & Parker (1973); Wong & Sackett (1978)
5. Aerobic respiration — Degens (1969); Parker (1973)
6. Fractionation between CH_4 and CO_2 by Methanogenesis via acetate fermentation pathway or reduction of CO_2 by H_2 (Rosenfeld & Silverman 1959; Meinschein et al. 1974; Games et al. 1978; La Zerte 1981; Woltemate et al. 1984)
7. Methane oxidation (Barker & Fritz 1981; Coleman et al. 1981)

inorganic carbon (DIC) may be transferred to and from the organic carbon pools (particulate and dissolved — POC and DOC) through photosynthesis and respiration and degradation within the water column and sediments. A better understanding of these interactions may be possible by utilizing the natural variations of the two stable isotopes of carbon (^{12}C and ^{13}C) in the various carbon pools.

The stable isotopes of carbon in freshwater systems are fractionated by such processes as gas exchange, photosynthesis, methanogenesis and methane oxidation. As may be seen in the compilation of published data in Table 1, the fractionation factors for the various processes are dependent on temperature and P_{CO_2}. By measuring the time rate of change of $DI^{12}C$, $DI^{13}C$ and the partial pressure of carbon dioxide (P_{CO2}) and the isotopic composition of particulate organic carbon ($\delta^{13}C_{POC}$), a mass balance of carbon for the epilimnion and hypolimnion could be constructed from which estimates of the net CO_2 flux from the surface water to the atmosphere and the net conversion of inorganic carbon to organic carbon could be made. For the hypolimnion, the mass balance gives a first order estimate of the DIC produced by rapid breakdown of organic carbon at or near the sediment-water interface plus that derived by diffusion from sediment porewaters. Quay et al. (1986) applied the ^{12}C-^{13}C mass balance approach to an investigation of the carbon cycle in Lake Washington (ΣAlk $\approx$ 700 μeq/l) and a similar approach is used here for Mohonk Lake (ΣAlk $\approx$ 130 μeq/l).

A better knowledge of carbon cycling in lakes is important for many reasons. The first defense mechanism of lake water from acidification is the dissolved bicarbonate and carbonate ion which usually comprise the largest component of the alkalinity balance. A better understanding is needed of all of the important transformations of carbon and nutrients in order to predict the impact of human activities on lake ecosystems. For isotopic studies bearing on paleolimnology, one must have a good knowledge of the lake carbon cycle and early diagenesis of organic carbon in the sediments and the behaviour of carbon isotopes in modern systems in order to apply them to sediments of Quaternary age or older. The information in this paper will also be important to those studying carbon isotopes for lake productivity, assessment and management.

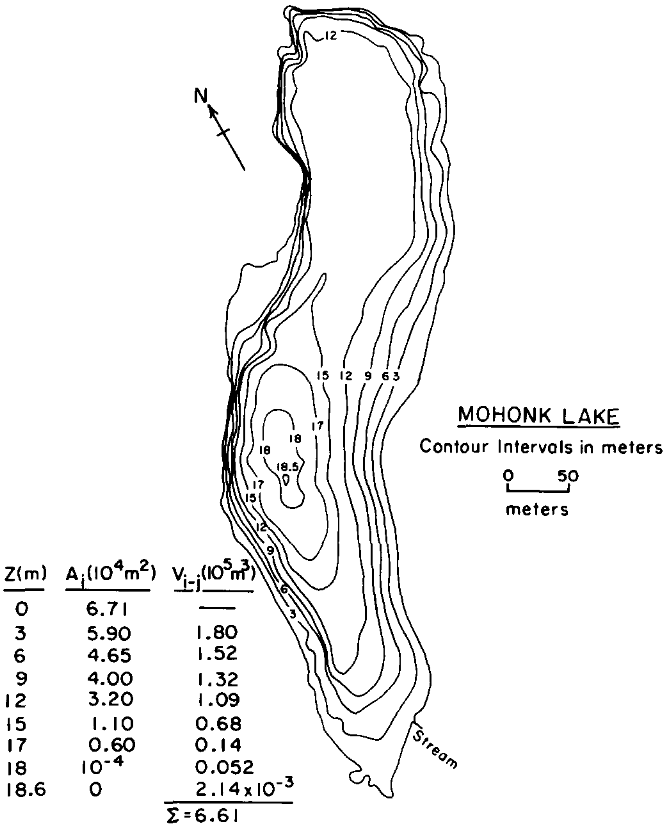
Previous work

A number of investigators have utilized the stable isotope geochemistry of carbon to delineate various biogeochemical processes in lacustrine systems. Some of the earliest limnological work using ^{12}C and ^{13}C as tracers was done by Oana & Deevey (1960) and Deevey & Stuiver (1964). They attempted a mass balance for the hypolimnion of a lake using ^{12}C, ^{13}C and ^{14}C to determine the relative importance of DIC fluxes from particulate organic carbon degradation (δ^{13}C = −20‰), pore water flux (δ^{13}C = −5‰) and groundwater input (δ^{13}C = 0‰, δ^{14}C = −1000‰). Weiler & Nriagu (1978) and McKenzie (1982) documented an increase in δ^{13}C in the epilimnion of hardwater lakes during the summer and interpreted this to the preferential photosynthetic fixation of ^{12}C by phytoplankton. There was a concomitant decrease of the ^{13}C/^{12}C ratio in the hypolimnion due to degradation and oxidation of this organic matter in the deep waters. δ^{13}C studies in an oligotrophic, softwater lake (Rau 1978) revealed exceptionally ^{13}C depleted carbon in both the DIC and POC pools. Rau postulated that the major DIC source was recycled organic matter presumably derived from the terrestrial drainage basin and that gas exchange was a trival source of CO$_2$ for the phytoplankton or zooplankton. A thorough survey of the δ^{13}C distribution in several New Zealand lakes by McCabe (1985) showed extreme variations in the carbon isotope ratio of DIC in some dystrophic and eutrophic lakes. This study builds on the above investigations, and the work of Quay et al. (1986) on Lake Washington, by using stable carbon isotopes as a means of quantifying DIC fluxes in a lake of low DIC concentration.

Table 2. Mohonk Lake vital statistics (after Rubin 1980).

Latitude	41°46′N
Longitude	74°09′W
Elevation	380 m
Maximum length	646 m
Maximum width	163 m
Total volume (at 0 on surface marker)	$6.6 \times 10^5\,\mathrm{m}^3$
Surface area	$6.8 \times 10^4\,\mathrm{m}^2$
Mean depth	9.7 m
Maximum depth	18.6 m
Drainage area (excluding lake surface)	$17 \times 10^4\,\mathrm{m}^2$
Mean precipitation during ice-free season[1]	100 cm
Evaporation rate[1]	0.7 m/yr

[1] D. Smiley (unpublished data)



Z(m)	$A_i(10^4 m^2)$	$V_{i-j}(10^5 m^3)$
0	6.71	—
3	5.90	1.80
6	4.65	1.52
9	4.00	1.32
12	3.20	1.09
15	1.10	0.68
17	0.60	0.14
18	10^{-4}	0.052
18.6	0	2.14×10^{-3}
		$\Sigma = 6.61$

Fig. 1. Morphometry of Mohonk Lake (adapted from unpublished data by D. Smiley & J. Parker). Nominal volume and surface area at selected depths adapted from Hellerman (1965).

Lake description

Mohonk Lake is a small, deep, glacially carved basin situated at 380 m elevation in the Shawangunk Mountains about 150 km north of New York City. A summary of physical parameters of the lake are given in Table 2. The lake is elongate with a maximum depth of 18.6 m, mean depth of 9.7 m with steep sides in the epilimnion region (see Fig. 1). Water residence time calculated from evaporation and outflow measurements (D. Smiley, unpublished data) is on the order of 4 years. The bedrock of the terrestrial drainage basin is about 70% quartzite-conglomerate and 30% shale (1-7% $CaCO_3$) and is covered by thin soil. Inflow to the lake is mostly by direct precipitation on the surface and runoff from the terrestrial drainage basin. Two ephemeral streams near the southern end of the lake supply some water (mostly in the springtime) and carry a large amount of dissolved inorganic and organic carbon. Water loss is by controlled outflow at the northern end of the lake and evaporation. The evaporative loss is estimated at 0.7 m/yr (D. Smiley, unpublished data). Subsurface seepage is considered to be minimal (Egemeier 1981).

The lake water is characterized by low conductivity, low alkalinity ($\sim 130\,\mu$eq/l), circumneutral pH and is undersaturated with respect to $CaCO_3$ by at least two orders of magnitude. The low total dissolved solids content is due to the chemically resistant nature of the bedrock which provides little in the way of base cations but the small amount of calcium carbonate (1–10%) in the shale within the drainage basin presumably acts as a buffer to the effects of the local acidic precipitation (pH $\approx$ 4.2 — D. Smiley, unpublished data).

The ice-free season for 1984 was from mid-April to the end of December and the lake was thermally well stratified from May to October (Fig. 2). As documented below, overturn events occurred both in the spring (April) and autumn (November). Three algal blooms were inferred from Secchi disk readings (Fig. 3), the most intense and prolonged in mid-summer at which time calculated mid-morning pH's exceeded 9 due to depression of the P_{CO_2} of surface water by rapid phytoplankton growth.

Sampling and analytical methods

Water samples were collected in a 1.5 l Niskin bottle from a pier near the northern end of the lake where the water column was 13 m deep. Samples for DIC and $\delta^{13}C_{DIC}$ analysis were transferred to 250 ml pyrex bottles fitted with ground glass stoppers, 1-2 mls of saturated $HgCl_2$ were added and they were stored in a cool, dark container for transport to the laboratory. For P_{CO_2} samples, water was transferred to a 2.5 l container for pre-processing in

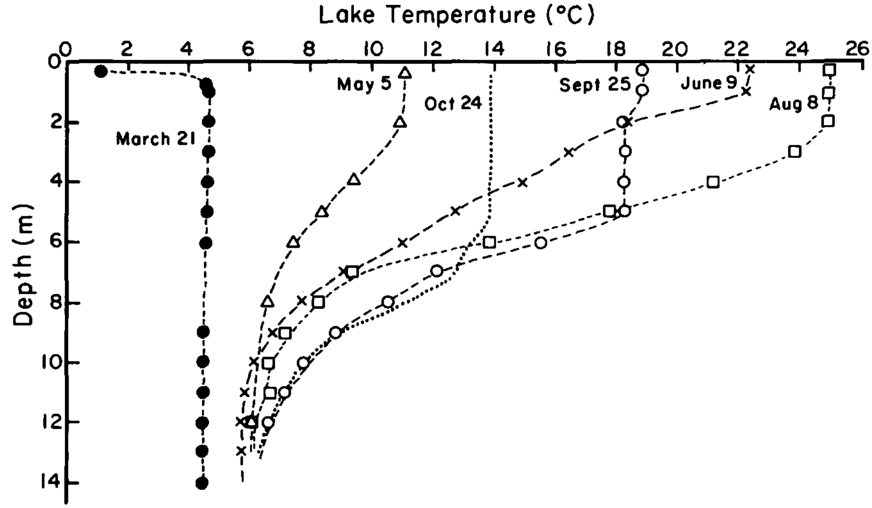


Fig. 2. Mohonk Lake temperature profiles throughout the 1984 ice-free season.

the field (see below). Particulate matter was collected by filtering about 1 l of water through a pre-combusted quartz fiber filter. The filters were dried and stored frozen prior to combustion for the POC analysis. Several gravity cores were taken in the lake prior to fall overturn for sediment pore waters. Within hours of collection, one to three cm core slices were centrifuged at ~7000 rpm in sealed containers and the pore water extracted with 5 ml Glasspak® syringes and refrigerated at 4°C. Extraction of CO_2 for pore water DIC and $\delta^{13}C$ analysis was done within 48 h of core collection.

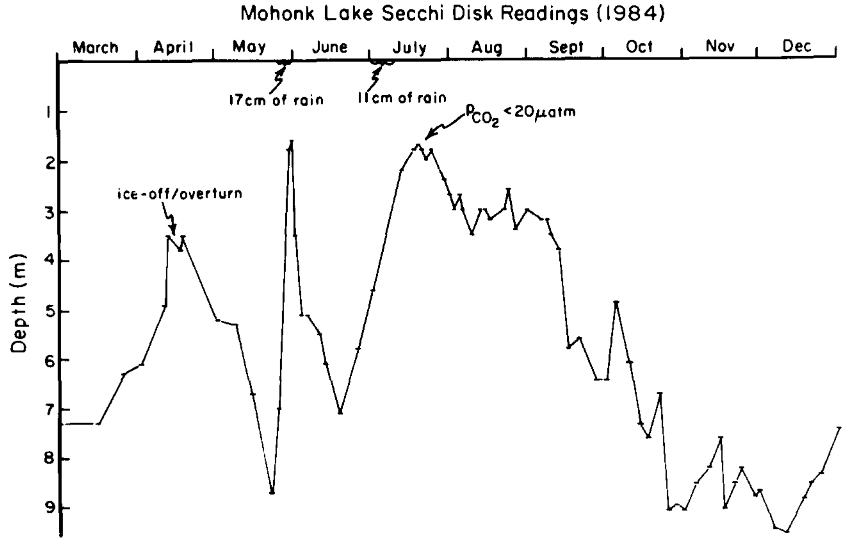


Fig. 3. Secchi disk readings at Mohonk Lake during 1984.

Dissolved inorganic carbon (DIC)

The concentration of DIC was determined by coulometry. This is an electrochemical technique based on the electrolytic generation of strong base used to titrate a weak acid formed by reaction of CO_2 and ethanolamine (see Johnson et al. 1985 for complete description). Briefly, 50 ml of water was injected through a septum into a glass column containing ~ 1 ml of CO_2-free concentrated phosphoric acid. The solution was bubbled with pure N_2 gas and the evolved CO_2 gas stripped (Coulometrics® Inc. Model 5030 scrubber) into an organic solution. The reaction between the CO_2 and the organic solution changes the optical properties (i.e. absorption of light) of the Coulometrics® cell solution which is detected by a photodiode. When there is excess CO_2 present, the solution becomes clear and the solution is automatically titrated. The current that passes through the cell in response to the added base is proportional to the CO_2 absorbed by the organic solution. The detector and the current meter was a Coulometrics® Inc. 5010 coulometer. DIC concentration in the water samples was calculated from the calibrated volume of the pipet and the amount of evolved CO_2 inferred from base addition. Replicate analyses for Mohonk Lake water were always within 1%.

Partial pressure of CO_2 (P_{CO2})

About 400 ml of ambient air was recirculated through 2.4 l of water in a closed system for 20 min. The equilibration was performed at a temperature held constant to within 0.2°C. A complete description of the equilibration procedure is presented in more detail in Herczeg & Hesslein (1984) and Herczeg (1985). An aliquot of the air was returned to the lab for CO_2 analysis on a Perkin-Elmer® Gas Chromatograph equipped with a ruthenium catalyst and a flame ionization detector. Analyses of P_{CO_2} from replicate equilibrations were precise to within 1%.

Total alkalinity (ΣAlk)

50 ml of lake water (or 1 ml of pore water) was titrated potentiometrically with 0.04 N HCl to a pH $\approx$ 3.5. The volumetric end point was calculated using the Gran extrapolation method (see Stumm & Morgan 1981) with replicate titrations agreeing to within 1%.

Hydrogen ion concentration (pH)

The pH values quoted here were calculated from the DIC and P_{CO_2} data according to the method of Herczeg & Hesslein (1984). Because of large random and systematic errors inherent in the electrode determination of pH in softwater lakes (see Herczeg & Hesslein 1984) the *in situ* hydrogen ion activity can only be determined with adequate precision (i.e. within 5%) using the method referred to above. Electrometric pH value in Mohonk Lake were always lower (by up to 0.5 pH units) than pH calculated from DIC and P_{CO_2}.

Isotopic composition of DIC ($\delta^{13}C_{DIC}$)

The $\delta^{13}C$ determination of DIC was made following the principles set out by Kroopnick (1974). 50–100 ml of water (or 5–10 ml of pore water) was injected into an evacuated glass reaction vessel containing ~2 ml of phosphoric acid. Helium gas was passed through a fritted disk at the base of the stripping column for about 10 min thereby removing CO_2 from the water. The He/CO_2 mixture passed through two water traps (dry ice/propanol) and the CO_2 trapped at liquid nitrogen temperature as the helium was pumped away. The CO_2 was transferred to a pre-combusted 6 mm diameter glass tube and then flame sealed.

The breakseal containing the CO_2 gas samples was cracked open in a closed, evacuated system and the CO_2 introduced into a MICROMASS® 903 mass spectrometer. The $^{13}C/^{12}C$ ratio of the CO_2 was determined relative to a secondary Bahama oolite standard and the appropriate ^{17}O correction applied to the mass 45 peak. The results are all expressed relative to the international Peedee belemnite standard according to the expression:

$$\delta^{13}C\ (\text{PBD}, ‰) = \left[\frac{(^{13}C/^{12}C)_{\text{sample}}}{(^{13}C/^{12}C)_{\text{standard}}} - 1\right] \times 1000$$

The precision for replicate CO_2 extraction and mass spectrometric determinations reported here was always better than ±0.2‰. The relatively large uncertainty was thought to be caused by decomposition of organic carbon during transport and storage of these poorly buffered waters.

Isotopic composition of particulate organic carbon ($\delta^{13}C_{POC}$)

Filters containing the particulate matter were cut into thin strips and placed in 0.94 cm diameter quartz tubes containing about 3 g of copper oxide and a small twist of silver wire. The tubes were evacuated overnight, sealed with an oxy/propane torch and then combusted in an oven at 800°C for two h to convert all the POC to CO_2 (Boutton et al. 1983). Oven temperature was

Table 3. Carbonate chemistry and carbon isotope data for Mohonk Lake waters during the ice-free season of 1984.

Date	Depth meters	Temp. °C	[DIC] μmol/l	[CO_2(aq)] μmol/l	P_{CO2} in situ μatm	pH	ΣAlk μeq/l	$\delta^{13}C_{DIC}$ (‰, PDB)	$\delta^{13}C_{POC}$ (‰, PDB)
April 9	1	5.3	213	66	1030	6.72	115		
	10	4.4	220	106	1612	6.41	141		
April 17	1	6.1	155	82	1335	6.33	128	−9.3	−30
	12	5.0	142	85	1312	6.21	128	−9.7	
April 26	1	7.2	156				150	−7.9	
	12	5.6	169				134	−12.3	
May 5	1	11.1	155	35	665	6.92	134	−5.8	−30
	6	7.2	181				132	−5.9	
	12	6.1	239	41	660	7.07	134	−10.4	
May 15	1	12.5	151				124	−4.6	
	12	6.9	261				133	−12.2	
June 5	1	18.9	131	9.5	173	7.49	122	−2.7	−31
	6	10.6	162					−4.6	
	12	7.8	280				141	−16.3	−30
June 15	1	22.2	142	18.1	487	7.49	129	−5.3	
	6	11.9	152				136	−2.6	
	12	8.3	285	71	1255		140	−15.2	
June 22	1	22.2	135	14.8	398	7.29	126	−5.0	−33
	6	11.1	159					−4.1	
	12	8.3	301	82	1455			−14.5	
July 3	1	23.3	128				123	−3.6	
	6	12.5	147				129	−2.8	
	12	8.6	357				133	−15.9	
July 16	1	25.6	106	0.3	12	9.52		−8.8	−18
	6	14.4	156				142	−3.2	−24
	12	7.8	388	83	1471	6.95		−17.0	
July 31	1	24.4	129					−7.8	
	6	14.7	171				138	−4.2	
	12	7.8	348				156	−18.0	
Aug 17	1	25.5	118	1.4	36	8.30		−2.9	
	6	14.2	186					−5.1	
	12	8.3	365	174	3092	6.42		−16.6	
Sept 25	1	21.1	141	14.4	370	7.33		−2.7	−26
	6	16.7	185	44	967	6.88		−6.3	
	12	8.9	556	209	3718	6.60		−19.2	
Oct 24	1	13.9	156	41	808	6.84	126	−3.9	
	6	13.6	164	57	1129	6.66	129	−3.5	
	12	7.2	504	277	4529	6.30	178	−18.3	

reduced gradually to room temperature to avoid cracking of the tubes. The amount of CO_2 evolved was measured manometrically (after removal of non-condensable gases) and the $\delta^{13}C$ of the CO_2 determined on the mass spectrometer as described above.

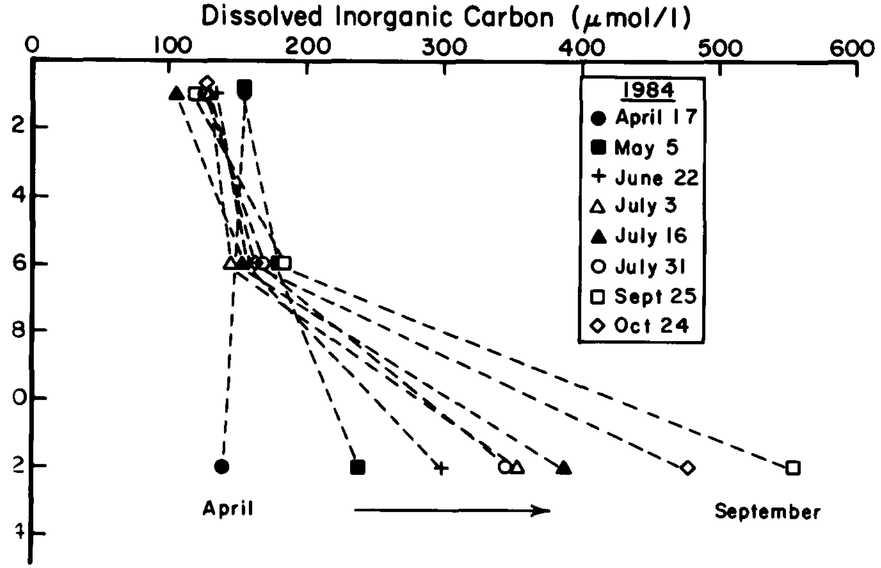


Fig. 4. DIC depth profiles at Mohonk Lake, 1984.

Results and discussion

Seasonal variation of DIC, P_{CO_2}, $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$

The DIC data presented in Table 3 and depicted as depth profiles in Fig. 4 show a DIC spring overturn (April 9) epilimnion concentration of 200 μmol/l that decreases to around 108 μmol/l in mid-summer then increases to a concentration greater than 200 μmol/l by the time of fall overturn in mid-November. The hypolimnion DIC concentration increases from a uniform value of 200 μmol/l recorded at spring overturn to greater than 500 μmol/l by early autumn. Similar trends have been observed by other workers (eg. McKenzie 1982; Quay et al. 1986) and result from CO_2 loss by gas evasion and uptake of CO_2 by phytoplankton in the surface water and the subsequent sinking and oxidation of the POC in the deeper waters. Because the lake is thermally stratified in the summer, the CO_2 released by POC oxidation in deep water cannot rapidly escape back into the epilimnion.

Variation in P_{CO_2} rather than in DIC provides the most sensitive indicator of biological processes associated with consumption and production of CO_2. The P_{CO_2} of the epilimnion is affected by gas exchange, photosynthesis and respiration, and entrainment of deep water. During early spring and late

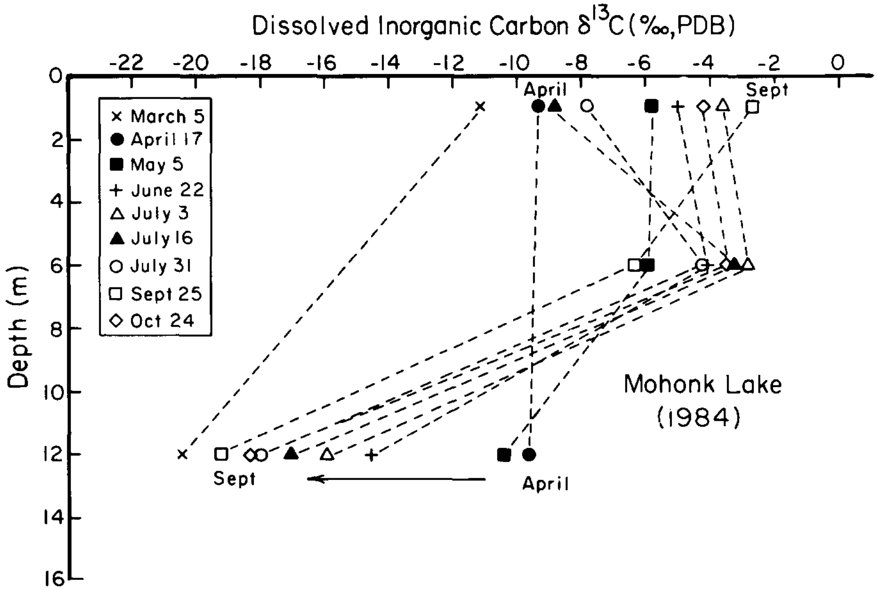


Fig. 5. $\delta^{13}C_{DIC}$ depth profiles at Mohonk Lake, 1984.

autumn the P_{CO_2} of surface water was supersaturated with respect to atmospheric P_{CO_2} due to entrainment of deep water where P_{CO_2}'s were greater than 4000 μatm (i.e. > 10 times the atmospheric concentration of ~ 340 μatm — Table 3). Photosynthesis during summer stratification depressed the P_{CO_2} to values below 20 μatm when CO_2 invasion could not keep up with CO_2 phytoplankton uptake. The hypolimnetic P_{CO_2} increased by more than a factor of five over the course of the summer due to *in situ* organic carbon degradation as well as a CO_2 flux from the sediment pore waters.

The $\delta^{13}C_{DIC}$ time trend for Mohonk Lake (Table 3, Fig. 5) is, in general, consistent with the interpretation of the processes controlling the DIC and P_{CO_2} values described above. In late winter and early spring the $\delta^{13}C$ values of the surface and deep water were relatively light (− 11.5 to − 9.3‰ – surface; − 21 to − 9.7‰ – deep) due to accumulation of CO_2 via oxidation of organic carbon under ice during winter. Additional "light" DIC was contributed by the large amount of DIC in runoff during spring melt which had a $\delta^{13}C$ of ~ − 16‰. Throughout spring and summer the DIC of surface water became progressively enriched in ^{13}C (i.e. acquired less negative $\delta^{13}C$ values) excluding two temporary reversals in this trend, due to preferential fixation of ^{12}C by the phytoplankton and to CO_2 gas exchange with the atmosphere. Some of the particulate matter produced in the euphotic zone ($\delta^{13}C$ = − 18 to − 32‰) rained through to the thermocline and hypolimnion and was oxidized to CO_2 causing the hypolimnion DIC to get progress-

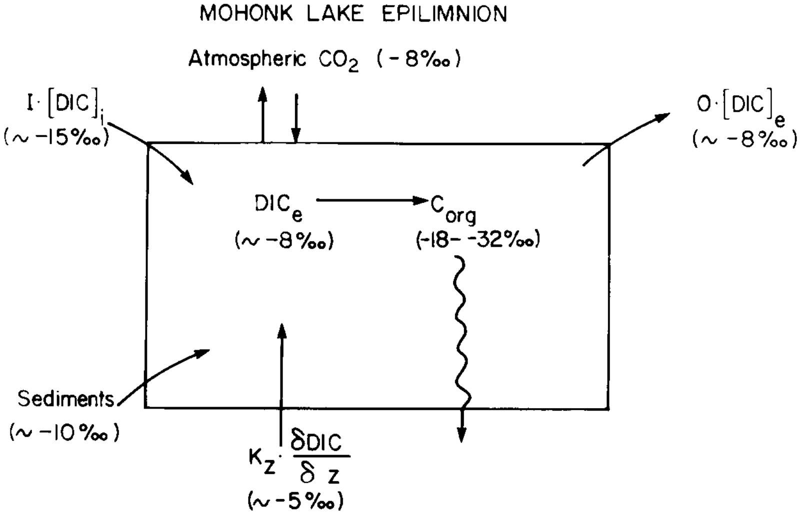


Fig. 6. Box model for $DI^{12}C$–$DI^{13}C$ mass-balance in the Mohonk Lake epilimnion. Fluxes are depicted as inflow (I.$[DIC]_i$), outflow (O.$[DIC]_e$), gas exchange, net photosynthesis (P), and diffusion of CO_2 from sediments or thermocline ($K_z\{\delta DIC/\delta z\}$). Approximate average $\delta^{13}C$ values are denoted in brackets.

ively "lighter" throughout the summer and autumn. The thermocline became slightly more enriched in ^{13}C through summer indicating that more $^{12}CO_2$ was fixed by phytoplankton at 6 m than was released by organic matter respiration or oxidation.

The two reversals in the $\delta^{13}C$ trend described above occurred around June 15 and July 16. The first of the reversals occurred soon after an algal bloom and must have resulted from respiration of light DIC as indicated by a concomitant increase in DIC concentration. The values for DIC and $\delta^{13}C$ recorded in mid-July could not have been caused by net respiration of light carbon because there was not a concomitant increase in DIC (Table 3). For example, a reduction of epilimnion $\delta^{13}C$ by 4‰ using added DIC from autochthonous POC respiration ($\delta^{13}C \approx -18‰$) should result in about a 40% increase in DIC concentration. In the first two weeks of July, the DIC in the Mohonk Lake epilimnion *decreased* by about 20% (Table 3).

The observed decrease in $\delta^{13}C$ during early July was apparently caused by a change in the isotopic fractionation between atmospheric CO_2 and DIC (via the reaction $CO_2 + OH^- \rightarrow HCO_3^-$) at the high pH ($> 9.5$) induced by intense photosynthesis. Because CO_2 invasion must have been chemically enhanced by reaction with OH^- during the time of peak productivity, the invasion fractionation factor approximated that for invasion into a hydroxide solution ($-15‰$ — Craig 1953) compared with about $+8‰$ for atmospheric equilibrium conditions (Table 1). Therefore, for the first two weeks of July the isotopic composition of CO_2 invading the lake was about −21‰. Since the CO_2 lost via photosynthesis was −18‰ (Table 3), the CO_2 invading the lake was 3‰ lighter than that lost by photosynthesis resulting in a decrease in epilmnetic $\delta^{13}C$ during that time interval. This phenomena is discussed in greater detail in another paper (Herczeg & Fairbanks 1987).

Changes in $\delta^{13}C_{POC}$ over the course of the year were caused by variation in the photosynthetic fractionation factor which in turn is a function of P_{CO_2} of surface water. This phenomenon has been observed by several workers (eg. Degens et al. 1968; Deuser et al. 1968; Calder & Parker 1973; Rau et al. 1982). The mid-summer $\delta^{13}C_{POC}$ values were about 1‰ more negative than $CO_2(aq)$ when P_{CO_2}'s were much lower than atmospheric CO_2. The difference in $\delta^{13}C$ between dissolved CO_2 and POC was as much as 18‰ during spring when P_{CO_2} of surface water was several times supersaturated with respect to CO_2.

Epilimnion ^{12}C-^{13}C mass balance calculations

The change in DIC and $\delta^{13}C$ of the epilimnion of Mohonk Lake over any given time interval may be expressed as a balance of the input and output of $DI^{12}C$ and $DI^{13}C$. These fluxes are depicted in Fig. 6 as input by inflow plus runoff ($I[DIC]_i$), invasion from the atmosphere, sediment pore water flux and eddy diffusion through the thermocline while the loss terms are outflow ($O[DIC]_e$), gas evasion and net conversion of DIC to C_{org} by photosynthesis. Using two equations, one each for $DI^{12}C$ and $DI^{13}C$, a unique solution can be obtained for any two unknowns provided all other parameters are known. The two unknown parameters that are the largest in magnitude and the most difficult to quantify are the net rate of photosynthesis (conversion of DIC to C_{org}) and the net flux of CO_2 across the air-water interface.

The $DI^{12}C$ mass balance may be expressed as:

$$\frac{\Delta([DIC]_e V_e)}{\Delta t} = \Sigma I[DIC]_i - \Sigma O[DIC]_e + K^*\{P_{CO_2}(atm)K_H - [CO_2(aq)]_e\}A_L - \text{net P} + \Phi D_s\left(\frac{\Delta DIC}{\Delta z}\right)_s A_{sed} + \left(\frac{\Delta DIC}{\Delta z}\right)_{th} K_z A_{th} \qquad (1)$$

where:

$\frac{\Delta[DIC]_e}{\Delta t}$ = change in DIC concentration of the epilimnion during time interval Δt

V_e = volume of the epilimnion

I and O = inflow of water to, and outflow of water from, the epilimnion. For constant V_e, any imbalance between I and O during time interval Δt implies displacement or entrainment of an equivalent amount of water to or from the thermocline

$[DIC]_i$ and $[DIC]_e$ = average concentration of DIC in the inflow and the epilimnion over time interval t

K^* = gas exchange coefficient

A_L, A_{sed} and A_{th} = area of lake surface, epilimnetic sediments and thermocline/epilimnion boundary

P_{CO_2} (atm) = partial pressure of CO_2 in the atmosphere above the lake

K_H = solubility of CO_2 at the temperature of surface water (Stumm & Morgan 1981)

$[CO_2(aq)]_e$ = concentration of dissolved CO_2 in the epilimnion

net P = net conversion of DIC to C_{org} (i.e. Σ photosynthesis — light respiration — dark respiration — degradation of C_{org} to DIC in the epilimnion)

D_s = diffusion coefficient of CO_2 in the sediment pore water corrected for tortuosity and porosity $\approx D.\Phi^2$ (Berner 1978)

D = diffusion coefficient of CO_2 in pure water at surface water temperature ($D = 1.06 \times 10^{-5} cm^2 sec^{-1}$ at

5°C; $D = 1.9 \times 10^{-5}\,\mathrm{cm^2\,sec^{-1}}$ at 25°C — Lerman 1979)

Φ = porosity of the upper 2 cm of sediment

$\left(\frac{\Delta DIC}{\Delta z}\right)_s$ = DIC concentration gradient at the upper 2 cm of sediment

$\left(\frac{\Delta DIC}{\Delta z}\right)_{th}$ = DIC concentration gradient through the thermocline

and K_z = eddy diffusivity through the thermocline = 5×10^{-4} to $10^{-2}\,\mathrm{cm^2\,sec^{-1}}$ based on data from Quay et al. (1980).

The gas exchange term on the right-hand side of equation (1) represents the net flux of CO_2 across the air-water interface as defined by the stagnant film model of Lewis & Whitman (1924). This model envisages the resistance to gas transfer between a well mixed air and water reservoir as diffusion across an imaginary boundary film. Net CO_2 flux is then controlled by — the exchange coefficient, K*, which is a bulk term for the expression $D.\beta/z^*$ where β is the chemical enhancement factor for CO_2 exchange (Emerson 1975a) and z* is the thickness of the imaginary film at the air-water interface, — the concentration gradient of CO_2 across the interface calculated from the measured P_{CO_2} in the atmosphere and surface water.

The $DI^{13}C$ mass balance is expressed in the same manner as equation (1) with the respective $^{13}C/^{12}C$ ratios attached to each of the DIC flux terms. That is:

$$\frac{\Delta([DIC]_e R_e V_e)}{\Delta t} = \Sigma I[DIC]R_i - O[DIC]_e R_e$$

$$+ K^* \{P_{CO_2}\,(atm)\, K_H R_{atm} \alpha_{inv} - [CO_2(aq)]_e R_e \alpha_{ev}\} A_L$$

$$- \text{net } P \cdot R_{POC} + \Phi D_s \left(\frac{\Delta DIC}{\Delta z}\right)_s R_s A_s + K_z \left(\frac{\Delta DIC}{\Delta z}\right)_{th} R_{th} \qquad (2)$$

where

$$R = \frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{standard}} = \frac{\delta^{13}C}{1000} + 1$$

and: α_{inv} and α_{ev} are the fractionation factors for CO_2 invasion and evasion respectively (see Table 1).

The two unknowns, K* and net P, may be calculated by isolating net P in equation (1) then substituting that expression for net P in equation (2) to solve for K* and hence the net gas exchange rate. Substituting the net CO_2 flux back into the DIC balance (equation 1) gives the net rate of conversion of DIC to C_{org} (i.e. P). This mass-balance approach was only applicable for the time interval mid-May to late September when the water column was thermally stratified (Fig. 2) and thus entrainment of deep water was negligible. All of the other parameters were measured or estimated as stated below.

The concentration and isotopic comosition of DIC in inflow water was measured during spring and early summer (Herczeg 1985) and this inflow ceased after mid-July. Total input of water from the drainage basin (ΣI) was estimated from the water balance:

$$\Sigma I = \frac{\Delta V_L}{\Delta t} + O + E$$

where:

$\frac{\Delta V_L}{\Delta t}$ = change in lake volume estimated from changes in lake level

O = outflow from controlled outflow measurements

E = evaporation rate estimated at 70 cm/yr from class A evaporation pan (D. Smiley, unpublished data).

The total terrestrial input of DIC was calculated by multiplying ΣI times $[DIC]_i$ and is considered accurate to within 50%.

The pore water $DI^{12}C$ and $DI^{13}C$ fluxes were estimated from one sediment pore water profile taken in the epilimnetic sediments in early November (Fig. 7). Diffusional fluxes using the upper two centimeters of sediment yields a DIC flux from pore waters to the epilimnion of 28 moles DIC d^{-1}. The highest DIC flux from sediment pore waters to the epilimnion probably occurred in early autumn due to deposition of fresh organic material during the preceding summer months. Therefore the pore water fluxes input to the model were scaled from near zero in early spring to a maximum prior to fall overturn. These estimates may be in error because some evidence from chambers suggests that sediment DIC fluxes determined from pore water gradients are two low by about a factor of two (Hesslein 1980; J. Rudd,

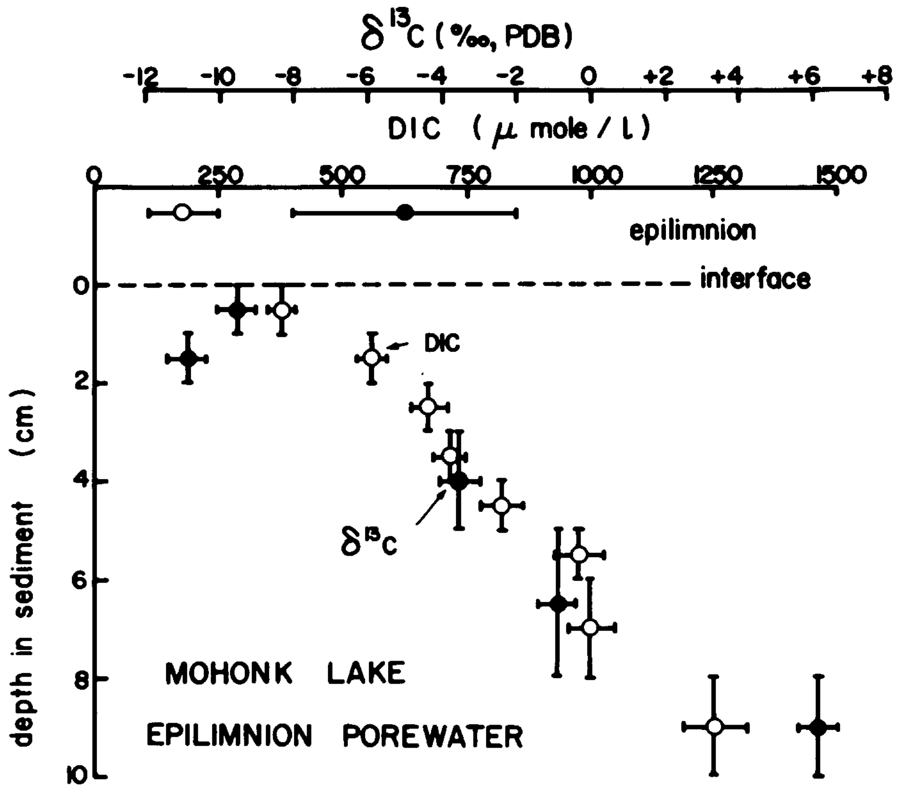


Fig. 7. DIC concentration and $\delta^{13}C_{DIC}$ of epilimnion porewaters. Waters were extracted from a core retrieved 3 weeks prior to Fall overturn.

unpublished data). However, this potential error would not change the conclusions of this work because the combined sediment plus hypolimnetic contribution to the epilimnetic DIC budget is less than 8% of the total flux. The $\delta^{13}C$ flux from epilimnetic sediments was assigned the value measured at the sediment-water interface and assumed to be −10‰ throughout summer. Pore water DIC fluxes were generally small relative to the total DIC input (see below) partly because of the steep sided nature of the lake in the epilimnion region (Fig. 3) that exposes only a small fraction of the epilimnion to sediments. Diffusion of CO_2 through the thermocline contributed less than 5% to the epilimnion DIC budget (see below) while the lake was well stratified.

Model results and sensitivity

The results of the $DI^{12}C$-$DI^{13}C$ mass balance calculations are given in Table 4 and an example of sensitivity of errors of input values given for one of the

Table 4. Summary of ^{13}C–^{12}C mass balance calculations for DIC fluxes into and out of the Mohonk Lake epilimnion during the ice-free season, 1984. ΔDIC and $\Delta\delta^{13}C$ = change in DIC concentration and $\delta^{13}C$ respectively over time interval; ΔP_{CO2} = mean CO_2 partial pressure gradient across the air water interface; Inf, Of and S + Th = estimated fluxes of DIC via inflow, outflow and sediment porewater plus thermocline flux respectively; K* = exchange coefficient. Positive values for net gas exchange indicate invasion of CO_2 from the atmosphere; positive values for net photosynthesis indicate net conversion of DIC to C_{org}. The quoted errors are propagated errors derived from uncertainties in the measured or estimated input parameters and are caused largely by uncertainties in estimates of ΔP_{CO2}, ΔDIC and $\Delta\delta^{13}C_{DIC}$ (see Table 5).

	# days	ΔDIC	$\Delta\delta^{13}C$	ΔP_{CO_2}	Inf	Of	S + Th	K*	Net Inv	net P
		µmol/l	‰, PDB	µatm	moles DIC/day			m/day	moles DIC/d (mmol/m^2 day)	
May 16–June 5	21	−20	+1.9	−90	300	−130	13	−1.7 ± 0.8	96 ± 34 (1.4 ± 0.5)	565 ± 182 (8.3 ± 2.7)
June 6–June 15	10	+11	−2.6	+20	100	−83	13	−0.1 ± 0.5	−5 ± 39 (−0.1 ± 0.6)	−194 ± 124 (−2.9 ± 1.8)
June 16–June 22	7	−7	+0.3	−10	100	−83	18	−1.1 ± 1.3	113 ± 160 (1.7 ± 2.4)	346 ± 163 (5.1 ± 2.4)
June 23–July 3	11	−7	+1.4	+10	100	−4	18	0.7 ± 0.4	52 ± 30 (0.8 ± 0.4)	294 ± 59 (4.3 ± 0.9)
July 4–July 16	13	−22	−5.2	+320	50	−4	22	2.6 ± 0.6	1820 ± 420 (26.8 ± 6.2)	2070 ± 510 (30.4 ± 7.5)
July 17–July 31	15	+23	+1.0	+290	–	−4	28	0.6 ± 0.2	430 ± 180 (6.3 ± 2.6)	160 ± 51 (2.4 ± 0.8)
Aug. 1–Aug. 17	17	−11	+4.9	+160	15	–	32	0.4 ± 0.2	230 ± 50 (3.4 ± 0.7)	410 ± 125 (6.0 ± 1.8)
Aug. 18–Sept. 25	39	+23	+0.2	+40	5	–	48	0.7 ± 0.2	121 ± 42 (1.8 ± 0.6)	70 ± 25 (1.0 ± 0.4)

Table 5. Sensitivity of calculated rates of invasion and net photosynthesis to uncertainties in some of the input parameters. The calculations presented in the table are for the data obtained for June 23–July 3, 1984. Each set of calculated values below the top line represents a change in only one of the input values.

parameter changed	ΔDIC μmol/l	$\Delta\delta^{13}C_{DIC}$ ‰, PDB	ΔP_{CO_2} μatm	$\delta^{13}C_{POC}$ ‰, PDB	K* m/day	net Inv moles DIC/day	net P
–	−7	+1.4	+10	−32	0.7	52	294
ΔDIC	−5	+1.4	+10	−32	0.3	24	227
$\Delta\delta^{13}C_{DIC}$	−7	+1.0	+10	−32	1.0	71	311
$\Delta^{P}CO_2$	−7	+1.4	−40	−32	0.8	−132	183
$\Delta^{P}CO_2$	−7	+1.4	+60	−32	0.1	2	242
$^{13}C_{POC}$	−7	+1.4	+10	−30	0.5	38	279

time intervals in Table 5. Calculated CO_2 exchange coefficients, K*, range from −1.7 m/d to 2.6 m/day. The mean exchange coefficient was 0.6 m/d (neglecting negative values). The value of 2.6 m/day corresponds to a period of intense photosynthetic activity when P_{CO_2}'s were less than 10% of the atmosphere and surface water pH's approached 9.8. Thus, chemical enhancement of CO_2 invasion must have occurred at this time. The value of 2.6 m/day represents both diffusive transport across the air-water interface and reaction of CO_2 with OH^- within the stagnant boundary layer. Negative values of K* which were calculated for the first three time intervals are not realistic because the exchange coefficient is an absolute quantity where the direction of gas exchange is determined by the P_{CO_2} gradient across the air-water interface. These negative values must result from inaccuracies in estimated DIC fluxes from the drainage basin and the estimate of the size of the epilimnion DIC pool. Episodes of high rainfall and runoff experienced in May and June lead to large uncertainties in the amount of DIC derived from the drainage basin. Reasonably accurate and precise estimates of K* could only be obtained over the 95 days from late June to late September when inflow was small or well quantified and the epilimnion volume fairly stable. Although there is considerable variability in calculated K* values, the mean compares favourably with exchange coefficients calculated from purposeful tracer experiments done in other lakes of similar size (eg. Emerson 1975b; Hesslein et al. 1980; Torgersen et al. 1982; Wanninkhof et al. 1985, see Table 6). Surprisingly enough, the exchange coefficient determined for two much larger lakes in eastern California (Wanninkhof 1986) gave about the same exchange coefficient as the small lakes mentioned above. One would expect large lakes to have a greater wind fetch and therefore higher exchange coefficient than the small lakes. The ^{12}C-^{13}C mass balance provides a means of obtaining long term averaged exchange coefficients in lakes with water residence times greater than 6 months during periods of stable thermal stratification.

Table 6. Comparison of the mean exchange coefficient (K*) calculated for Mohonk Lake with those determined in other lakes.

Place	K* (meters/day)	Method	Reference
Mohonk Lake	Mean = 0.6* Range (− 1.7–2.6)	^{13}C–^{12}C mass balance	this work
Rockland Lake	Mean = 0.53 Range (− 0.04–1.9)	SF_6 tracer	(1)
ELA Lakes	0.5–2.0	$^{222}Rn/^{226}Ra$, ^{14}C tracer $^3He/^3H$	(2)–(4)
Pyramid Lake	1.0		
Walker Lake	3.3	Bomb ^{14}C	(5)
Mono Lake	8.3		
Mono Lake	Mean = 0.6 Range (− 1.1–3.7)	SF_6 tracer	(6)
Crowley Lake	Mean = 0.6 Range (0.3–5.0)	SF_6 tracer	(6)
Ocean	~ 5	Natural ^{14}C	(7)

* Mean value calculated from positive values for K* in Table 4 (see text); (1) Wanninkhof et al., (1985); (2) Emerson (1975b); (3) Hesslein et al., (1980); (4) Torgersen et al., (1982); (5) Peng and Broecker (1980); (6) Wanninkhof (1986); (7) Peng et al., (1979)

The calculated CO_2 exchange rates range from − 0.1 to 27 mmoles $m^{-2}d^{-1}$ (Table 4). The fluxes calculated for the first three time intervals are in the opposite sense to measured P_{CO_2} gradients. Since the CO_2 gas fluxes are calculated from the product of K* and ΔP_{CO_2} these results must be ascribed to errors in one or more of the measured input values giving rise to negative K* values. Mean net CO_2 invasion from June 3 to September 25 was 6.2 ± 1.8 mmoles $m^{-2}d^{-1}$. About the same amount of carbon was converted to C_{org} via net photosynthesis (6.5 ± 1.8 mmoles $m^{-2}d^{-1}$) over the same time interval.

Uncertainties for K*, net gas exchange and net photosynthesis given in Table 4 were calculated by propagation of uncertainties of some of the critical input parameters through the mass balance calculations. The results are most sensitive to uncertainties in measured DIC, $\delta^{13}C$ and P_{CO_2} of surface water. An example of the sensitivity to variations in these values is given in Table 5 for the time interval June 23–July 3. Each calculation shows the result for a change in one of the input parameters to a value twice the analytical uncertainty away from the measured value. These results indicate that the model calculations are especially sensitive to estimations of the CO_2 concentration gradient across the air-water interface. Because of the dynamic nature of the photosynthesis/respiration cycle in moderate to highly productive lakes, average P_{CO_2} of surface water over time intervals on the order of weeks can probably be estimated to no better than ± 30% using discrete measurements over weekly (or less) intervals. Uncertainties in the mass balance calculations can therefore be no better than the propagation of the P_{CO_2} error which amounts to about 30% in most instances (i.e. there is a linear correlation between ΔP_{CO_2} and net gas exchange). Although P_{CO_2} can conceivably be calculated from pH and bicarbonate alkalinity measurements, the large systematic errors inherent in glass electrode pH measurements in softwaters ($\sim$0.4 pH units lower than "true" pH — eg., Herczeg & Hesslein 1984) mean that only direct P_{CO_2} measurements can yield results with better than 30% uncertainty for CO_2 flux calculations. Frequent and accurate P_{CO_2} determinations in the waters of lake are essential if a serious carbon budget is to be attempted.

Exchange of CO_2 across the air-water interface

As discussed above, the rate of net transfer of CO_2 across the air-water interface is dependent on the concentration gradient of CO_2 between the air and water and the value of the exchange coefficient which is in turn dependent on wind speed (eg. Wanninkhof et al. 1985). Although the P_{CO_2} of Mohonk Lake surface water was measured periodically from April to November, reliable estimates of K^* could be calculated only from June 23 to September 25. Qualitative assessment of the direction and magnitude of CO_2 flux can be inferred for the remainder of the ice-free season from P_{CO_2} data.

Surface water P_{CO_2} data (Table 3) show that there must have been a significant loss of CO_2 to the atmosphere from ice-off (April 9) to at least mid-May when P_{CO_2}'s were up to four times that of atmospheric P_{CO_2}. There was a concomitant decrease in DIC (Fig. 4) and increase in $\delta^{13}C$ (Fig. 5) which is consistent with inferred evasion of CO_2. The source of this "escess" CO_2 was probably due to the accumulation of degraded and oxidized POC under ice plus addition of inflow water supersaturated in CO_2.

In early June a P_{CO_2} of 173 μatm was recorded which was about half that of atmospheric equilibrium and occurred simultaneously with an algal bloom as inferred from Secchi disk readings (Fig. 3). The enhanced algal activity was stimulated by nutrient input from a large rain even at the end of May ($\sim$17 cm). The return to supersaturated levels of P_{CO_2} by June 15 may be a reflection of respiration plus oxidation of the phytoplankton produced in the preceding time interval. This is consistent with the increase in Secchi depth observed in mid-June.

From early July to mid-August there was a large amount of net CO_2 invasion as borne out by surface water highly undersaturated with respect to P_{CO_2} ($P_{CO_2} \approx 12\,\mu$atm — see Table 3) and mass balance calculations (Table 4). Net CO_2 invasion was 27 ± 7 mmoles $m^{-2} d^{-1}$ for the first two weeks in July and the following two time intervals the values were 6.4 ± 2.5

and 3.4 ± 0.7 mmoles $m^{-2} d^{-1}$ respectively. The depression in P_{CO_2} was apparently induced by an algal bloom (inferred from Secchi disk readings — Fig. 3). Calculated rates of photosynthesis were also very high (Table 4 and see below) during these time intervals.

For the remaining six weeks of summer (August 17–September 25) net invasion was reduced to 1.8 ± 0.6 mmoles $m^{-2} d^{-1}$ and surface water P_{CO_2}'s returned to about equilibrium with the atmosphere. As the mixed layer deepened from September onward (Fig. 2) surface water P_{CO_2} increased (Table 3) due to the entrainment of deep water where CO_2 had accumulated from oxidation of particulate organic carbon. There must have been evasion of CO_2 at least until fall overturn in late November when surface water P_{CO_2}'s were greater than 3 times atmospheric P_{CO_2} (Herczeg 1985).

Net photosynthesis

Calculations for net photosynthesis (i.e. net conversion of DIC to C_{org}) were done simultaneously with that for net gas exchange using the mass balance equations (1) and (2). Calculated rates of net P range from −1.6 ± 0.6 mmoles $m^{-2} d^{-1}$ (i.e. net respiration) in early June to 30 ± 8 mmoles $m^{-2} d^{-1}$ in July (Table 4). The results agree in a qualitative sense with Secchi disk observations (Fig. 3); that is, rapid growth of phytoplankton in late May followed by a decline in the standing crop in early June. From late June to mid-July the Secchi visibility decreased to ~ 1.5 m corresponding to the highest rates of calculated net photosynthesis. The algal population remained at quasi steady-state through the rest of summer (inferred from Fig. 3) though there was continued net photosynthesis (Table 4). Therefore about as much DIC was converted to C_{org} during this time interval as was lost by settling of autochthonous POC through the thermocline.

A short lived algal bloom that was inferred from Secchi disk observations (Fig. 3) occurred soon after ice-out (5th April). The primary source of carbon for these phytoplankton was probably derived from recycled carbon that had accumulated under-ice and was mixed to the surface from the hypolimnion. A second, more intense bloom occurred in late May (in response to an episode of high rainfall and runoff) when net photosynthesis was 8.3 ± 2.7 mmoles $m^{-2} d^{-1}$ (Table 4). About 20% of DIC was derived from the atmosphere, 50% from DIC brought in by inflow from the terrestrial drainage basin and the remaining 30% from the decrease in the epilimnion DIC pool.

From early July to mid-August the average net photosynthesis in the epilimnion was calculated as 12 ± 5 mmol $m^{-2} d^{-1}$. When integrated over the six weeks it amounts to 65 ± 15% of the total net production of organic carbon from mid-May to late September (Table 7). In particular, net

Table 7. Measured and calculated fluxes of DIC for the Mohonk Lake epilimnion for each given time interval. The term Δ storage refers to an increase (+) or decrease (−) of DIC in the epilimnion. Positive values for net photosynthesis (net P) indicate net respiration and negative values represent loss of DIC from the system via conversion to C_{org}. S + Th are the combined sediment and thermocline flux of DIC as calculated by first order diffusion across the measured concentration gradient. Inf and Of are DIC flux via inflow and outflow respectively.

	Δ storage	Inf	Of	S + Th	net Inv	Net P
			moles DIC × 10^3			
May 16–June 5	−6.0	6.3	−2.7	0.3	2.0	−11.9
June 6–June 15	+2.2	1.0	−0.8	0.1	−0.1	1.9
June 16–June 22	−1.4	0.7	−0.6	0.1	0.8	−2.4
June 23–July 3	−1.4	1.1	−0.04	0.2	0.6	−3.2
July 4–July 16	−2.2	0.7	−0.05	0.3	23.7	−26.9
July 17–July 31	+4.6	–	−0.06	0.4	6.5	−2.40
Aug 1–Aug 17	−2.2	0.3	–	0.5	3.9	−7.0
Aug 18–Sept 25	+4.6	0.2	–	1.9	4.7	−2.7
Total	−1.8	10.2	−4.3	3.9	42.1	−54.7

photosynthesis during the first two weeks of July corresponded to 50 ± 15% of net conversion of DIC to C_{org} during the time that the lake was thermally stratified. There was continued net photosynthesis from mid-July through to the end of mid-September (Table 4) though at considerably lower rates than those of mid-summer. Only about 5% of net conversion of DIC to C_{org} for the stratified period occurred during these last six weeks.

Relationship between net photosynthesis and gas exchange

There has been some controversy over the past two decades on whether the main source of carbon for lake phytoplankton is derived from the atmosphere (e.g. Schindler et al. 1973; Talling 1976; Bower 1981; Quay et al. 1986) or from the recycled terrestrial organic carbon (e.g. Wetzel et al. 1972; Wissmar et al. 1977; Rau 1978). If the atmosphere can provide sufficient CO_2 for phytoplankton growth in the presence of excess phosphorus and nitrogen, then carbon is never a limiting nutrient. DIC for primary producers may be derived from the above-mentioned external sources (i.e. atmospheric CO_2 or terrestrial DIC) or from recycled C_{org} accumulated in the hypolimnion and mixed to the surface during the breakdown of thermal stratification. The relative importance of all three sources is related to differences from lake to lake of water residence time, ratios of drainage basin area to lake surface area and to trophic state. For example, the highly negative $\delta^{13}C_{POC}$ and $\delta^{13}C_{DIC}$ values measured in Findlay Lake, Washington (Rau 1978) were interpreted as being derived from respired carbon from the

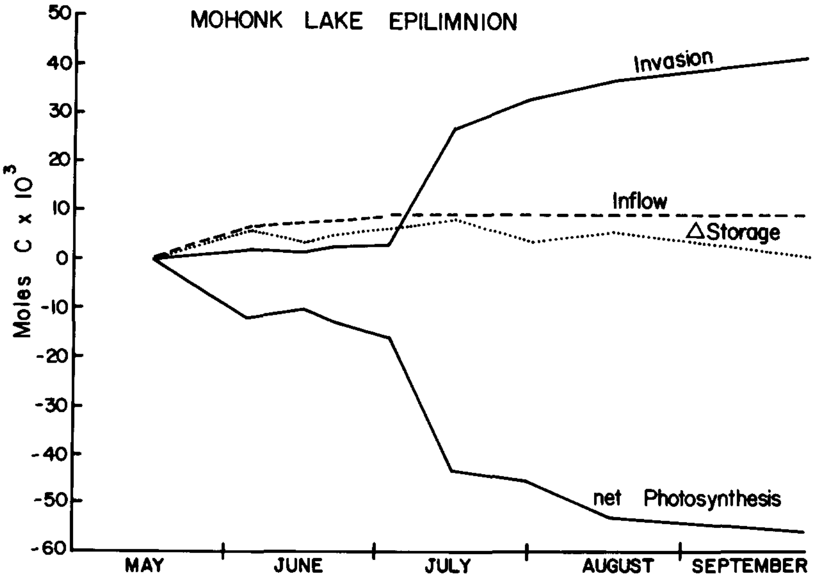


Fig. 8. Inventory of calculated DIC fluxes via invasion, inflow, change in storage and loss of DIC from conversion of DIC to C_{org}.

terrestrial drainage basin. These measurements were made in the two months following ice-off and the lake had approximately a two month water residence time. Under these circumstances where large quantities of terrestrially derived DIC enters a lake it is unlikely that the DIC would have had an opportunity to equilibrate chemically or isotopically with atmospheric CO_2 even in a lake with very low DIC concentration. Extrapolating the conclusions derived from the $\delta^{13}C$ results of Findlay Lake to lakes with longer water residence times or greater primary productivity is not justified. Furthermore, the $\delta^{13}C$ of POC by itself is not diagnostic of carbon source because of the variation of the photosynthetic fractionation factor with P_{CO_2} (see above and Table 1).

Sources of DIC phytoplankton from ice-off to mid-May in Lake Mohonk were inferred from surface water P_{CO_2} data and from the amount of DIC entering from the drainage basin. P_{CO_2} of surface water was consistently greater than twice atmospheric CO_2 during this time period (Table 3). These high values must have been maintained by a combination of entrainment of deep water, stream input and seepage through soils (Herczeg 1985). Therefore the main source for phytoplankton during spring must have been recycled terrestrial or autochthonous carbon since CO_2 invasion was minimal.

Figure 8 displays the calculated cumulative carbon fluxes (compiled from calculations given in Table 7) for net CO_2 invasion, DIC inflow, changes in DIC storage and net conversion of DIC to C_{org} for the epilimnion during the time the lake was thermally stratified. Change in epilimnion DIC storage is depicted on the upper (positive) axis for comparative purposes because a decrease in DIC storage is potentially a source of DIC for photosynthesis. From mid-May to early July the atmosphere supplied less than 20% of DIC that was converted to C_{org}. Input from the drainage basin and decrease in epilimnion DIC storage supplied about 50% and 30% respectively. The situation changed dramatically from July 3 onwards. As described above calculated rates of net photosynthesis were about equal to calculated rates of net CO_2 invasion. Sources of DIC other than atmospheric CO_2 cannot have contributed more than 10% to net photosynthesis after July 3 (Table 7). These results show that Mohonk Lake underwent substantial changes in trophic state and in turn carbon sources for photosynthesis throughout the ice-free season of 1984.

Hypolimnion $DI^{12}C$–$DI^{13}C$ mass balance

During thermal stratification, the hypolimnion of a lake is effectively isolated from the epilimnion and accumulates organic carbon degradation products. The evolution of the $\delta^{13}D_{DIC}$ of the hypolimnion as a function of DIC concentration is depicted in Fig. 9. The lower left most point is the measured $\delta^{13}C$ and DIC of the hypolimnion at the onset of summer stratification (~ 15th May) and shows a $\delta^{13}C$ decrease with increasing DIC concentration. A model curve respresenting complete oxidation of POC in Mohonk Lake follows the upper curve where the $\delta^{13}C$ of oxidized C_{org} is −32‰ during spring increasing to −18‰ during July and back to −28‰ in August–September. These values represent the $\delta^{13}C$ of POC measured in the epilimnion during these time intervals. The data points for the Mohonk Lake hypolimnion fall below the trend defined by POC oxidation alone. The estimated $\delta^{13}C$ of DIC predicted by this curve alone is about −22‰. If one of the end-members producing the observed trend in the hypolimnion is about −26‰, there must be an additional source of DIC with a $\delta^{13}C$ less negative than −22‰ to complete an isotopic mass balance; that is, a mixture of DIC from POC oxidation plus a "heavy" $\delta^{13}C$ source. Sources of this heavy DIC may be:

— HCO_3^- derived from dissolution of carbonate minerals, or
— CO_2 derived as a by-product of methanogenesis

The first scenario is unlikely because the alkalinity of the hypolimnion did not increase to the extent that would have resulted from addition of the Ca^{2+} and CO_3^{2-} to make up the measured accumulation of DIC. Methanogenesis must have occurred in the deep sediments of Mohonk Lake as confirmed by "heavy" $\delta^{13}C$ of DIC in the hypolimnion sediment pore waters (−7‰ to +3‰ — Fig. 10) where CO_2 produced as a by-product of methanogenesis

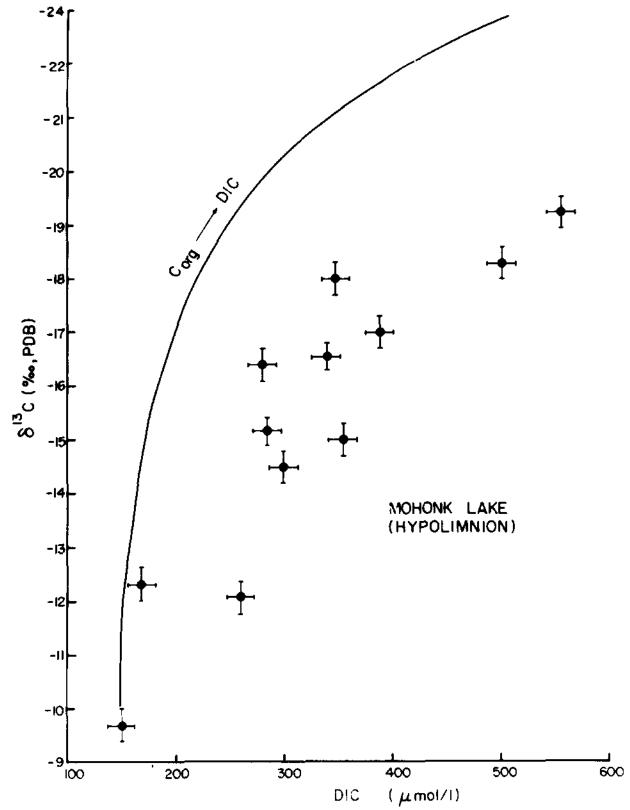


Fig. 9. Evolution of $\delta^{13}C_{DIC}$ of Mohonk Lake hypolimnion expressed as a function of DIC concentration. The solid curve represents the expected approximate trend followed by the $\delta^{13}C_{DIC}$ if the accumulated DIC had been derived solely from breakdown of POC.

can have a $\delta^{13}C$ greater than $+20‰$ (Rosenfeld & Silverman 1959; Games et al. 1978; Schoell 1980; Woltemate et al. 1984). A value of $-7‰$ was assumed for the $\delta^{13}C$ of pore water DIC entering the hypolimnion which was equal to that measured at the sediment-water interface.

The fluxes of DIC into and out of the lake hypolimnia are depicted in Fig. 11 with approximate $\delta^{13}C$ values as measured in Mohonk Lake. The mass-balance for $DI^{12}C$ in the Mohonk Lake hypolimnion may be written as:

$$\frac{\Delta(DIC)_h}{\Delta t} V_h = D_{ox} + SA_s + M_{ox} - K_z \left(\frac{\Delta DIC}{\Delta z}\right) A_{th} \qquad (3)$$

where:

V_h = volume of hypolimnion

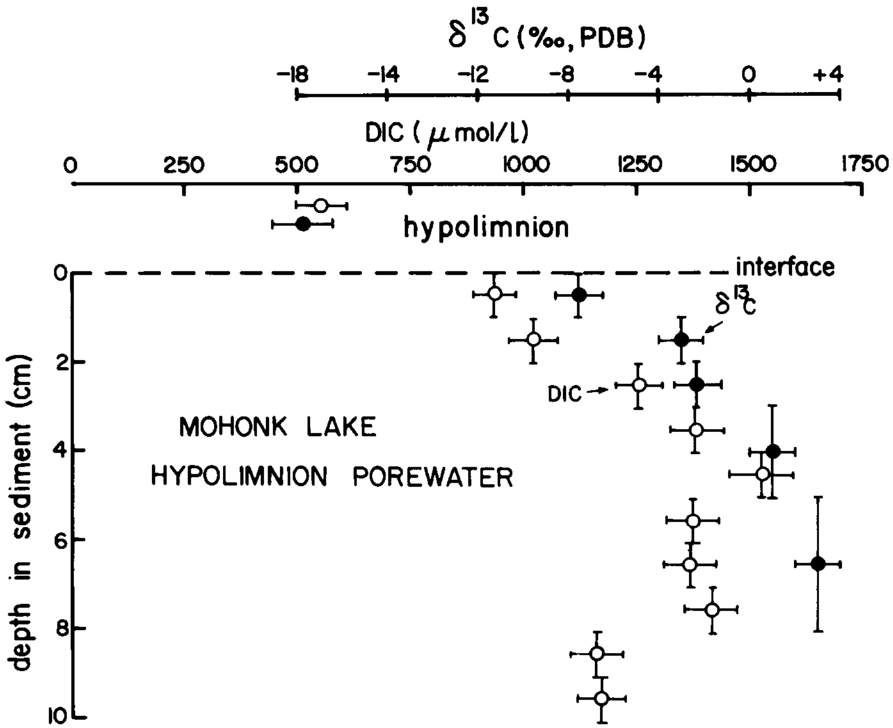


Fig. 10. DIC concentration and $\delta^{13}C_{DIC}$ of hypolimnion porewaters. Water samples were extracted from a core taken at 13 meters depth 3 weeks prior to Fall overturn.

D_{ox} = rate of DIC production by organic matter oxidation

S = pore water DIC flux

A_s = surface area of hypolimnetic sediment

M_{ox} = DIC produced by methane oxidation

$K_z\left(\frac{\Delta DIC}{\Delta z}\right)A_{th}$ = flux of DIC across the hypolimnion-thermocline boundary

The DI^{13}C mass balance for the hypolimnion is expressed as:

$$\frac{\Delta(DIC_hR_h)}{\Delta t}V_h = D_{ox}R_{POC} + SR_sA_s + M_{ox}R_m - K_z\left(\frac{\Delta DIC}{\Delta z}\right)R_h \cdot A_{th} \qquad (4)$$

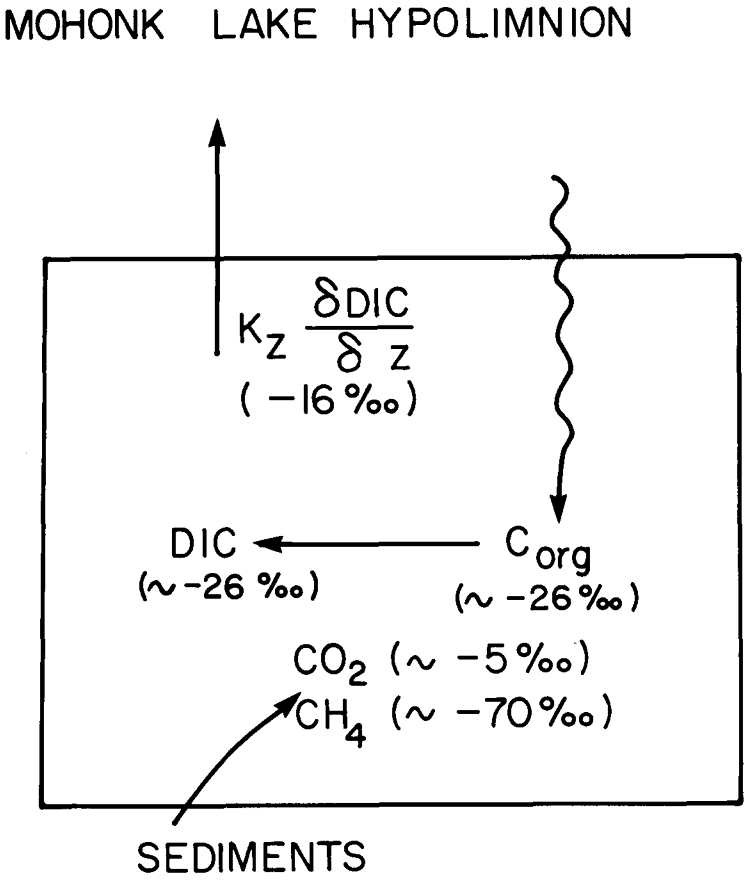


Fig. 11. Box model of $DI^{12}C$–$DI^{13}C$ balance in the Mohonk Lake hypolimnion. Input is from oxidation of C_{org} to DIC and diffusion of CO_2 and HCO_3^- from sediment porewaters; loss occurs via eddy diffusivity of DIC through the thermocline. Approximate mean $\delta^{13}C$ values are denoted in brackets.

where:

R represents the $^{13}C/^{12}C$ ratios for subscripts:

h = hypolimnion

POC = particulate organic carbon

s = hypolimnion sediment pore water

m = DIC from methane oxidation

The bacterially mediated destruction of land derived plant matter within the hypolimnion during summer is assumed to be small compared with autochthonous POC oxidation. Organic matter derived from the terrestrial drainage basin is probably more refractory and hence less metabolically favourable than algae, therefore the $^{13}C/^{12}C$ value assigned for R_{POC} is equivalent to that for autochthonous POC. Because the hypolimnion was anoxic throughout the summer, any methane that diffused from the sediment pore waters is presumed to have behaved conservatively rather than oxidized to CO_2 (eg. Rudd & Hamilton 1978). Therefore the third term on the right hand side of equations (3) and (4) (i.e. M_{ox}) need not be included in the mass balance calculations. Equations (3) and (4) can then be solved simultaneously for the two remaining unknowns; D_{ox}, the amount of organic matter oxidized to DIC, and S, the DIC flux from sediment pore waters.

Solving the mass balance equations for the time interval 24th of May to the 24th of October reveal that 80 ± 10% of DIC produced in the hypolimnion was derived from POC oxidation and the rest by diffusion of "heavy" CO_2 from sediment pore water. As some of the pore water CO_2 was derived as a by-product of methanogenesis, the fate of methane diffusing to the hypolimnion from the pore waters must ultimately be accounted for. A methane mass balance constructed by Rudd & Hamilton (1978) for a soft water lake in northwest Ontario, Canada gave the following account for CH_4 that had accumulated in the hypolimnion over summer; about one thrid was oxidized to CO_2 at fall overturn, one third lost to the atmosphere by evasion and the remainder converted to bacterial cellular material which may have been consumed by grazers. Whether a similar scenario applies to Mohonk Lake cannot be determined from the data available, however the results of Rudd & Hamilton (1978) imply that CH_4 and CO_2 produced as a by-product of methanogenesis most likely accumulate in the anoxic hypolimnia of soft water lakes during summer stratification. Therefore the addition of isotopically heavy DIC to the hypolimnion by this mechanism is a reasonable scenario.

Conclusions

The dynamic nature of the DIC cycle in Mohonk Lake is reflected in large variations in DIC, P_{CO_2} and $\delta^{13}C_{DIC}$ in the epilimnion and hypolimnion waters throughout the ice-free season. DIC and P_{CO_2} concentrations range over an order of magnitude and $\delta^{13}C$ values span over nerly 10 per mil. Evasion of CO_2 to the atmosphere and uptake of CO_2 by phytoplankton caused the epilimnion DIC concentration to decrease through spring and summer with a concomitant increase in $\delta^{13}C_{DIC}$. Degradation of C_{org} in the hypolimnion was responsible for the decrease in $\delta^{13}C_{DIC}$ of the deep waters over the course of the ice-free season.

Net gas exchange and net conversion of DIC to C_{org} were quantified by a $DI^{12}C$–$DI^{13}C$ mass balance for the epilimnion from May 15 to September 25. Approximately 80% of net photosynthesis in the epilimnion was supported by CO_2 invasion from the atmosphere through the time of summer stratification. About 50% of the total net photosynthesis occurred during an algal bloom over a two week interval (July 3–July 17) and was almost entirely supported by CO_2 invasion.

A model for the evolution of $\delta^{13}C_{DIC}$ in the hypolimnion showed that the accumulated DIC must have been derived from two sources — about 80% from rapid degradation of particulate organic carbon and the remaining 20% from diffusion of CO_2 from sediment pore waters. The pore water DIC was produced in part as a by-product of methanogenesis as indicated by relatively enriched $\delta^{13}C$ values of DIC at the hypolimnion water-sediment interface.

Acknowledgements

This work represents a portion of a PhD thesis completed at Columbia University, New York, under the direction of W.S. Broecker. Discussions during the course of the work and comments on earlier versions of the manuscript by R. Anderson, R. Bopp, T. Takahashi, M. Wahlen, P. Duby and W.B. Lyons are greatly appreciated.

Constructive reviews by R. Hesslein, J. McKenzie and one anonymous referee were also valuable. Analytical facilities for the stable carbon isotope work were generously made available by R. Fairbanks and those for DIC and P_{CO_2} analyses by T. Takahashi and D. Chipman.

Access to Mohonk Lake and ancillary data were provided by P. Huth and D. Smiley of Mohonk Preserve. The assistance and companionship in the field of S. Schiff, B. Deck and E. Catanzaro are appreciated.

The manuscript was typed by J. Stringer, V. Costello and M. Stevenson and figures drafted by P. Catanzaro and J. Cowley. Financial support provided in part by NSF grant DEB 8017639. LDGO contribution number 4134.

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