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Redox reactions of organic matter decomposition in a soft water lake

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Abstract. During a three year study (1985—1987) we used a mass balance approach to study the oxidation and reduction reactions related to decomposition of organic carbon in Mirror Lake, New Hampshire. The stoichiometry of the reactions allows us to calculate an electron transfer budget for the summer stratification period in the lake, as well as in benthic chambers and sealed jars.

The average decomposition rate measured as dissolved inorganic carbon (DIC) production was 5.33 mmol m^{-2} d^{-1}. The proportions of decomposition accounted for by the various electron acceptors varied both during the summer, as well as from year to year. On average, oxygen accounted for 43% of DIC production, while the processes involving sulfate, nitrate, iron and methane formation together accounted for 20%. Despite conservative assumptions we could not account for 37% of the DIC production. The general pattern, including excess DIC production, was also observed in chamber studies conducted over shallow-water sediments and in sealed-jar experiments.

Data on burial rates of reduced iron minerals indicate that such minerals are not sufficient to account for the discrepancy in the electron budget. Our analysis suggests that another electron acceptor such as organic carbon reduction, either via fermentation or selective oxidation, is the most likely explanation of excess DIC production.

Introduction

Under conditions of thermal stratification, the redox reactions involved in the oxidation of organic carbon can be studied in essentially “closed” volumes within the lower portion, or hypolimnion of a lake which are isolated from atmospheric exchange (Birge & Juday 1911; Hutchinson 1941; Ohle 1956). When the respiratory quotient (RQ), or the ratio of DIC produced to oxygen consumed exceeds 0.85, the excess DIC production generally is assumed to represent DIC production from anaerobic bacterial decomposition (e.g. Hutchinson 1957; Wetzel 1983). Recent studies have attempted to balance the oxidation of organic carbon with the reduction of electron acceptors for such anaerobic reactions involving sulfate, nitrate, iron, manganese and methane (Jones & Simon 1980; Schafran & Driscoll 1987; Kelly et al. 1988). Because the electrons involved in the reactions are simply transferred (they are conservative) we can use the valence of the products and reactants to calculate a 'mass' balance of electrons within the volume of the hypolimnion over time. Because all systems must maintain charge balance, the electron budget must balance exactly. By studying such budgets we hope to identify the relative importance of the various electron acceptors and their associated bacterial communities, to the overall metabolism of the ecosystem.

Previous investigations on decomposition in Mirror Lake, a soft-water lake in New Hampshire (Zmax = 11 m) indicated that there is a large proportion of anaerobic decomposition in the hypolimnetic waters (Rich & Devol 1978). This large amount of anaerobic decomposition, implied by the accumulation of DIC, is unusual considering that there is little methane accumulation (Jordan 1985) and the lake has very low concentrations of nitrate (ca. 1.5 μeq/l) and sulfate (ca. 119 μeq/l) (Likens et al. 1985), which limit the amount of decomposition attributed to those electron acceptors. This study investigated the overall production and decomposition processes in Mirror Lake and attempted to balance the oxidation rate of organic matter with the reduction rates of the known electron acceptors within the hypolimnetic volume and in the shallow water sediments. Additional information on the lake is available in Likens (1985).

Methods

Hypolimnetic studies

Complete details on sampling and analytical methods are given elsewhere (Mattson 1989). Briefly, water samples were collected at approximate monthly intervals during the summers of 1985, 1986 and 1987 at 1-m depth intervals within the hypolimnion. Samples were collected with a weighted sampling tube and peristaltic pump while tethered to the central buoy in the lake. Changes in the depth of sampling relative to the bottom of the lake, caused by lake-level fluctuations (continuously recorded and always less than 15 cm during each summer), were corrected for by interpolation of concentration vs depth profiles (see calculations, below). The hypolimnetic volume is defined here as the bottom three meters of the water column (8 to 11-m depth).

DIC was determined by the gas-headspace procedure of Stainton

(1973). Fifteen ml of subsamples in syringes were acidified with 0.1 ml 1N HCl to protonate bicarbonate and sulfide ions, then 15 ml of He gas was added; the syringes were shaken for sixty seconds. The partitioned headspace gases were analyzed on a dual column (Poropak Q, molecular sieve) Schimadzu gas chromatograph against both DIC and bottled gas standards. This method was tested extensively with standards from several sources and replicate samples for DIC and methane agreed within 6% and 10%, respectively. DIC calculated from pH and ANC is slightly higher (typically 10%) than DIC measured directly; this difference is to be expected when organic anions contribute to the ANC. Inorganic anions were determined on a Dionex ion chromatograph. Major cations were determined by atomic absorption. Acid-soluble iron and manganese were determined from unfiltered, water samples acidified with HCl to pH < 2.2, and analyzed by ICP plasma emission spectrometry. Dissolved oxygen was determined by Winkler titration. A standardized Beckman pH meter equipped with separate pH and reference electrodes was used to determine pH and acid neutralizing capacity (ANC) by the Gran titration method (Gran 1952). Methane ebullition was measured by collecting bubbles continuously in inverted funnel traps (diameter 82.5 cm) based on the design of Chau et al. (1977). Each funnel trap had a 2-liter bottle for gas storage with a plastic, gas-sampling tube running from the top of the bottle to the surface of the lake where the tube was sealed with a three-way stopcock attached to a subsurface float (Mattson 1989). The traps were sampled every 2 to 6 days and the gas returned to the lab for analysis within 2 hours. The gases were analyzed as described above (also see Mattson 1989).

Chamber studies

Benthic chambers were used to calculate redox electron budgets for epilimnetic sediments. The chambers were constructed from sections of PVC pipe (44.4 cm dia.) and contained 22 liters of water when the chambers were inserted into the sediments. To minimize disturbance, the chambers without lids, were placed in the sediments 24 hours prior to the beginning of incubation experiments. The lids were replaced and samples for redox-active, chemical species were taken at 0 and 24 hours and analyzed as described above for hypolimnetic studies. Four chambers were used in each incubation experiment.

In vitro incubations

During 1987 homogenized seston (5.2 mmol C/L) collected from sediment traps was incubated in 24 glass jars with no headspace. Eight of the jars had 1-ml washed sandy sediments added. The jars with silicone grease applied to the lips had plexiglass lids fitted with dual three-way stop-cocks (Pharmaseal) and were screwed on tightly. To monitor the initial oxygen consumption rate the same suspension was also placed in a BOD bottle with a probe attached to a calibrated oxygen meter. The jars were incubated in the dark at 19 °C on a shaker table which gently shook the jars for 30 minutes every four hours.

After 26 hours the dissolved oxygen was depleted to less than 30 μM and six jars were sampled for dissolved gases and ions as described previously. The remaining 18 jars were divided into three treatments: Two replicate aerobic series, I and II; Two replicate anaerobic series without mineral sediments, anaerobic I and II; and two replicate anaerobic series with mineral sediments, anaerobic III and IV. The anaerobic jars were also injected with a tiny amount (100 μL) of anoxic porewater from Mirror Lake as a seed source for anaerobic bacteria. A 5-ml gas headspace was flushed and analyzed periodically by injecting fresh gas (either air or He, depending on treatment), and the jars were destructively sampled for complete chemistry on days 7, 35 and 70. Details are available in Mattson (1989).

Calculations

The accumulation of DIC is assumed to represent the net oxidation of organic carbon to CO_2. The net electron budgets were calculated from the mass balance of DIC compared to the equivalent balance of dissolved inorganic chemical species based on the equations of Richards (1965) (Table 1) modified as described by Mattson (1989). Since nitrate does not accumulate in the lake (it is often below the limit of detection) the equations used here imply that organic nitrogen (R-NH_3) is neither oxidized nor denitrified. In addition, ammonium (NH_4^+) does not accumulate in the lake and is very low in concentration (2 μeq/L) (Likens et al. 1985) and we assume it is insignificant in the alkalinity and electron budgets.

We tested for the possibility that sulfides present in samples could oxidize during storage and add to measured sulfate concentrations. Hydrogen sulfide was not detected in the gas samples and comparisons of hypolimnetic sulfate concentrations in the sulfide-stripped samples vs regular samples showed no significant differences. We conclude that sulfides were insignificant and did not interfere with later measurements of sulfate. In any case, sulfate reduction was determined from the depletion of sulfate, rather than sulfide accumulation. Reduced sulfur in Mirror Lake sediments is present as iron minerals (mostly pyrite, see Giblin et al.

Table 1. REDOX REACTIONS. A summary of simplified redox reactions involved in the decomposition of organic matter in aquatic systems. The DIC equivalents per mole may be positive or negative depending on whether or not the measured species is a product or reactant (see Mattson 1989).

REACTION # 1 TYPE: AEROBIC $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 106\ O_2$	REACTANT SPECIES: O_2; DIC EQUIVALENTS PER MOLE: −1 $> 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 106\ H_2O$
REACTION # 2 TYPE: DENITRIFICATION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8\ HNO_3$	REACTANT SPECIES: NO_3^-; DIC EQUIVALENTS PER MOLE: −1.25 $> 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 42.4\ N_2 + 148.4\ H_2O$
REACTION # 3 TYPE: MANGANESE REDUCTION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 212\ MnO_2 + 424\ H^+$	PRODUCT SPECIES: Mn^{2+}; DIC EQUIVALENTS PER MOLE: 0.5 $> 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 212\ Mn^{2+} + 318\ H_2O$
REACTION # 4 TYPE: IRON REDUCTION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 424\ FeOOH + 848\ H^+$	PRODUCT SPECIES: Fe^{2+}; DIC EQUIVALENTS PER MOLE: 0.25 $> 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 424\ Fe^{2+} + 742\ H_2O$
REACTION # 5 TYPE: SULFATE REDUCTION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53\ SO_4^=$	REACTANT SPECIES: $SO_4^=$; DIC EQUIVALENTS PER MOLE: −2 $> 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 53\ S^= + 106\ H_2O$
REACTION # 6 TYPE: IRON & SULFATE REDUCTION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 47.1\ FeOOH + 47.1\ SO_4^= + 94.2\ H^+$	REACTANT SPECIES: $SO_4^=$; DIC EQUIVALENTS PER MOLE: −2.25 $> 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 47.1\ FeS + 176.6\ H_2O$
REACTION # 7 TYPE: METHANOGENESIS $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$	PRODUCT SPECIES: CH_4; DIC EQUIVALENTS PER MOLE: 1 $> 53\ CO_2 + 16\ NH_3 + H_3PO_4 + 53\ CH_4$
REACTION # 8 TYPE: FERMENTATION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$	PRODUCT SPECIES: DOC; DIC EQUIVALENTS PER MOLE: 0.5 $> 35.3\ CO_2 + 16\ NH_3 + H_3PO_4 + 35.3\ C_2H_5OH$
REACTION # 9 TYPE: HUMIFICATION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$	PRODUCT SPECIES: DOC; DIC EQUIVALENTS PER MOLE: 0.5 $> 35.3\ CO_2 + (C_2H_5OH)_{35.3}(NH_3)_{16}H_3PO_4$
REACTION # 10 TYPE: MAGNETITE FORMATION $(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 1272\ FeOOH$	PRODUCT SPECIES: Fe_3O_4; DIC EQUIVALENTS PER MOLE: 0.25 $> 106\ CO_2 + 16\ NH_3 + H_3PO_4 + 424\ Fe_3O_4 + 742\ H_2O$

1990). For the purposes of calculating the summer stratification electron budget we will assume the sulfur is stored as iron sulfides (Equation 6 in Table 1). Fe and Mn were measured on acidified, unfiltered water samples which we assume represent the reduced forms. Thus, in our calculations we are maximizing the possible electrons attributed to Fe and Mn reduction reactions. All of the assumptions listed may result in overestimates of the reduction rate of electron acceptors and thus our conclusions with respect to the missing electron acceptors (or equivalently, the calculated excess DIC) will be conservative.

Mass balances for dissolved chemical species DIC, O_2, $SO_4^=$, Fe, Mn, and CH_4 were calculated for the hypolimnetic volume below 8-m (the 8-m hypolimnion). Since lake volume, temperature, and chemistry change rapidly with depth, but are relatively linear below 8 m we used linear interpolation to correct for changes in concentrations due to changes in lake level before mass balances were calculated. These corrections were small (e.g. maximum adjustment for DIC was less than 10 percent). The volume of the lake was estimated in 0.2-m depth intervals from a curve of area vs depth, and mass balances for each 0.2-m depth interval was calculated by the product of the average interpolated concentration and the volume (Mattson 1989). For example, the 8.2—8.4-m depth interval was calculated from the concentrations interpolated from the 8-m and 9-m data. For depths below 10 m, the 10-m concentrations were used.

Since the upper boundary of the hypolimnion is arbitrary, the calculations were repeated for the 9 to 11-m volume to determine the effect of the choice of the upper boundary of the hypolimnion on the conclusions. Sampling dates are reported as the day of the year, where 1 = 1 Jan.

The eddy diffusion transport of ions across the upper hypolimnetic boundary were calculated from the slope of the concentration profiles multiplied by the respective coefficients of eddy diffusion. Eddy diffusion coefficients were calculated from the heat-flux gradient method of Jassby and Powell (1975) as described in Mattson (1989). Methane ebullition loss rates were added to the methane accumulation rates in the hypolimnion when calculating net methane generation.

Decomposition rates for the chamber incubations were calculated from simple mass balances within the chambers and expressed as DIC equivalents on an areal basis. For jar incubations the change in mass calculations also included the collected headspace gases. For each jar, the total change in mass of each redox-active species was used in the calculations of the electron budgets for the jars and the results presented as μM DIC equivalents.

Results

Chemical profiles

In all years DIC concentrations in the hypolimnion increased far more than dissolved oxygen concentrations decreased. An example of the chemical profiles in the lake are shown for the summer of 1987 in Fig. 1. In 1985, 1986 and 1987, DIC concentrations at 10 m increased by 314, 444 and 544 μM, respectively, compared to decreases in oxygen concentrations of 0, 191 and 71 μM, respectively. Sulfate was depleted by approximately 25 μM at the 10-m depth during the late summer in each of the years of the study. Dissolved methane never appeared in the hypolimnetic waters until the onset of anoxia. Maximum concentrations of dissolved methane (87 μM at the 10-m depth) occurred on 20 Sept. 1985, just prior to overturn. Significant concentrations of acid-soluble iron appeared only at the 10-m depths during late stratification, reaching a maximum concentration of 136 μM on day 253 in late summer of 1987. Acid-soluble manganese never exceeded concentrations of 20 μM even at the deepest depths and can be considered negligible in terms of the electron budget.

Methane ebullition

No measurements were taken in 1985, but for the purposes of calculating the electron budget we estimated methane ebullition from the dissolved methane and the ratio of methane ebullition to dissolved methane accumulation in later years. In 1986 and 1987 rates were low, averaging 0.09 and 0.32 mmol m^{-2} d^{-1} during summer stratification, respectively. Ebullition accounted for about one half (50—56%) of the net methane efflux from the hypolimnetic sediments during these periods. Rates of ebullition tended to increase until overturn, at which time rates sharply declined. All sites of methane ebullition exhibited a marked synchrony in the timing of bubble release which was significantly related to changes in air pressure associated with passing storm systems (Mattson & Likens 1990).

Electron budgets

The electron balance for the three years is presented as a time series for both the 8 to 11-m (Fig. 2 panels a, c, and e) and 9 to 11-m (Fig. 2 panels b, d, and f) hypolimnia. Both the 8 to 11-m and 9 to 11-m hypolimnetic electron budgets were never balanced in any year. In all cases rates of DIC accumulation exceeded the combined rate of reduction of the electron acceptors. In general, the budgets were unbalanced only slightly during early stratification, but as the dissolved oxygen was depleted, large electron imbalances occurred, with a 10 to 67 percent excess of DIC production.

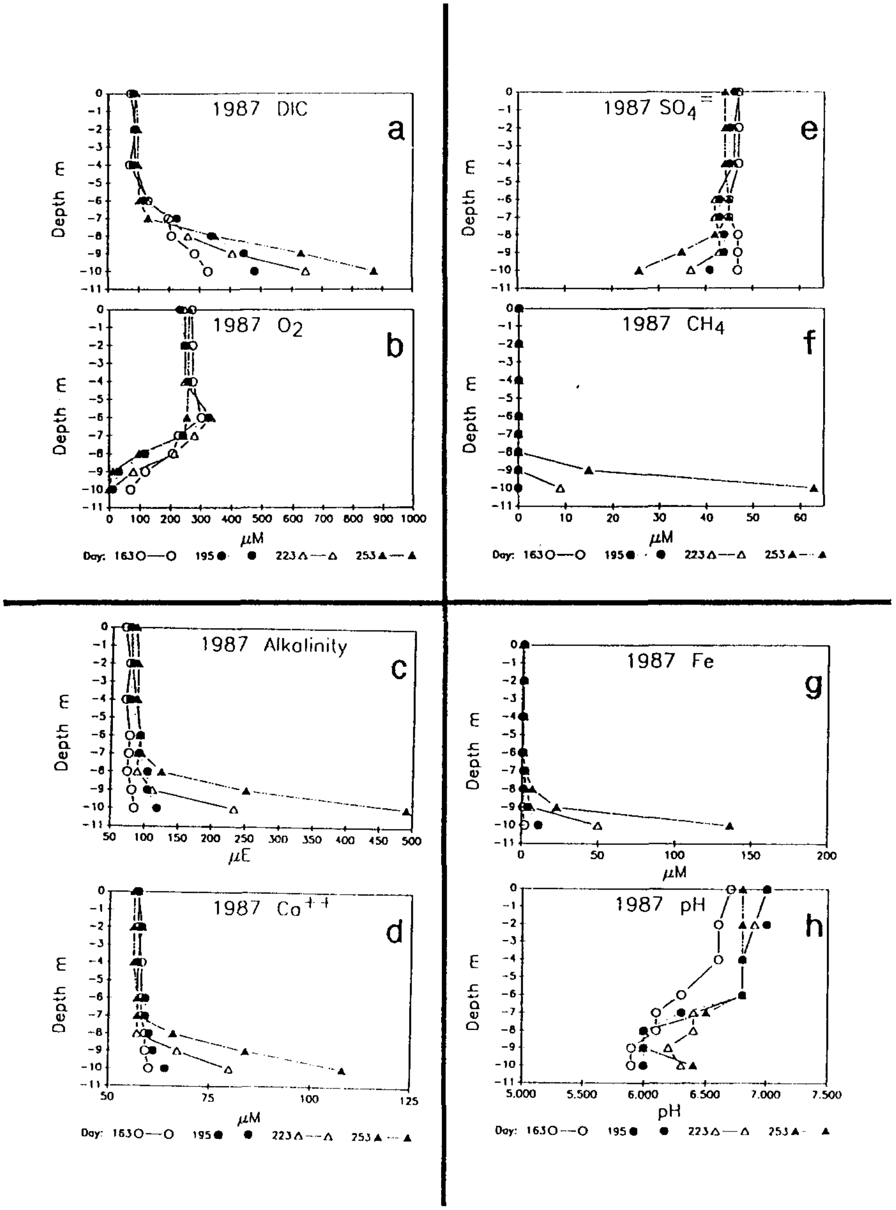

Fig. 1. Profiles of selected chemistry in Mirror Lake during summer stratification of 1987. Symbols and day of year are given in each panel. Panels: a — DIC; b — O_2; c — Alkalinity; d — Ca^{+2}; e — $SO_4^=$; f — CH_4; g — Acid soluble iron; h — pH.

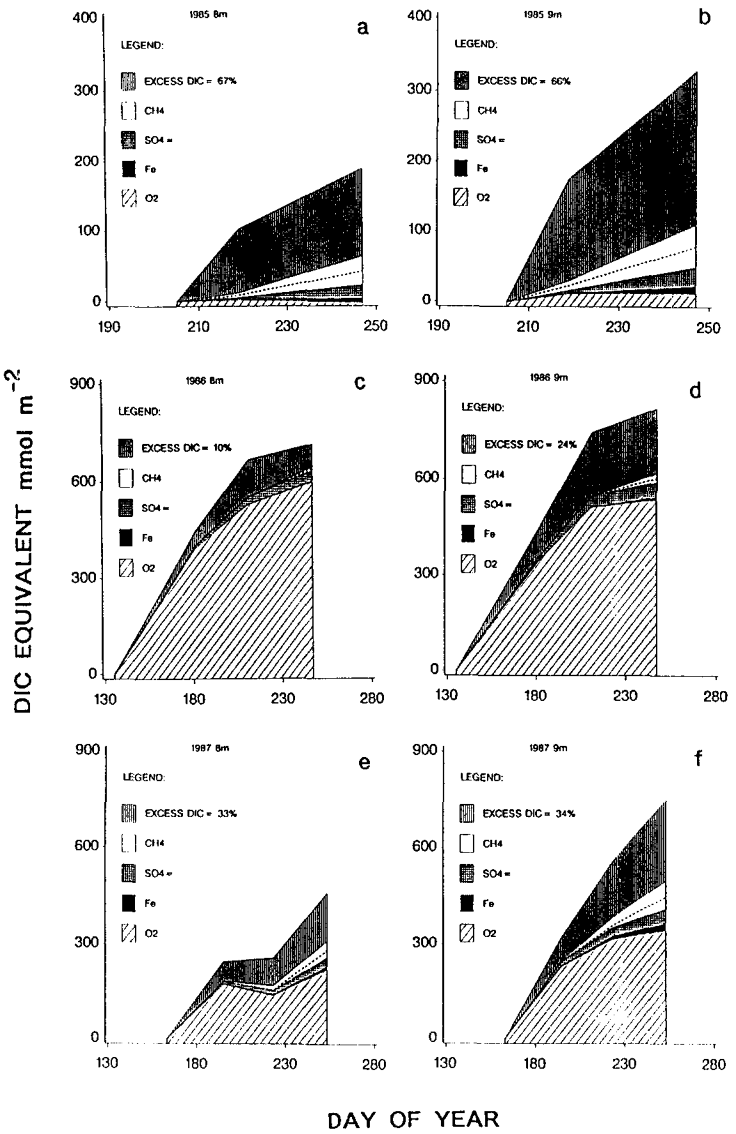

Fig. 2. Organic decomposition accounted for by various electron acceptor reactions in the 8—11 and 9 to 11-m hypolimnion of Mirror Lake during 1985—1987. The top line indicates the amount of DIC production observed during sampling intervals shown as day of year on the abscissa. Each of the shaded areas represents the DIC accounted for by the indicated electron acceptor or end-product in order from the bottom of the graph: oxygen, iron, sulfate, methane (dotted line separates the dissolved methane, below, from methane ebullition above). The excess DIC production unaccounted for by the various electron acceptors for the summer period is shown as vertical shading above the electron acceptors. Panels a, c and e show results for the 8 to 11-m hypolimnion and panels b, d, and f show results for the 9 to 11-m hypolimnion for the years 1985, 1986 and 1987 respectively.

1985

In 1985 the bottom waters of the lake were nearly anoxic by the time of the first chemical sampling on day 205. Apparently the lake did not circulate fully in the spring which may account for the low dissolved oxygen concentrations observed in this year. The observed decomposition rates were only 4.5 and 6.2 mmol m^{-2} d^{-1} for the 8 to 11-m and 9 to 11-m hypolimnia, respectively, somewhat lower than those measured in 1986 and 1987. The mass of DIC produced was lower in 1985 because of the shorter time between sample collections. By the time of the first collection, the hypolimnion was for the most part anoxic, and the final electron balance showed a large excess of DIC; 67% and 66% of the total in the 8 to 11-m and 9 to 11-m hypolimnia, respectively. The overall decomposition rate appeared to be decreasing toward the end of the stratification period (Figs. 2a and 2b).

1986

The electron balance for 1986 was also unbalanced, but to a lesser degree than in 1985. For example, the excess DIC was 24% in the 9 to 11-m hypolimnion and only 10% in the 8 to 11-m hypolimnion. An imbalance of this magnitude ($<10\%$) may be due to cumulative errors in the analysis (see Mattson 1989).

The overall decomposition rate was 7.3 mmol DIC m^{-2} d^{-1} for the 9 to 11-m hypolimnion, but a decline in the rate was observed after day 211 which coincided with the abrupt decrease in the oxygen consumption rate (Fig. 2d). A similar drop in the DIC accumulation rate can also be seen in the 8 to 11-m hypolimnion (Fig. 2c).

1987

During 1987, DIC showed a linear accumulation in the 9 to 11-m hypolimnion at an overall rate of 8.3 mmol m^{-2} d^{-1} with only a slight decline in the rate during late summer (Fig. 2f). Oxygen consumption accounted for 72% of the carbon oxidation during the early summer, but declined to only 46% by the end of summer stratification. During the late summer, as oxygen was depleted, other electron acceptors such as sulfate, iron and methane each accounted for small percentages of total decomposition, 6%, 3% and 12%, respectively, but a large excess of DIC (34%) was unexplained (Fig. 2f).

During 1987 the overall decomposition rate for the 8 to 11-m hypolimnion was 5.1 mmol DIC m^{-2} d^{-1}, slightly less than that estimated for the deeper (9 to 11-m) hypolimnion. The budget was again unbalanced with a 33% excess of DIC over the known electron acceptors. The temporal pattern of decomposition in the 8 to 11-m hypolimnion was similar to that observed at 9 to 11-m except that there was an obvious break in the hypolimnetic accumulation rate of DIC between days 195 and 223 (Fig. 2e). At the 8 m and 9 m depths during this time interval, DIC decreased in concentration while dissolved oxygen increased (Figs. 1a and 1b).

Chamber studies

Results from benthic chambers showed excellent replication between the four chambers and only averages are presented here. In general, the proportions of DIC production accounted for by the various electron acceptors was similar to the hypolimnetic studies. The overall rate of decomposition was higher in the chamber studies and appeared to be related to the presence of organic material on the sediment surface. Two shallow sites with leaf detritus and all sites below 6 m (organic surface sediments) had decomposition rates greater than 15 mmol m^{-2} d^{-1}. The shallow sites with inorganic sediments all had decomposition rates less than 13 mmol m^{-2} d^{-1}. The 24-hour electron balance for all the sites is shown in Fig. 3. Oxygen was the major electron acceptor as expected, but in sites with relatively high decomposition rates there was a large excess of DIC production.

In vitro jar results

The decomposition rates were much higher in the aerobic jars (3500 μM DIC in 70 days) than in the anaerobic jars (810 μM DIC in 70 days) as shown in Fig. 4. Some sulfate depletion was seen at day 70 in the aerobic jars suggesting that they became anoxic despite the air flushing. We did not calculate electron budgets for the aerobic jars and we assume oxygen accounted for the high decomposition rates. The electron budgets for the anaerobic jars were very similar to that in hypolimnetic studies and benthic chamber studies. Initially the decomposition rates were high and the initial supply of dissolved oxygen could account for all the DIC. After the first day however, the anaerobic jars were depleted of dissolved oxygen and the decomposition rates slowed (Fig. 4). By day 7 a large portion of the DIC could not be accounted for by the measured electron acceptors. Between day 7 and 35 the sulfate was depleted and methane began to increase and subsequently accounted for the remaining DIC production until the end of the incubation on day 70. There was no effect

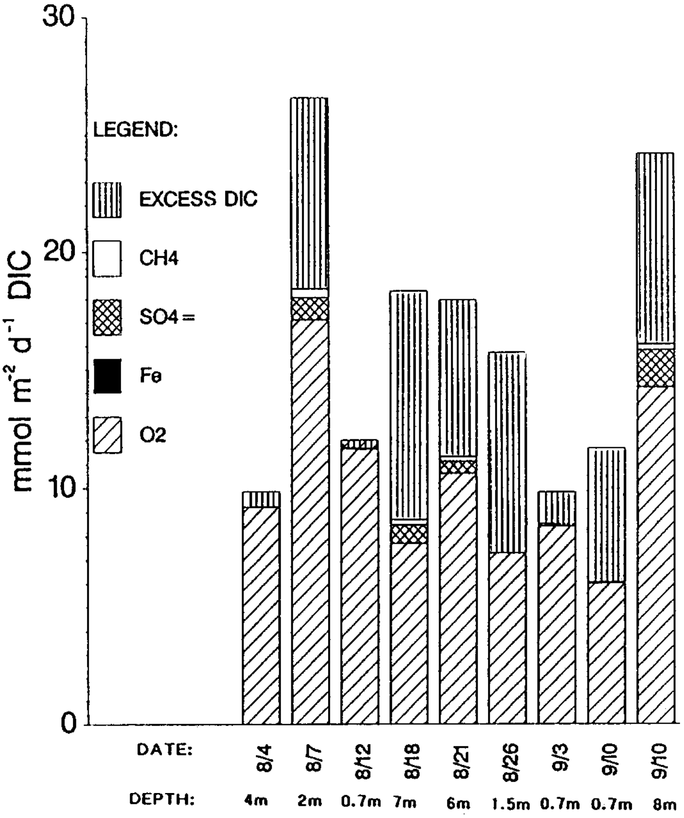

Fig. 3. Organic decomposition accounted for by various electron acceptor reactions during chamber incubations over shallow water sediments in Mirror Lake during 1986. The chambers replicated very well (average coefficient of variation for the decomposition rate was 10%) and only the averages for each site are presented. Month and day of the incubation are indicated below each bar along with the water depth at the site. Shading for each of the electron acceptors as in Fig. 2.

of the addition of mineral sediments to the jars other than the appearance of a tiny amount of dissolved iron (ca 1% of the DIC production).

Discussion

Previous studies in Mirror Lake

The average 8 to 11-m hypolimnetic decomposition rate of 5.3 mmol DIC m^{-2} d^{-1} reported here agrees well with a previous estimate of 5.6 mmol

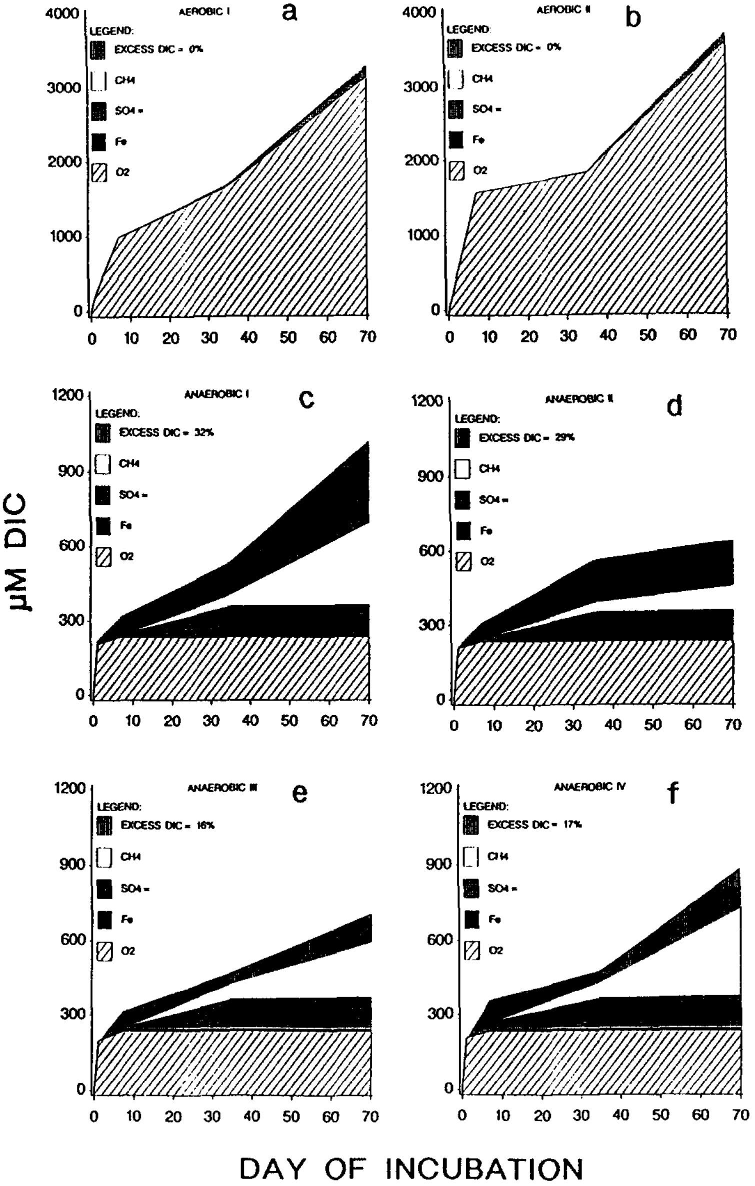

Fig. 4. Incubation studies of seston decomposition accounted for by various electron acceptor reactions. The results are presented in μM DIC equivalents with shading as in Fig. 2. The top two panels (a and b) are the incubations with air added periodically. The middle two panels (c and d) are anaerobic incubations, and the bottom panels (e and f) are anaerobic incubation with 1 gm of mineral sediment present.

DIC m^{-2} d^{-1} determined by CO_2 accumulations in sediment cores, within the hypolimnion and under the ice of Mirror Lake (Jordan et al. 1985). It is higher than the rate of 3.5 mmol DIC m^{-2} d^{-1} estimated by Caraco et al. (1988), however they did not include eddy diffusion losses of DIC from the hypolimnion, which we assume would increase their estimate of DIC production by about 47 percent and thus would agree closely with our results. Our estimate is much lower than the decomposition rate of 25.25 mmol m^{-2} d^{-1} reported for the hypolimnion (below 7-m) of Mirror Lake by Rich & Devol (1978). Rich & Devol (1978) used the McEwen method (see Hutchinson 1941) to estimate the eddy diffusion coefficient at 7-m but this method has been shown to be in error by Powell & Jassby (1974). Thus Rich & Devol's (1978) estimate of eddy diffusion transport of DIC may be erroneously high.

The electron imbalance

The electron budget for the hypolimnion does not balance for either the 8 to 11-m or the 9 to 11-m hypolimnia during any of the budgetary periods. The excess DIC appears to be larger in the deeper hypolimnion and in the latter stages of stratification. These observations suggest that excess DIC is related to anoxic conditions which predominate at depth in late stratification. More importantly, conclusions based on hypolimnetic electron budgets are sensitive to the time period and the upper boundary chosen for the hypolimnion, and extrapolations of these results should be made with caution. The slight decline in the decomposition rates at the end of the summer stratification period may be due to the slower kinetics of decomposition under anoxic conditions (Alexander 1971; Otsuki & Hanya 1972; but also see Howarth & Hobbie 1982).

Alkalinity constraints

The generation of alkalinity (ANC) provides an independent check on the electron balance because many of the redox active ions also affect alkalinity (e.g. Giblin & Howarth 1984; Carmouze 1986; Anderson & Schiff 1987; Schafran & Driscoll 1987; Kelly et al. 1988). The overall rate of alkalinity generation below 8 m was 2.3 and 1.8 meq m^{-2} d^{-1} during 1987 and 1986 respectively. Measured alkalinity increased as much as 406 μeq l^{-1} at the 10-m depth during 1987.

Most of the alkalinity generation can be accounted for by changes in the measured base cations and strong acid anions as shown in Fig. 5 for 1987 between days 163 and 253. Slightly underestimated on day 194 and overestimated on day 223, by day 253 the alkalinity generation as

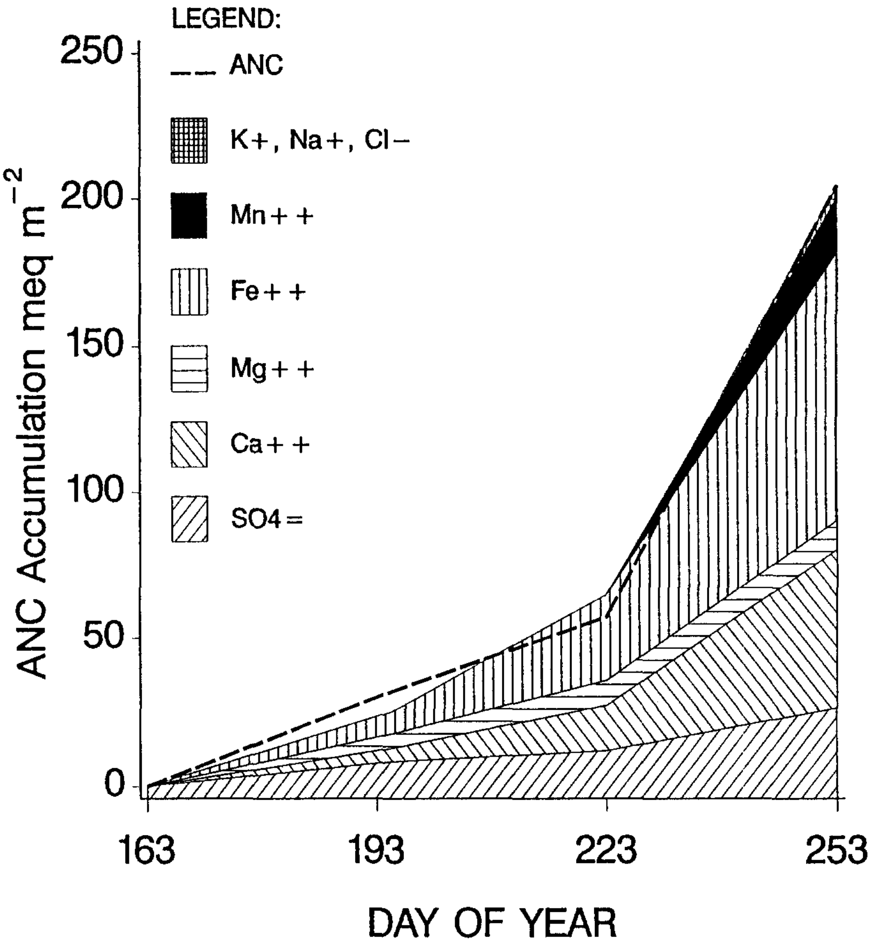

Fig. 5. ANC generation in the 8 to 11-m hypolimnion of Mirror Lake during 1987 from day 163 through 253. The solid areas represent alkalinity generated from accumulation of base cations and depletions of acid anions. Titration ANC is shown as a dashed line.

measured by Gran titration was accounted for to within 1%, with most of the generation occurring in the latter stages of summer stratification (Fig. 5). The increases in alkalinity could be accounted for by increases in iron (44.4 percent), magnesium (4.9 percent), calcium (26.5 percent), and manganese (9.3 percent). The depletion of sulfate could account for an additional 12.9 percent. The remaining 2% was due to small changes in potassium, sodium and chloride concentrations (J. S. Eaton, unpub. data). Due to the relatively high pH of the hypolimnion (6—6.5) we do not expect aluminum to be significant in the alkalinity budget (Schafran & Driscoll 1987). Because the alkalinity budget balances and all of the above mentioned ions are either accounted for in our electron budget or do not participate in redox reactions we conclude the excess DIC generation (2.0 mmol m^{-2} d^{-1}) is due to a process which does not generate alkalinity.

Benthic chambers

The high rate of decomposition observed in shallow sediments (average 16.3 mmol m^{-2} d^{-1}) compares well with previous chamber studies in this lake (Walter 1985) and is considerably higher than the average hypolimnetic rates for the 8 to 11-m and 9-m hypolimnetic sediments (5.3 and 7.3 mmol m^{-2} d^{-1}, respectively). The higher rates may be due to higher temperatures and higher dissolved oxygen concentrations in the epilimnion (Likens 1985). Large production of excess DIC was seen only when decomposition rates exceed 15 mmol m^{-2} d^{-1} in organic-rich sediments. Apparently the rate of oxygen diffusion into the sediments at these shallow sites was not rapid enough to maintain aerobic decomposition.

Jar experiments

The jar experiments show that algal decomposition is faster under oxic conditions, a finding also reported by Otsuki & Hanya (1972). The electron budget showed similar patterns to those observed in the lake. Initial high rates of decomposition can be accounted for by oxygen: The average RQ was 0.98 ± 0.13, which is not different from the DIC/O_2 ratio of 1 as shown in Table 1. In the anaerobic jars the excess DIC averaged 23.5% by the end of the experiment, but it is interesting to note that most of this excess DIC appeared immediately after anoxia and prior to sulfate reduction and methanogenesis. This sequence would be expected since sulfate reducers require simple organic acids (Brock 1979) which are the products of fermentation. Later in the incubations it appears that methanogenesis can account for most of the DIC production.

Comparison to other lakes

We could find only three other studies which have relatively complete hypolimnetic budgets for redox active chemical species (Jones & Simon 1980; Schafran & Driscoll 1987; Kelly et al. 1988). All of these studies used similar stoichiometric equations for the major electron acceptors (Table 1), based on the work of Richards (1965). The analysis of Kelly et al. (1988) was balanced by difference, assuming the stoichiometric coefficient for methanogenesis is variable (between 0.4 and 1.4 per unit DIC). With carbohydrate type carbon it is impossible to obtain a ratio other than

1 unless an additional reduced (or oxidized) carbon end product is included as shown in reactions 8 or 9 of Table 1. In our reanalysis of Kelly et al. (1988), we have assumed that the net production ratio of DIC to methane during decomposition is 1.0. Furthermore, for the data reported by Kelly et al. (1988), we have assumed that the nitrate produced from the oxidation of organic matter was subsequently denitrified, since the mass of nitrate nitrogen decreased rather than increased in their study. The resulting data are summarized in Table 2. Manganese reduction is omitted from the table because it contributed less than 1% to the total electron budget in all studies where it was measured.

The overall electron budgets for the lakes compared (Table 2) vary from a 60 percent excess of electron acceptors in Lake 226N, Ontario, to a 37 percent deficit in Mirror Lake. Only the study of Dart's Lake in the Adirondack Mountains of New York, balances within 1 percent (Schafran & Driscoll 1987). Dart's Lake is the only lake studied that had dissolved oxygen continuously present throughout the hypolimnion, and this may be an important factor in the balance of the electron budget. The large discrepancies in the electron budgets for Mirror Lake occurred after dissolved oxygen was depleted.

The Canadian lakes studied by Kelly et al. (1988) have much higher percentages of decomposition attributed to methane production than the other, presumably more oxic lakes which show dissolved oxygen to be the major electron acceptor. Sulfate reduction also appears to be higher in the Canadian Lakes. Nitrate reduction is variable, but always less than 20 percent. Iron reduction also appears to be negligible in the DIC production of the lakes (Table 2).

Possible errors

Possible explanations for the budget discrepancy in Mirror Lake fall into three categories: (1) Non-organic sources of DIC, including groundwater inputs, eddy diffusion inputs from the epilimnion and carbonate dissolution from the sediments. (2) Calculation errors including analytical errors, sampling errors and errors in stoichiometry. (3) Alternate electron acceptors and/or storage of reduced products in sediments.

Sodium budgets indicate that groundwater inputs are not significant in the hypolimnion, therefore, DIC inputs from groundwater are also unlikely (Mattson 1989). Previous studies have also indicated that significant seepage through the thick organic sediments lying below the hypolimnion of Mirror Lake is unlikely (Asbury 1990). Carbonates have not been found in Mirror Lake sediments (Likens & Moeller 1985), thus DIC production from carbonate dissolution is unlikely. Errors could occur in

Table 2. Comparison of hypolimnetic electron budgets from several lakes. Data include the carbon sedimentation rate and DIC production rate during summer stratification. The portion of DIC accumulation accounted for by each electron acceptor is given as a percent. Manganese reduction is not reported here, see text for additional details. The percent of total electron acceptors and percent excess DIC may not add to 100 due to rounding errors.

Lake Name	Carbon input	DIC accum.	O_2	$SO_4^=$	NO_3^-	CH_4	Fe	Total	Excess	Reference
	mmol m^{-2} d^{-1}		Electron acceptor as percent of DIC accumulation							
Blelham Tarn	38.2	10.7	42	2	17	25	ND	86	14	Jones & Simon (1980).[1]
L226N	ND	8.10	47	25	13	71	3	160	−60	Kelly et al. (1988).[2]
L227	21.0	7.38	5.5	30	1	68	2	106	−6	" "
L223	ND	7.62	9	30	1	42	6	88	11	" "
Mirror	10.0	5.33	43	7	0	11	2	63	37	This study.[3]
Dart's	ND	4.70	81	4	15	ND	0.2	100	0	Schafran & Driscoll (1987).[4]

[1] Sulfate reduction estimated by sulfide accumulation.

[2] Data for the three lakes recalculated with equations in Table 1. Implied nitrate production from oxic metabolism was added to denitrification estimates.

[3] Average for three years for the 8 to 11-m hypolimnion.

[4] Methane not determined but believed to be negligible, C. Driscoll, pers. comm.

ND = Not Determined.

the estimates of the eddy diffusion exchange of chemicals across the thermocline. The average eddy diffusion calculated for the three summer periods was 0.017 m^2 d^{-1} for the 8-m depth and 0.046 m^2 d^{-1} at 9-m depth (Mattson 1989). In Mirror Lake however, the two major redox-active chemical species (DIC and dissolved oxygen), have nearly identical concentration gradients with opposite slopes. Thus the gain of oxygen generally is balanced by the loss of DIC across the thermocline. As a result, if eddy diffusion were zero over the three years of the study, the estimated average decomposition rate for the 8 to 11-m hypolimnion would decrease from 5.33 to 3.6 mmol DIC m^{-2} d^{-1} (a 32% decline), but the net electron budget would show only a slight increase in the DIC excess, from 37% to 43%. On the other hand, if eddy diffusion were 5-fold higher than estimated, the average calculated decomposition rate would increase to 12.2 mmol DIC m^{-2} d^{-1} and the electron budget would still show an average DIC excess of 27 percent. Thus, it is not likely that errors in the eddy diffusion estimates could account for the excess DIC production. Sampling errors in the vertical location of the sampling tube are small. For example, the average DIC slope at 9 m during 1987 was 152 μM m^{-1} compared to average concentrations of 442 μM. Thus a sampling error of 0.1 m would result in a DIC error of 15 μM, or about 3%. The fact that we see excess DIC production in both chamber and jar experiments also indicates that the results are not due to sampling errors or failures in the assumptions of the hypolimnetic budgets.

Analytical errors are less than 10% for all major ions and an extensive Monte Carlo simulation of analytical error propagation shows that random errors even as great as 20% are not likely to change the conclusions of this study (Mattson 1989). Stoichiometric errors (incorrect assumptions for equations in Table 1) are unlikely to account for the excess DIC since the assumptions made regarding the electron acceptors would tend to overestimate the reduction rates, leading to a lack of DIC with respect to that expected.

Redox reactions between the known, measured electron acceptors would not affect the total electron balance. Some additional, as yet unmeasured, reduced chemical species would need to be exported, or be accumulated in the hypolimnetic waters or sediments and not contribute to alkalinity generation.

The excess DIC accumulates at an average rate of about 2 mmol m^{-2} d^{-1}. This rate of excess DIC accumulation could be explained by the accumulation below the 8 to 11-m depth of an unknown reduced end product with a volume-weighted concentration of 160 μM (expressed as DIC redox equivalent) over a 90-day period. If 2 liters of methane (at 0 °C and 1 atmosphere pressure) were stored per m^2 of sediment in a 90-day period this would account for 50 percent of the excess DIC. Methane stored in the sediments could diffuse out and be oxidized at other times of the year (Rudd & Hamilton 1978).

If other fermentation reactions were occurring in the hypolimnion of Mirror Lake we would expect to observe either an accumulation or a conversion of DOC to a form which is more reduced than the original organic matter. Hypolimnetic DOC concentrations (volume weighted) increased from 206 μM to 241 μM during the three summers. Most of the increase in DOC concentration occurred at the 10-m depth during late stratification. If we assume that 240 μM of DOC were reduced by an average valence of -0.5, we would account for about 20 percent of the excess DIC (see Reaction 8, Table 1).

Electrons may also be stored within reduced forms of particulate organic carbon. Assuming half of all permanently buried carbon were effectively reduced by one electron (an average valence change of -0.5) during three months of the summer stratification period, we would account for a DIC production rate of 2.2 mmol m^{-2} d^{-1}, more than enough to account for the excess DIC production rate.

Another example of a reaction which does not necessarily alter alkalinity would be the bacterial formation of a solid mineral such as magnetite (Lovely et al. 1987). Such reactions would not alter alkalinity in the water column if the DIC were produced as CO_2 (or equivalently $HCO_3^- + H^+$) as in Table 1, and both the oxidized reactant and reduced end product were stored in the sediments (possibly as solid minerals as in reaction 10). However, the accumulation rate of iron in the recent sediments of Mirror Lake (Likens & Moeller 1985; Moeller 1985) could account for only 0.06 mmol m^{-2} d^{-1} of excess DIC even if the entire yearly input of iron were reduced within a 90-day period.

There is a possibility of seasonal formation of reduced iron minerals which are reoxidized during turnover and during the winter. Previous studies have shown that the oxidized zone is shallow (2 cm or less) in other lake sediments (e.g. Mortimer 1971; Kelly & Rudd 1984; Carlton & Wetzel 1988). If one third of all the iron to a depth of 2 cm were reduced in a 90-day period (and later reoxidized), iron reduction would account for about 0.8 mmol m^{-2} d^{-1} DIC production (about 40 percent of the excess DIC). Again, such a seasonal reduction and reoxidation of iron particulates (e.g. ferric oxyhydroxides ↔ magnetite; reaction #10 in Table 1) in the surface sediments would not affect the alkalinity budget of the water column since both the reactant and product are iron minerals stored as solids in the sediments. A similar seasonal reduction and reoxidation system already has been described for a salt marsh system for sulfur as well as iron (see Howarth & Teal 1979, and Giblin & Howarth 1984).

We have considered several possibilities to explain the excess DIC. The most likely possibilities include seasonal iron reduction in the sediments and the storage of reduced organics, probably as a combination of gaseous (methane), dissolved, and particulate forms. Future studies should include measurements of iron reduction rates in the sediments and measurements of the changes in the C:H:O ratio of organic matter in Mirror Lake during summer stratification.

Summary

Decomposition in the hypolimnion of Mirror Lake is highly variable from year to year and these differences appear to be related to the dissolved oxygen supply. The accumulation rate of DIC is relatively rapid and linear when dissolved oxygen is present (typically during early stratification). When dissolved oxygen is present most of the oxidation of organic carbon can be accounted for by redox transformations of known electron acceptors in the water column. However, once oxygen is depleted at the bottom of the hypolimnion, the rate of DIC accumulation tends to decline slightly and the redox reactions of the known electron acceptors cannot account for the oxidation of organic carbon.

During the three summers of this study an average of 63 percent of the decomposition in the hypolimnion of Mirror Lake could be accounted for (mainly by oxygen), while 37 percent remains unexplained. It is unlikely that errors in the calculations could result in the magnitude of the observed discrepancies. The results imply that additional, as yet unknown redox reactions are occurring, and these reactions probably are associated with the storage of reduced compounds in the sediments.

Over 90 percent of the alkalinity generated within the hypolimnion of Mirror Lake can be accounted for by changes in concentrations of iron, calcium, manganese and sulfate. Therefore, the excess DIC probably is due to a process which does not produce alkalinity. These process could include seasonal solid phase iron and manganese reduction, as well as the accumulation of reduced organics. Of these, we believe the most likely possibility to explain the excess DIC is the accumulation of reduced organics.

The electron budgets of several other lakes reported in the literature vary considerably, with some lakes showing an excess of DIC, and some showing an excess of electron acceptors (Table 2). The electron budgets of these lakes are more nearly in balance when oxic conditions prevail, a trend we also observed in Mirror Lake. The imbalance in our electron budgets suggest that the assumptions typically made during hypolimnetic studies are in error. In particular, carbon budgets based on the balance of electron acceptors may be in serious error. Our models for decomposition in anoxic freshwater systems may have to be re-evaluated to include such non-traditional decomposition pathways such as fermentation.

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