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Disruption of sulfur cycling and acid neutralization in lakes at low pH

C. A. KELLY[1], J. A. AMARAL[1], M. A. TURNER[2], J. W. M. RUDD[2],
D. W. SCHINDLER[3] and M. P. STAINTON[2]
[1] *Department of Microbiology, University of Manitoba, Winnipeg, Manitoba R3T 2N2;*
[2] *Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, Manitoba R3T 2N6;*
[3] *Departments of Zoology and Botany, University of Alberta, Edmonton, Alberta, Canada*

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Abstract. Experimental acidification of a softwater lake to below pH 5 fundamentally changed the sulfur cycle and lowered internal alkalinity generation (IAG). Prior to reaching pH 4.5, the balance of sulfur reduction and oxidation reactions within the lake was in favour of reduction, and the lake was a net sink for sulfate. In the four years at pH 4.5 the balance of reduction and oxidation reactions was in favour of oxidation, and there was a net production of sulfate (SO_4^{2-}) within the lake. Evidence indicating a decrease in net SO_4^{2-} reduction at pH 4.5 was also obtained in an anthropogenically acidified lake that had been acidified for many decades. In both lakes, the decrease in net SO_4^{2-} reduction appeared to be linked not to a simple inhibition of SO_4^{2-} reduction but rather to changes in benthic ecosystem structure, especially the development of metaphytic filamentous green algae, which altered the balance between SO_4^{2-} reduction and sulfur oxidation.

At pH's above 4.5, net SO_4^{2-} reduction was the major contributor to IAG in the experimental lake, as it is in many previously studied lakes at pH 5 and above. At pH 4.5, the change in net annual SO_4^{2-} reduction (a decrease of 110%) resulted in a 38% decrease in total IAG. Because of the important role of net SO_4^{2-} reduction in acid neutralization in softwater lakes, models for predicting acidification and recovery of lakes may need to be modified for lakes acidified to pH < 5.

Key words: acidification, alkalinity generation, metaphyton, sulfur, sulfate reduction

Introduction

It has been shown previously that the nitrogen cycle in lakes is disrupted by acidification to pH 5.4–5.6, through inhibition of nitrification (Rudd et al. 1988). Also, the carbon cycle may be affected by inhibition of decomposition at pH 5 and below (McKinley & Vestal 1982; Kelly et al. 1984; Schindler 1990), and by changes in benthic photosynthesis in the littoral zone (Turner et al. 1987; Turner et al. 1991). Inhibition of processes in the sulfur cycle at low pH has not been shown previously, although a previous study indicated unusual patterns in the balance between oxidation and reduction of sulfur species in sediments that were at pH 4.5 (Rudd et al. 1986b).

Sulfate reduction has been recognized as an important acid-neutralization mechanism for a number of years, as shown in whole lake acidification experiments (Schindler et al. 1980; Cook et al. 1986; Rudd et al. 1990; Sampson et al. 1994) and in many anthropogenically acidified lakes (Baker et al. 1988). The term 'sulfate reduction' is most often used to refer to dissimilatory SO_4^{2-} reduction, which is a bacterial process that occurs in lakes in anoxic sediments, both epilimnetic and hypolimnetic (Kelly & Rudd 1984), and leads to the formation of a variety of reduced inorganic and organic sulfur compounds (e.g. Rudd et al. 1986b; Cook & Kelly 1991). This term can also include assimilatory SO_4^{2-} reduction, which serves biosynthetic functions (amino acids, etc.), and which is carried out by both bacteria and algae, in both the water column and the sediments (e.g. Baker et al. 1989; Rudd et al. 1990). In this paper, we will use the term to include both dissimilatory and assimilatory processes, because both result in acid neutralization by the removal of 2 equivalents of H^+ with each equivalent of SO_4^{2-} reduced (e.g. Anderson & Schiff 1987). Thus, both mechanisms can be effective in neutralizing acidity.

Bacterial denitrification and the abiological process of cation exchange of hydrogen ion with base cations in sediments are also important to varying degrees in neutralizing acid inputs to lakes (Schindler et al. 1986; Cook et al. 1986; Schiff & Anderson 1987; Rudd et al. 1990; Kelly et al. 1990; Sampson et al. 1994). Together these in-lake processes can add significantly to acid neutralization that occurs in the watersheds of lakes (Schindler 1986; Cook et al. 1986) and are referred to collectively as internal alkalinity generation (IAG). In-lake processes are more important in lakes that have longer water residence times or are shallower in depth (Baker et al. 1986; Kelly et al. 1987).

Past studies have indicated that net rates of bacterially-mediated IAG increase as SO_4^{2-} and nitrate inputs increase, because both SO_4^{2-} reduction and denitrification are first-order reactions (Cook & Schindler 1983; Kelly & Rudd 1984; Herlihy & Mills 1986; Rudd et al. 1990). These studies have been further developed into models now in use for prediction of acidification of lakes at different acid loadings (Baker et al. 1986; Kelly et al. 1987; Kelly et al. 1990). However, these studies relied on data sets where the lakes were above pH 5. In this paper, we examine the relationship between pH and net annual SO_4^{2-} reduction (the balance between reduction and oxidation over the whole year) as a lake was experimentally acidified from pH 6.7 to 4.5. Changes in the relative contribution of SO_4^{2-} reduction and other-in-lake processes to IAG were measured as the pH was lowered. Also, we studied the role of algal mat development as a contributor to changes in net SO_4^{2-} reduction in this and in an anthropogenically acidified lake (Lake Hovvatn).

Materials and methods

Lake descriptions

Lake 302S is the southern, upstream basin of a double basin lake located in the Experimental Lakes Area, northwestern Ontario. Its area is 10.9 ha, and its mean depth is 5 m. It receives runoff from an undisturbed, forested 43.4 ha watershed. It is separated from the downstream basin (L. 302N) by an island that has shallow sills on each side (4 m and 1.5 m deep), and curtains of polyethylene-covered nylon restrict water circulation between the two basins. This downstream basin (L. 302N) was acidified with nitric acid in 1982–1988 (Rudd et al. 1990).

Experimental acidification of L. 302S began in 1982. The methods of acid addition and water chemistry analyses, chemical budgets and microbial studies obtained on this lake in the years 1981 (pre-acidification) through 1986, are presented in Rudd et al. (1990). Biological results through 1991 are in Schindler et al. (1991); Turner et al. (1987); Turner et al. (1991).

Lake Hovvatn is located in southern Norway, and has been acidified since the 1920's or 1930's (Wright 1985). This lake was sampled in 1984 (Rudd et al. 1986b) and in 1985, reported here.

The method for calculating chemical budgets for L. 302S is described in Rudd et al. (1990). Briefly, measurement of direct precipitation was by continuous bulk collection, with water for chemical analyses taken from collection containers within hours of the end of each wet precipitation event. Water flows from the south to the north basin, and there is a single outflow stream at the north end of the north basin, which is monitored continuously at a V-notch weir. Outflow from the south basin alone was assumed to be 0.53 of the measured outflow from the north basin, because the area of the south basin watershed is 0.53 of the entire lake watershed. Direct runoff to the south basin was estimated by using measured stream flow from a nearby watershed (L. 239 northwest inflow stream) and adjusting for differences in watershed area. The L. 239 northwest inflow (L. 239 NWIF) watershed is similar to the watershed of L. 302S in slope, surficial geology, and vegetation (Rudd et al. 1990).

Chemical analyses of L. 302S outflow were done on a bi-weekly basis, using methods described in Stainton et al. (1977). Watershed runoff was analyzed approximately bi-weekly, depending on flow. Analyses of precipitation were done on an event basis. These analyses, together with precipitation and flow volumes, were used to calculate direct precipitation onto the lake surface, direct runoff, and outflow of ionic species.

In-lake flux (consumption or production of each ionic species within the lake), in units of equivalents per lake basin per year, was calculated from

$$\text{Flux} = \text{change in mass} + \text{outputs} - \text{inputs} \qquad (1)$$

Change in mass (sometimes called change in storage) for each year was determined from the difference in average lake mass measured in the previous year and average lake mass in the year being calculated. Inputs and outputs were determined as described above. When this flux is negative, it means that the ion is being consumed within the lake. When it is positive, the ion is being produced within the lake.

As discussed in Rudd et al. (1990), the major source of uncertainty in the ion budgets and flux calculations is the direct runoff component of the input term in the chemical and water budgets, due to differences between the gauged (L. 239NWIF) watershed and the ungauged (L. 302S) watershed. For chloride ion, which should have little flux (uptake or release) within the lake, the input-output measurements and direct runoff estimates explained 92% of the observed changes in mass of Cl^- within the lake (the mass changed considerably over the years 1980–1992 due to large changes in water residence time). For other ions, where in-lake fluxes may be significant, it is not possible to do the same evaluation. However, mass balance budgets where inputs are natural (i.e. there is not an experimental input), have been estimated in the past to have an uncertainty of about 20% (Rudd et al. 1990). For ions where the inputs are dominated by experimental inputs (in this case H^+ and SO_4^{2-}), flux estimates have a smaller uncertainty because the largest input is the experimental addition, which is accurately known.

The contribution of the flux of each ion to IAG depends on the nature of the ion and its charge. Fluxes that contribute positively to IAG are positive fluxes of base cations and negative fluxes of acid anions (e.g. Cook et al. 1986).

Porewater samples for determination of SO_4^{2-} gradients within metaphytic algal masses and sediments were obtained with polycarbonate membrane (Nuclepore) samplers, with chambers at 1 cm intervals (Hesslein 1976). Membranes were soaked and washed in distilled, deionized (SuperQ) water to remove residual SO_4^{2-}, and the samplers were deoxygenated before insertion into the sediments by diver (Kelly & Rudd 1984). After equilibration (7–10 days), porewater samples were removed using glass syringes and transferred to small glass bottles with screw caps with Teflon septa, which minimized evaporation and contamination prior to analysis by ion chromatography (Dionex).

Table 1. Sulfuric acid additions to L. 302S and time-weighted epilimnetic mean pH's for the years 1980–1990.

Year	kg H_2SO_4	Mean pH
1980	0	6.7
1981	0	6.6
1982	2075.8	6.2
1983	1872.5	5.9
1984	1947.1	5.6
1985	2106.1	5.3
1986	2207.1	5.0
1987	2479.5	4.8
1988	3454.2	4.6
1989	2086.2	4.5
1990	1496.3	4.5
1991	1898.1	4.5

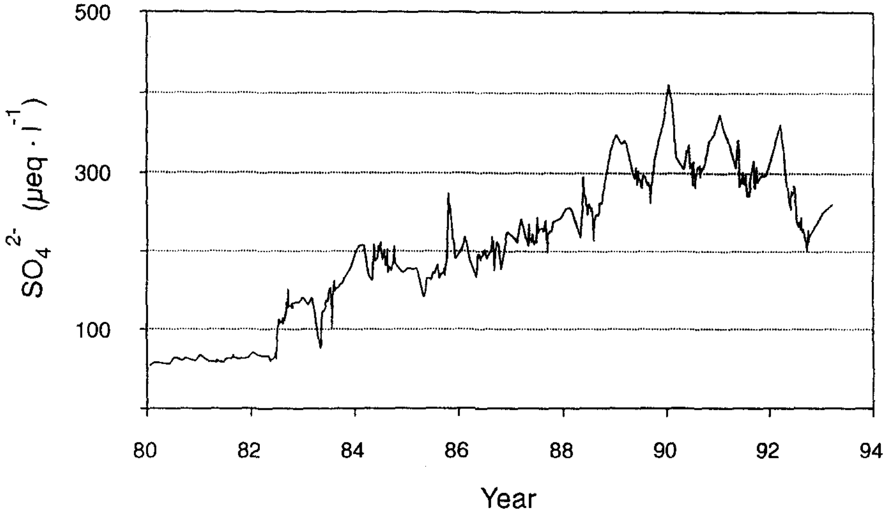

Fig. 1. Epilimnetic (1 m) sulfate concentrations in L. 302S from 1980–1990.

Results and discussion

Whole lake observations

Experimental additions of sulfuric acid to L. 302S decreased the mean, open-water pH from the pre-acidification range of 6.6–6.7 in 1980 and 1981 to pH

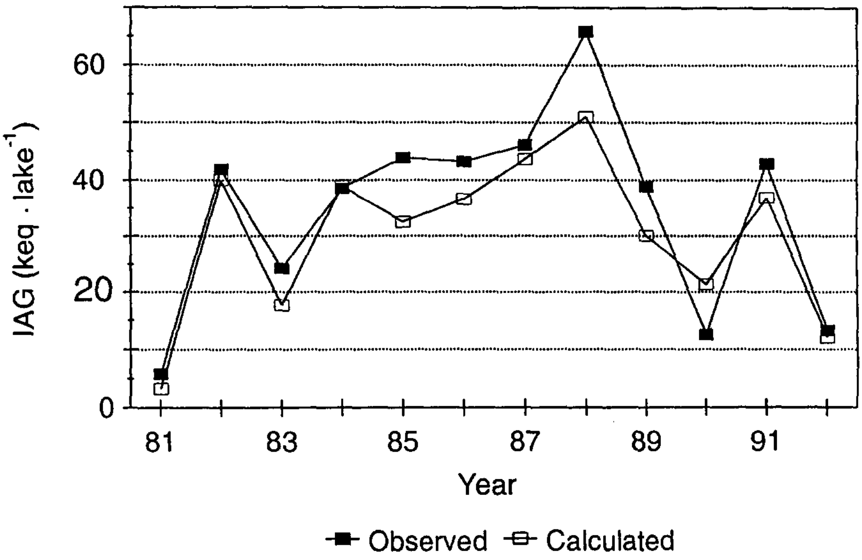

Fig. 2a. Internal alkalinity generation (IAG) calculated by summing the IAG contribution of each individual ion (shown in Fig. 2b) in L. 302S from 1980–1992 (open squares). IAG was also calculated from Gran alkalinity data (closed squares). Sulfuric acid additions were begun in 1982.

4.5 in 1989, where it was held for three years (Table 1). In 1992, acid additions were decreased, allowing the pH to increase to 4.8. Due to the sulfuric acid additions, SO_4^{2-} concentrations generally increased from year to year (Fig. 1).

Each year, the IAG due to within-lake gains or losses of individual chemical species (SO_4^{2-}, Ca^{2+}, NH_4^+, etc.) was calculated as described above, and the sum of IAG from all these species was compared to IAG calculated from the Gran alkalinity analyses (Fig. 2a). Year to year agreement of these two calculations was good ($r^2 = 0.89$; $n = 12$, significant at 1% level).

From the pre-acidification years (1980 and 1981) through the first year at pH 4.5 (1988), net annual SO_4^{2-} reduction generally increased, with some year-to-year variability (Table 2; Fig. 2b). This increase was expected in response to the increase in SO_4^{2-} concentrations (Fig. 1; Baker et al. 1986; Kelly et al. 1987). SO_4^{2-} reduction was the single largest contributor to IAG (61%) during these years (Fig. 2b).

The increase in SO_4^{2-} reduction, and its large contribution to IAG in L. 302S during 1982–88, were similar to a previous experimental acidification (with sulfuric acid) to pH 5 in L. 223 (Cook et al. 1986), where SO_4^{2-} reduction accounted for 85% of IAG. Also, SO_4^{2-} porewater profiles measured in L. 302S during 1982–1986 (Rudd et al. 1990) were similar to profiles measured

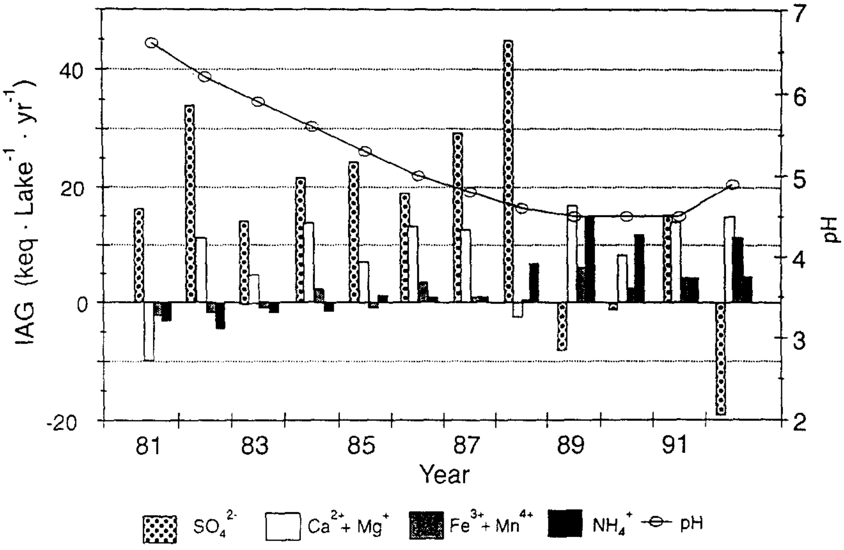

Fig. 2b. IAG due to individual chemical species (bars) and mean annual pH (circles) in L. 302S.

in L. 223 as well as a variety of other acid lakes above pH 5 (Rudd et al. 1986b).

Beginning in 1989, the second year at pH 4.5, there was a marked change in net SO_4^{2-} reduction and associated H^+ consumption (Table 2, Fig. 2b). Rather than net annual SO_4^{2-} reduction within the lake (i.e. negative SO_4^{2-} fluxes), during the years 1989–1992, net annual SO_4^{2-} fluxes were positive in 3 out of 4 years (Table 2). This showed that SO_4^{2-} was being produced within the lake, most likely from oxidation of reduced S stored within the sediments during previous years.

Directly related to this change in net SO_4^{2-} reduction at pH 4.5 was a decline in total IAG (Table 2; Fig. 2a). During the years 1989–92 average IAG was only 26.9 keq/year, 38% lower than during the years 1982–88 when the pH was being lowered from 6.6 to 4.6. Also, rather than contributing positively to IAG during 1989–92, SO_4^{2-} reactions subtracted from IAG (Fig. 2b). The loss of IAG due to the loss of net SO_4^{2-} reduction was somewhat offset by increased IAG from calcium release (in 1989) and ammonium accumulation (in 1989 and 1990; Figs. 2a and 2b). The increased ammonium accumulation was caused by the termination of nitrification below pH 5.6 (Rudd et al. 1988). The reason for the particularly high calcium release in 1989 (Fig. 1) is not known. One possibility is that increased NH_4^+ caused displacement of Ca^{2+}

Table 2. Annual inputs, outputs, change in mass, and flux of chemical species in L. 302S, 1981–1990. All units are keq/lake.

SO_4^{2-}						
Year	Mean mass	Additions	Precipitation	Runoff	Outflow	Flux
1980	31.98	0.00	1.70	10.58	0.13	−9.76
1981	34.27	0.00	1.73	19.43	3.03	−15.85
1982	50.11	42.36	2.52	17.94	13.56	−33.42
1983	74.46	38.21	2.00	8.00	9.76	−14.11
1984	90.90	39.74	2.66	9.30	13.99	−21.26
1985	93.68	42.98	2.14	14.26	32.61	−23.99
1986	107.78	45.04	1.71	5.68	19.77	−18.57
1987	122.06	50.60	1.30	3.65	12.43	−28.85
1988	142.57	70.48	2.05	5.13	12.78	−44.38
1989	172.47	42.58	1.37	8.05	30.19	8.08
1990	186.42	30.54	1.55	4.29	23.28	0.86
1991	172.38	38.74	1.55	9.43	48.94	−14.82
1992	148.86	7.68	2.17	10.26	62.56	18.93
Alkalinity						
1980	33.4	0.00	0.001	0.355	0.000	2.26
1981	36.7	0.00	0.000	0.293	2.82	5.85
1982	28.4	−42.4	−0.806	0.481	7.55	41.9
1983	12.1	−38.2	−0.915	0.466	1.87	24.2
1984	10.3	−39.7	0.175	0.470	1.26	38.5
1985	10.1	−43.0	−0.191	1.570	2.48	44.0
1986	7.04	−45.0	−0.932	0.451	0.829	43.3
1987	3.07	−50.6	−0.135	0.885	0.301	46.2
1988	−0.336	−70.5	0.610	0.336	−0.235	65.9
1989	0.881	−42.6	0.966	0.796	−3.16	38.9
1990	−12.8	−30.5	0.049	1.06	3.20	12.6
1991	−4.08	−38.7	−0.349	0.422	−4.46	42.9
1992	4.30	−7.68	−0.804	−0.352	−3.89	13.3

through ion exchange in the sediments, but NH_4^+ additions to sediment cores did not support this idea (L. Camerero & J. Rudd, unpublished data).

The decline in net annual SO_4^{2-} reduction in 1989–1992 (Table 2) was related to an increase in SO_4^{2-} return to the water column during the winters of 88–89, 89–90, and 90–91 (Fig. 1). Return of SO_4^{2-} during winter occurred to some degree during the early years of the experiment (Fig. 2), and is expected regardless of lake pH (Rudd et al. 1986a; Giblin et al. 1990; Kling et al. 1991). Thus, it was a change in the magnitude of the winter return at low pH in L. 302S that indicated a change had occurred in the sulfur cycle.

Mechanistic observations on Lake 302S

To explain the increased winter SO_4^{2-} return in L. 302S at pH 4.5 (Fig. 1), we looked first for changes in the epilimnetic sediments. The reason for this is that even though winter sulfur oxidation occurs in both epilimnetic (Rudd et al. 1986a) and hypolimnetic (Kling et al. 1991) sediments, epilimnetic sediments are quantitatively the most important site of SO_4^{2-} reduction (Cook et al. 1986). Also, one of the most obvious changes that occur in lakes as they become very acidic is the development of metaphytic algae in the epilimnion (Howell et al. 1990). Metaphytic algae are unattached, filamentous green algae that form balls, clouds, and/or patches over the surface of the sediment (Howell et al. 1990). In L. 302S, development of patches of filamentous green algae began as early as 1982 (Turner et al. 1987), but metaphytic blooms did not become extensive until the years at pH 4.5 (M. Turner, unpublished data). Metaphytic growth was uneven, with the epilimnetic sediments covered at some sites and not at others. The major metaphytic genus was *Zygogonium*, which is the same genus that dominates many acidic lakes in Ontario (Howell et al. 1990; Wei et al. 1989), and other experimentally acidified lakes (Schindler et al. 1991). Minor genera, not always present, were *Mougeotia* and *Oedogonium*.

In 1990, which was a cool year, metaphytic algal development in L. 302S did not reach its maximum until early fall (September). At this time we measured SO_4^{2-} profiles at epilimnetic sediment sites with and without algal coverage (Fig. 3a). These sites were only a few meters apart at 2 m depth. The profile at the bare site was similar to epilimnetic SO_4^{2-} profiles measured in this same lake during years when the pH was above 5.0 (Rudd et al. 1990), and in other acidic lakes, also above 5.0 (Rudd et al. 1986b; Sherman et al. 1994). In this 'normal' profile, the greatest decrease in SO_4^{2-} concentration occurred between 0 and 3 cm. At the algal-covered sites (Fig. 3a), profiles were quite different, with SO_4^{2-} either not decreasing as much with depth (algae #1) or increasing with depth (algae #2).

The difference in SO_4^{2-} profiles between bare and algal covered sites described above was likely due to algal production of oxygen during daylight hours, promoting sulfur oxidation and/or inhibiting SO_4^{2-} reduction. Our 10-day equilibration time for porewater sampling does not allow differentiation of changes in profiles that occur within diel periods. However, if there were a consistent net effect on the balance of SO_4^{2-} reduction and sulfur oxidation in

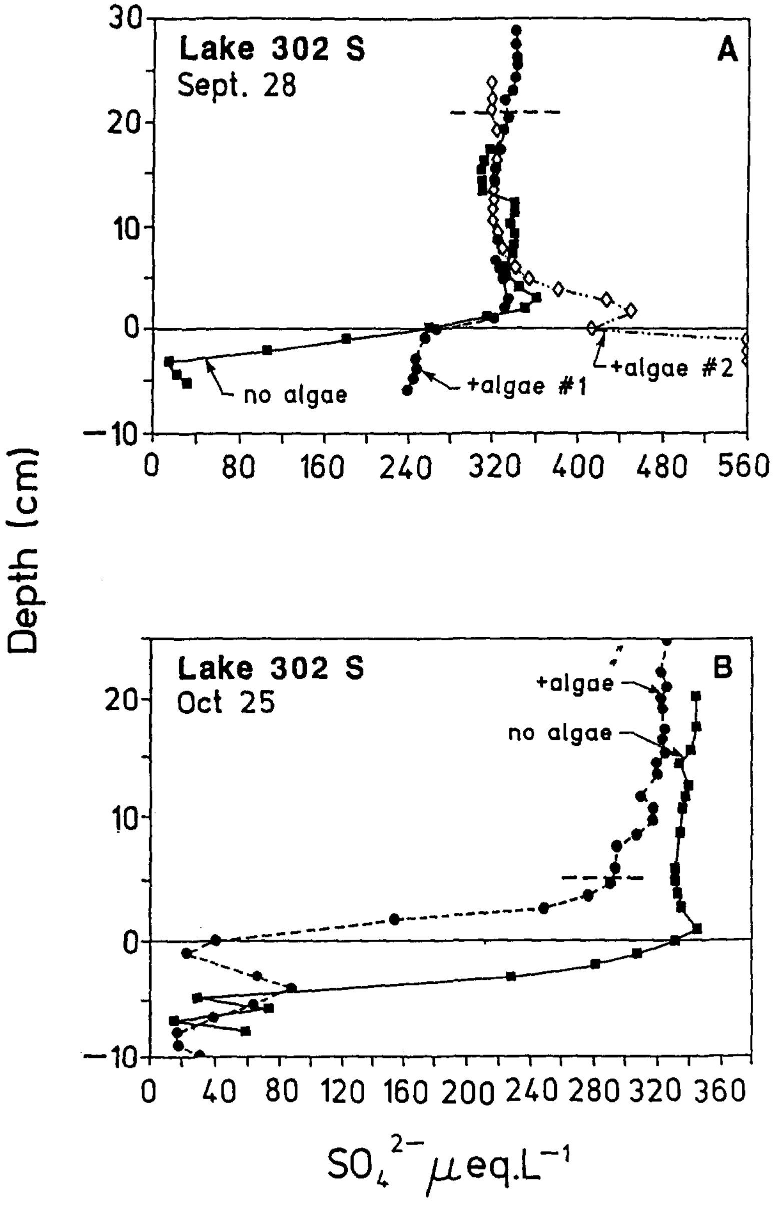

Fig. 3. a) Porewater sulfate profiles in L. 302S at a depth of 2 m, on September 28, 1990. All sites are only a few meters apart, and were either bare sediment ('no algae') or covered with algae that were viable and actively producing oxygen at this time (algae #1 and #2).

b) Porewater sulfate profiles in L. 302S at a depth of 2 m, on October 25, 1990. Sites were close together and were either bare sediment ('no algae') or covered with algae that were decaying ('algae').

each 24 hour period, this should be reflected in the longer term, equilibrated porewater SO_4^{2-} concentrations.

A much different effect of the metaphytic algae on SO_4^{2-} profiles was seen in October of 1990, when algae were senescing and decaying (Fig. 3b). At this time both the bare site and the site covered with algae had decreasing SO_4^{2-} concentrations with depth below either the sediment-water interface or the algal-water interface (Fig. 3b), indicating net SO_4^{2-} reduction. However, the two sites differed as to the depth of the zone of net SO_4^{2-} reduction with respect to the sediment-water interface. At the bare site, this zone was located between 0 and 5 cm *below* the sediment-water interface (Fig. 3b), slightly deeper than in the August profile at the bare site (Fig. 3a) and also similar to profiles measured in October during years when the lake was at a higher pH (unpublished data). In contrast, at the algal covered site, this zone was located 0–5 cm *above* the sediment-water interface (Fig. 3b), within the decaying mat. The same effect on the location of the SO_4^{2-} reduction zone (i.e. movement upward) can be produced in the laboratory by covering sediment with decaying algal material (Sweerts et al. 1986).

A change in the location of the zone of SO_4^{2-} reduction and solid sulfur accumulation, during the fall, can be expected to have consequences on the relative amount of sulfur that is oxidized the following winter in epilimnetic environments. Net oxidation of reduced sulfur in epilimnetic sediments occurs in the winter because oxygen penetrates further into the sediments as microbial respiration slows down (Kelly et al. 1984). We know from *in situ* ^{35}S experiments that winter loss of reduced sulfur occurs to a greater degree in sediments that are 0–3 cm below the sediment-water than at depths greater than 3 cm below the interface (Rudd et al. 1986a). Thus, SO_4^{2-} reduced and deposited at or just below the sediment-water interface at algal-covered sites should undergo greater re-oxidation over winter than sulfur that was deposited more deeply at the bare sites. Thus, as algal-covered sites became more prevalent in L. 302S in the years at pH 4.5, this likely caused more reduced S to be stored at or near the sediment-water interface during the fall, leading to the greater winter re-oxidation that was observed in the winters (Fig. 2).

Thus, there were likely two effects of the metaphytic algal development on net sulfur storage in L. 302S sediments: (1) decreased sulfate reduction in summer at sites covered by photosynthesizing (O_2-producing) algal patches and (2) an upward translocation of the SO_4^{2-} reduction zone in the fall at algal-covered sites, leading to increased susceptibility of the reduced S species the following winter.

Mechanistic observations in L. Hovvatn, Norway

Although L. 302S was kept at pH 4.5 for a relatively short period (4 years), observations in L. 302S are consistent with those in L. Hovvatn, Norway, which has been acidified by inputs from precipitation, and for a much longer time. L. Hovvatn was at pH 4.5 when sampled, and had metaphytic algae, mostly in the form of large drifting balls that were not particularly associated with specific sampling sites. We sampled L. Hovvatn in the summer, when algae are most actively producing oxygen. Porewater SO_4^{2-} profiles in L. Hovvatn followed diverse patterns: (1) SO_4^{2-} concentrations did not change with depth below the sediment-water interface, (2) concentrations decreased slightly or (3) concentrations increased (Fig. 4). Similar profile patterns were seen in two successive years (Fig. 4; Rudd et al. 1986b). All of these profiles were different from the commonly observed rapid decrease of SO_4^{2-} with depth seen in lakes above pH 5.0 (Rudd et al. 1986b). The L. Hovvatn profiles indicated that there was little or no net SO_4^{2-} reduction in these littoral sediments, or there was net sulfur oxidation, depending on the site. Incubations of L. Hovvatn sediment with $^{35}SO_4^{2-}$ showed that it was reduced at rates similar to other lakes (Rudd et al. 1986b). This means that the general lack of net SO_4^{2-} reduction shown by the porewater profiles was not due to a simple inhibition of SO_4^{2-} reduction, but rather an effect on the balance of reduction and oxidation.

The L. Hovvatn profiles were similar to profiles measured in L. 302S at the time of peak algal development in 1990 (September), at sites where there was obvious algal cover at the time of sampling (Fig. 3a). We do not have seasonal data on L. Hovvatn, so we do not know if it followed the same pattern of high SO_4 return in winter. What does seem evident is that the Hovvatn data showed a general lack of net SO_4^{2-} reduction in its sediments, whereas in L. 302S, which was at an earlier stage of acidification, this lack was associated specifically with algal cover.

While the porewater profiles from both lakes suggest that the metaphytic algae played a role in causing the changes seen in the sulfur cycle at low pH, other factors, such as the low pH itself, may also be important. Anaerobic microbial activities in sediments (SO_4^{2-} reduction, denitrification, ammonification, iron and manganese reduction) cause most sediments to be maintained at a higher pH than the overlying water (Herlihy & Mills 1985; Rudd et al. 1986b; Kuivala et al. 1989). These activities, as well as the maintenance of the anaerobic habitat necessary for SO_4^{2-} reduction, are all dependent on decomposition of organic carbon (e.g. Kelly et al. 1982), which can be inhibited at low pH (McKinley & Vestal 1982; Kelly et al. 1984; Schindler 1990). Over the long term, as very acidic water leads to greater penetration of acid con-

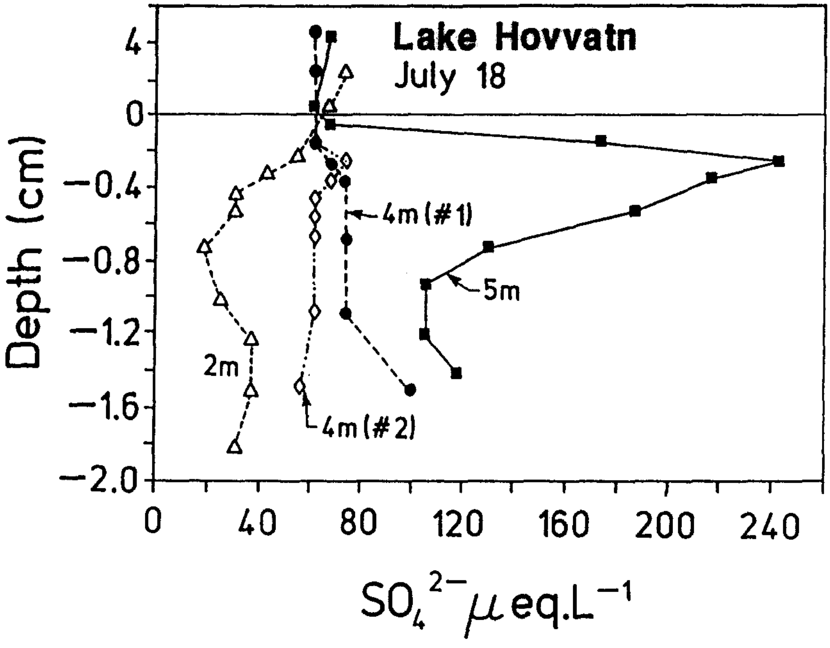

Fig. 4. Porewater sulfate profiles in Lake Hovvatn, Norway, on July 18, 1985, at depths of 2–5 m. This lake has a pH of 4.5 and has been acidified for decades.

ditions into the sediment, organic decomposition and the anaerobic habitats maintained by it may decrease.

There may be additional mechanisms underlying the decrease in net SO_4^{2-} reduction in L. 302S and L. Hovvatn at pH 4.5. However, the results presented here show that the community structure of epilimnetic sediments is an important consideration in understanding the factors controlling SO_4^{2-} reduction and IAG. The word ‘structure’ here means literally the physical placement of benthic species with respect to others. Demonstration of this type of controlling factor would be very difficult using laboratory experiments carried out on isolated parts, such as in incubations of sediment at different pH’s.

Implications for IAG models

In L. 302S, net SO_4^{2-} reduction, and the associated IAG, clearly changed as the lake reached pH 4.5. These results mean that models for predicting IAG (e.g. Baker et al. 1986; Kelly et al. 1987), which were originally based on data primarily from acidified lakes above pH 5, may need to be modified for lakes below pH 5. In these models the average mass transfer coefficient for SO_4^{2-} (S_S) is 0.5 ± 0.3 m/yr (Kelly et al. 1987; Baker & Brezonik 1988), similar to the measured coefficient for L. 302S during 1982–88 (Table 3). At pH 4.5,

Table 3. Average IAG, SO_4^{2-} flux, % retention of SO_4^{2-}, water residence time τ_w, and mass transfer coefficient (S_s) for the periods of pre-acidification (1980–81), acidification from pH 6.6 to pH 4.6 (1982–88) and acidification to pH 4.5 (1989–1992).

Years	pH	IAG keq/yr	SO_4^{2-} Flux keq/yr	SO_4^{2-} Retained %	τ_w yrs	S_s m/yr
1980–81	6.6–6.7	+4.1	−12.8	77	7.3	2.3
1982–88	6.2–4.6	+43.4	−26.4	45	5.8	0.73
1989–92	4.5–4.8	+26.9	+3.3	−8.3	4.2	−0.09

however, use of this value would obviously lead to erroneous prediction. (In the years prior to acidification, the high value for S_s was probably due to a greater proportion of SO_4^{2-} via algal uptake and sedimentation at low SO_4^{2-}, as previously suggested by Baker et al. 1989 and Rudd et al. 1990).

Because net SO_4^{2-} reduction and the storage of reduced S in sediments is a major mechanism that neutralizes acidity and assists lakes in recovering from acidification, its disruption increases the vulnerability of a lake to acidic precipitation. L. 302S is now in recovery, and early data suggest that its recovery is slower than for Lake 223 at the ELA (M. Turner, unpub. data), which had been experimentally acidified only to pH 5.0. Lakes below pH 5 are common in many European regions (Henriksen & Brakke 1988; Paetilae 1986), and effects on net SO_4^{2-} reduction in these lakes may play an important part in determining the degree of acidification and the rate of their recovery.

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