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Sulfur cycling in the water column of Little Rock Lake, Wisconsin

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Abstract. The S cycle in the water column of a small, soft-water lake was studied for 9 years as part of an experimental study of the effects of acid rain on lakes. The two basins of the lake were artificially separated, and one basin was experimentally acidified with sulfuric acid while the other served as a reference or control. Spatial and seasonal patterns of sulfate uptake by plankton (53–70 mmol m^{-2} yr^{-1}), deposition of sulfur to sediments in settling seston (53 mmol m^{-2} yr^{-1}), and sulfate diffusion (0–39 mmol m^{-2} yr^{-1}) into sediments were examined. Measurements of inputs (12–108 mmol m^{-2} yr^{-1}) and outputs (5.5–25 mmol m^{-2} yr^{-1}) allowed construction of a mass balance that was then compared with rates of S accumulation in sediments cores (10–28 mmol m^{-2} yr^{-1}) and measured fluxes of S into the sediments. Because of the low SO_4^{2-} concentrations (μmole L^{-1}) in the lake, annual uptake by plankton (53–70 mmol m^{-2} yr^{-1}) represented a large fraction (>50%) of the SO_4^{2-} inventory in the lake. Despite this large flux through the plankton, only small seasonal fluctuations in SO_4^{2-} concentrations (μmole L^{-1}) were observed; rapid mineralization of organic matter (half-life <3 months) prevented sulfate depletion in the water column. The turnover time for sulfate in the water column is only 1.4 yr; much less than the 11-yr turnover time of a conservative ion in this seepage lake. Sulfate diffusion into and reduction in the sediments (0–160 μmole m^{-2} d^{-1}) caused SO_4^{2-} depletion in the hypolimnion. Modeling of seasonal changes in lake-water SO_4^{2-} concentrations indicated that only 30–50% of the diffusive flux of sulfate to the sediments was permanently incorporated in solid phases, and about 15% of sulfur in settling seston was buried in the sediments. The utility of sulfur mass balances for seepage lakes would be enhanced if uncertainty about the deposition velocity for both sulfate aerosols and SO_2, uncertainty in calculation of a lake-wide rate of S accumulation in sediments, and uncertainty in the measured diffusive fluxes could be further constrained.

Introduction

The intricacies of microbial transformations of sulfur are appreciated (e.g., Jorgensen 1990), but sulfur (S) seldom is regarded as playing a critical role in non-meromictic lakes. Concentrations of sulfate in lakes are adequately high that S is seldom a limiting nutrient (Cook & Kelly 1992), but so low that SO_4^{2-} is thought to be unimportant as an electron acceptor for anaerobic respiration (Capone & Kiene 1988). Sulfur is required by organisms in amounts similar to phosphorus, but concentrations of SO_4^{2-} in lakes (25–300 μM) generally are 30- to 100-fold higher than those of P. Hence, sulfate depletion in epilimnetic waters is seldom observed (Hutchinson 1957). Depletion of SO_4^{2-} in the hypolimnion as a result of sulfate reduction and precipitation of iron sulfide in sediments is well known (e.g., Ohle 1934; Cook 1984). The widespread occurrence in lakes of sulfur-oxidizing bacteria, both phototrophic (e.g., Caldwell & Tiedje 1975; Davison & Finlay 1986) and (facultatively) aerobic (e.g., Strohl & Larkin 1978; Sweerts et al. 1990), is documented. However, there are few quantitative studies of rates and pathways of sulfur cycling in freshwater lakes (cf. Stuiver 1967; King & Klug 1982; Cook & Schindler 1983; Rudd et al. 1986a). This paper reports the rates of turnover of sulfur in the water column of a soft water lake.

Three major components of sulfur cycling in the water column are SO_4^{2-} uptake by phytoplankton, mineralization of phytoplankton that returns S to the water column, and S fluxes across the sediment-water interface. Sulfur is a major nutrient required by all organisms, and measurement of SO_4^{2-} uptake has been proposed as an alternative to thymidine uptake and ^{14}C assays as a means of measuring heterotrophic and primary production (Monheimer 1974, 1975; Jassby 1975). In Linsley Pond (Stuiver 1967) and Wintergreen Lake (King & Klug 1982), uptake by plankton was small in comparison to reservoirs of SO_4^{2-} in the water column. In some softwater German lakes, Ohle (1934) observed depletion of SO_4^{2-} in the epilimnion that may have resulted from uptake by plankton. In African lakes with very low SO_4^{2-} concentrations, phytoplankton uptake caused SO_4^{2-} turnover times to be as short as 10–14 days (Lehman & Branstrator 1994). We demonstrate here that phytoplankton uptake of SO_4^{2-} can cause rapid turnover of sulfate in small, soft water lakes.

Reduction of SO_4^{2-} in sediments and subsequent fixation of S as iron sulfide causes a diffusive flux of SO_4^{2-} from the lake water into the sediment pore waters (e.g., Cook 1984; Rudd et al. 1986b; Sherman et al. 1994). Despite low SO_4^{2-} concentrations in freshwater (1 to 3 orders of magnitude lower than in saltwaters), SO_4^{2-} reduction has been measured directly in numerous lakes (e.g., Sorokin 1975; Smith & Klug 1981; Rudd et al. 1986b). Freshwater sulfate-reducing bacteria have high affinities for SO_4^{2-} and acetate that allow them to outcompete methanogenic bacteria as long as concentrations of SO_4^{2-} are above a given threshold (5–20 μM; e.g., Schoenheit et al. 1982; Lovely et al. 1982; Ingvorsen et al. 1984). Whether the resultant sulfide is fixed in the sediments or reoxidized in the water column generally is thought to be a function of the availability of Fe (e.g., Cook 1984; Davison & Finlay 1986; Carignan & Tessier 1988). Fixation of microbially-reduced sulfur in sediments can be an important sink for SO_4^{2-} from the water column (e.g., Cook 1981; Schindler 1986; Schindler et al. 1986).

Sulfur in settling seston represents another loss of S from the water column. The relative importance of SO_4^{2-} diffusion and subsequent reduction versus seston deposition as sinks of sulfur from lakes remains unclear. Nriagu (1968) estimated that seston was the source for 50% of the total sediment S in eutrophic Lake Mendota. David and Mitchell (1985) observed that most S in sediments of South Lake was organic and concluded that seston must be the major source. However, lakes receiving large inputs of acid deposition exhibit large increases in S concentrations in recent sediments; this is inferred to have resulted from SO_4^{2-} diffusion into the sediments, subsequent reduction and fixation as Fe sulfides (e.g., Nriagu & Coker 1983, 1985; Mitchell et al. 1984, 1985; Carignan & Tessier 1988). When Fe is available, S fixation in sediments may be limited by SO_4^{2-} concentrations in lake waters (e.g., Baker et al. 1986; Kelly et al. 1987; Giblin et al. 1990; 1991) although there also is an interplay between sulfur fixation, the carbon content of the sediments, and the oxygen content of the bottom waters (e.g., Stauffer 1991; Norton et al. 1991). In this study we examine the relative importance of these two pathways for removal of S from the water column.

Not all sulfur that is removed from the water column to the sediments (via either settling of seston or diffusion into pore waters) remains permanently buried in the sediments. In the context of paleolimnology and acid rain, the net retention of S in sediments is more important than the initial flux into the sediment. Numerous attempts have been made to reconstruct previous lake or ocean conditions based on sediment profiles of S species (e.g., Mitchell et al. 1984; Nriagu & Soon 1985; Zaback & Pratt 1992); such reconstruction requires an understanding of the processes responsible for the incorporation and preservation of different S forms. Alkalinity to neutralize acid inputs to lakes will be generated by any processes that lead to permanent incorporation of S in the sediments (Anderson & Schiff 1987; Urban & Baker 1989). Retention of sulfur in sediments also is important as a means of immobilizing trace metals and mitigating their toxicity (e.g., DiToro et al. 1990, 1992). In this paper, we illustrate the dynamics of sulfur exchange across the sediment-water interface, and we determine the fraction of the original sulfur input to sediments that is retained in the sediments.

This paper summarizes the results of nine years of study of S-cycling processes in Little Rock Lake (LRL). The study comprised monitoring of inputs, outputs and water column conditions, as well as specific measurements of such processes as seston deposition and diffusion of SO_4^{2-} from the lake into sediment pore waters. This paper extends previous publications on Little Rock Lake (e.g., Baker et al. 1989; Baker et al. 1992; Brezonik et al. 1993; Sampson et al. 1994; Urban et al. 1994) by addressing the cycling of S within the water column.

Methods

Site description

Little Rock Lake is a small (18 ha) seepage lake situated in glacial outwash sands in northern Wisconsin (45°59′N, 89°42′W). The catchment (34 ha) is small, and the lake has no stream inlets or outlets. From 98% to 100% of water inputs come from direct precipitation; the remainder is from periodic groundwater inflow (Rose 1993). Consequently, the lake water is low in dissolved solids (ionic strength = 0.002 mol L^{-1}) and alkalinity (25 μeq L^{-1}; Brezonik et al. 1986). The long water-residence time (4–5 yr) combined with the minimal interaction with the catchment and ground water renders the lake ideal for studying internal processes and the effects of atmospheric inputs. All of the processes operating in this seepage lake occur also in drainage lakes; the sole difference is that the sulfate concentrations in drainage lakes typically are regulated by the water flushing rate and hence are not sensitive indicators of internal processes.

The lake has two basins of approximately equal area; the north basin (max. depth 10.5 m) is deeper than the south basin (max. depth 6.5 m). The lake is dimictic; holomixis occurs from November until ice formation (mid December) and again following ice melt (mid April) until early May. Both basins stratify weakly in winter, but the shallowness of the south basin prevents formation of any significant hypolimnion in summer. The small hypolimnion (8% of basin volume) in the north basin becomes anoxic in summer. The lake is oligotrophic; total phosphorus averages 12 μg L^{-1} and summer chlorophyll 5 μg L^{-1} (Wachtler 1987).

The lake was the site of an experimental acidification (Brezonik et al. 1986, 1993) starting in 1983. The two basins were divided from each other at a narrow point with a polyvinyl curtain in 1984. From 1985 to 1991, the north basin was acidified to successively lower pH values (5.6, 5.1, and 4.7 each for two-year periods) by addition of concentrated sulfuric acid. It has been left to recover by natural processes since then. Experimental acidification increased the sulfate concentration in the north basin from 28 to 80 μmole L^{-1}. The south basin received no acid and remained at its initial pH (6.1) and sulfate concentration (28 μmole L^{-1}). Additional information on the lake and experimental acidification is given elsewhere (Brezonik et al. 1986, 1987, 1993; Baker et al. 1989, 1992; Sampson et al. 1994; Urban et al. 1994).

Hydrologic budget

All components of the hydrologic budget (rainfall, evaporation, groundwater inflow, groundwater recharge) were monitored during this study (see Rose 1993). Precipitation amounts have been monitored with a standard rain gage since 1950 at Trout Lake station which is now part of the National Atmospheric Deposition Program (NADP). This site is located about 5 km from Little Rock Lake. From 1984–1990 a recording rain gage was located in a clearing 100 m northeast of the lake; this gage was operated during frost-free seasons. A nonrecording gage was maintained at the lake for November through to March. Lake evaporation was estimated from evaporation-pan data collected near Vandercook Lake (2.5 km southeast of Little Rock Lake). Water lever was measured daily in the pan; coefficients to convert to lake evaporation were based on comparison with a floating pan located at Rainbow Reservoir (20 km southeast of Little Rock Lake). Water levels in 59 piezometers (2 to 30 m depth) were measured monthly to assess groundwater flows. The forty nine sites were located within a 10-km^2 area around the lake. Slug tests were performed to estimate hydraulic conductivity. To account for the change in sediment area and the corresponding change in hydraulic conductivity of the littoral sediments as the lake level rose and fell, an empirical correction coefficient was applied that minimized the difference between calculated and observed change in lake storage. Details on calculations are presented in Rose (1993). Lake stage was monitored with a continuous digital recorder located at the northeast end of the south basin. Water levels remained identical in both basins even after installation of the curtain.

The hydrologic budgets for the individual basins contain one additional term not included in the budget for the entire lake; viz., transfer of water between the two basins. This flux was not measured directly, but was calculated by difference from measured fluxes according to the following equation (Rose 1993):

$$\begin{aligned}&\sum_{north} Inputs - \sum_{north} Outputs - \Delta Storage_{north} = residual = \\ &\sum_{south} Inputs - \sum_{south} Outputs - \Delta Storage_{south} \qquad (1)\end{aligned}$$

In this equation, transfer between the basins is an output for the south basin and an input to the north basin. The water year for the hydrologic and sulfate budgets is October 1 through September 30.

Water column monitoring, mass balance

The water column was sampled at 6-week (winter) or 4-week (ice-free season) intervals from August 1983 through December 1992. On each date, profiles with 2-m resolution were taken at the deepest locations in both basins. Measurements included temperature, conductivity, pH, alkalinity, major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}), major anions ($C1^{-}$, SO_4^{2-}, F^{-}), NH_4^+, NO_3^-, total and reactive phosphorus, silica, soluble Fe and Mn, chlorophyll, and color. Details on sampling and analytical techniques are given in Brezonik et al. (1990), Sampson et al. (1994), and Mach (1992).

In addition to monitoring the water column, measurements were made to construct element mass balances for the two lake basins (Eqn 2). Inputs to the water column include wet and dry atmospheric deposition (Atmos.Dep'n), groundwater inflow (GW_{in}), and litterfall (Litter) from the surrounding forest. Outputs consist of outseepage to groundwater (GW_{out}), net sedimentation, SO_4^{2-} diffusion into the sediments, and gas evasion. Gas evasion was assumed to be small and was ignored in this study. Interbasin transfer is an input to the north basin and an output from the south basin. The net burial of S in sediments (i.e., sedimentation plus diffusion minus release to the water column, Sed.Rxn) was calculated by difference from the other fluxes and then compared with measured rates of sediment S accumulation.

$$Atmos.Dep'n + GW_{in} + Litter \pm Ba \sin Transfer - GW_{out} - \Delta Storage = Sed.Rxn \tag{2}$$

Hydrologic fluxes were measured as discussed above (see Rose 1993). Precipitation chemistry was monitored at the Trout Lake station of the National Atmospheric Deposition Program (NADP) with a wet-only collector. Dry deposition was estimated from dry bucket measurements by the NADP as well as measurements made on site. In addition, 24-hr, high-volume air samples were filtered through Pallflex 2500 QAO quartz fiber filters for measurement of sulfate aerosols on twenty two occasions ($\sim$ monthly except in winter) between August 1984 and August 1987 (Tacconi 1988). Concentrations of SO_2 were measured in the same samples (teflon-coated quartz filters (Pallflex TX 40 HI20-WW) impregnated with 10% KOH and 5% glycerol). Groundwater chemistry was monitored in the relevant wells surrounding the lake, and leaf litter was collected in litter baskets along the shore and on the lake (Newsome 1987; Perry et al. 1987; Perry & Troelstrup 1989). Measurement of diffusive fluxes, sedimentation, and net S burial are discussed below.

Seston deposition

Sediment traps were used to measure seston deposition from July 1985 to December 1988 (Baker et al. 1988, 1989; Tacconi 1988) and again for 8 months in 1990. From four to six plastic cylinders (5.2 cm i.d.; height:width ratio of 3.7) were suspended together at each of three sites in the lake: at 5-m water depth in both basins, and at 9-m depth in the north basin. Traps were left in the lake for 7 days in summer, and 14 days in winter. New traps were set out every 14 days in summer, and every 30 days in winter. Material in the traps was filtered through pre-combusted and acid-washed glass fiber filters (GF/C), frozen until time of analysis, and then dried at 60 °C. Total sulfur and total carbon were measured with a LECO CS analyzer on subsamples from each filter from 1985–1987, and loss on ignition (550 °C) was measured on all samples. Precision for C and S analyses was 1%, and accuracy as assessed with NIST standards was within 5%.

Pore waters

Porewater equilibrators (Hesslein 1976) were installed at seven locations in the lake on multiple occasions (Perry 1987; Weir 1989; Sherman et al. 1994; Sampson et al. 1994). Sites included littoral (1–3.5 m water depths) and pelagic (5–9 m) sediments. Equilibrators, fitted with a plastic grate to hold them at a fixed depth in the soft, pelagic gyttja, were left in the lake for three weeks. Following their retrieval from the lake, porewater samples were withdrawn from the equilibrators by syringe within 45–60 min. and preserved immediately. Samples for redox-sensitive species (Fe, Mn, H_2S) were removed first, preserved (0.3 mole L^{-1} HCI for metals, 0.04 mole L^{-1} ZnAc for sulfide), and measured within two days. Diffusive fluxes were calculated with Fick's first law and the concentration gradient at the sediment surface. Diffusion coefficients (Li & Gregory 1974) were corrected for temperature and porosity.

Sediment cores

Sediment cores were retrieved from the lake in 1985 to quantify rates of sediment and element accumulation (Baker et al. 1992). Piston cores were taken from 9-, 7-, and 5-m depths in the north basin, and 5- and 3.5-m depths in the south basin. The cores were dated with ^{210}Pb, and sulfur present as acid-volatile sulfides (AVS), pyrite plus elemental sulfur (chromium-reducible S, CRS; Zhabina & Volkov 1978), hydriodic-acid-reducible sulfur (Johnson & Nishita 1952), and total sulfur (LECO CS Analyzer) was measured in freeze-dried sediments. All details on sediment core analyses and results were presented in Baker et al. (1992). Organic S will be defined operationally as

Table 1. Summary of average hydrologic fluxes (mean ± S.D.[c] in mm/yr) to and from Little Rock Lake.

Precipitation	Groundwater inflow	Evaporation	Groundwater outflow	Change in lake storage	Residual
Whole lake[a]					
824 ± 94	3 ± 3	546 ± 50	317 ± 47	92 ± 163	3 ± 41
North Basin[b]					
783 ± 116	75 ± 24	564 ± 52	391 ± 68	–92 ± 176	–4 ± 46
South Basin[b]					
783 ± 116	6 ± 8	564 ± 52	321 ± 52	–92 ± 176	–3 ± 45

[a] Time periods for each flux are different. Precipitation covers 1984–1997, Groundwater inflow, groundwater outflow, change in storage, and residual were from Rose (1993) and span 1984–1990, and evaporation covers 1984–1994.

[b] All fluxes for both the north and south basins are averaged over the years 1984–1990.

[c] The S.D. is the standard deviation in the annual flux calculated for the stated time periods.

total S minus CRS, and carbon-bonded S is calculated as Organic S minus hydriodic-acid-reducible S (HI-S or sulfate esters).

Results

In the following sections, we highlight the major features of each lake compartment or flux, and we point out any differences in interpretations or values between this and previous publications. As is often the case in any prolonged study, both 'average values' and interpretations of data have changed as new data were acquired.

Hydrologic budget

Precipitation to the lake surface dominates the hydrologic inputs to Little Rock Lake (Table 1). Because the period of study spanned a drought (precipitation in 1987–1989 was 80% of the 30-year mean), change in lake storage was a significant component of the hydrologic budget. The standard deviations reported in Table 1 reflect annual variability, not the measurement or calculation uncertainty. For precipitation, evaporation, and change in storage, the annual variability (10–177%) is larger than the estimated uncertainty in measurement ($<$5%). The errors in the groundwater flows are the major contributor to the residual term (i.e., the calculated minus observed change in lake storage) in the hydrologic budget. After application of an empirical correction for the change in surface area and hydraulic conductivity of littoral sediments resulting from changes in lake stage (Rose 1993), the residual error in the hydrologic budget amounts to 20 to 76 mm yr^{-1}. If these errors are not systematically related to lake stage, the uncertainty in the groundwater flux can be calculated to equal ~14%. The propagated error in the basin transfer for any one year (23%) reflects the uncertainty in all other fluxes because it is calculated by difference. The propagated uncertainty for the mean basin transfer (i.e., groundwater inflow and outflow for individual basins given in Table 1) however, is <10%.

Inputs and outputs

The major sulfur inputs to the lake are litterfall from the surrounding forest, atmospheric deposition, and groundwater inflow. As will be discussed below, sediments are both a source and a sink of S in the water column. Rain infiltration into the sandy soils of the catchment is rapid, and little or no surface or subsurface runoff occurs from the small catchment (catchment: lake area = 1.9) to the lake. The mass of litter inputs was estimated to be 6.4 g m^{-2} yr^{-1} (Newsome 1987); with an average S content of 50 μmol g^{-1}, this source contributes only 0.3 mmol S m^{-2} yr^{-1} to the lake (<2% of the total input).

Atmospheric deposition constitutes the largest input of S to LRL. Between 1984 and 1991, wet deposition of SO_4^{2-} averaged 11.1 ± 0.6 (S.E. of annual fluxes) mmol m^{-2} yr^{-1} (Table 2). The annual variability in this flux probably is larger than the measurement uncertainty. The average deposition of S to dry buckets over the period 1985–1987 was 3.6 ± 1.0 (S.E. of annual fluxes) mmol m^{-2} yr^{-1}. Dry deposition calculated from 22 aerosol measurements over the same period of time (deposition velocity 0.3 cm/s; Hicks 1986; Baker 1991) was 1.8 ± 0.3 (S.E. based on variance among 22 measured values) mmol m^{-2} yr^{-1} (Tacconi 1988). Ideally, dry buckets would measure both aerosol deposition and SO_2 deposition. However, it is well known that the buckets do not mimic natural surfaces and provide a poor estimate of fine aerosol deposition (e.g., Hicks et al. 1980) and underestimate deposition of SO_2 to lakes and canopies (e.g., Baker 1991; Zobrist et al. 1993). Although some SO_2 may adsorb onto the alkaline dust particles in the buckets, the plastic buckets themselves are thought to capture little SO_2 (Baker 1991). For this study, the SO_2 flux (1.8 ± 0.9 mmol $m^{-2}yr^{-1}$) was estimated by multiplying the mean of 22 measurements of SO_2 concentration (19.4 ± 10 (S.E.) mmol m^{-3}); (Tacconi 1988) by a deposition velocity of 0.3 cm s^{-1} (Baker et al. 1991). Total dry deposition (3.6 mmol m^{-2} yr^{-1}) was calculated as the sum of calculated SO_2 and aerosol deposition. The estimate of dry deposition represents 25% of the total atmospheric S deposition. Baker (1991) arrived at a similar estimate (27% of total S deposition) for the importance of dry deposition in the upper midwest of the U.S. The average atmospheric deposi-

Table 2. Summary of S mass balances (mmol $m^{-2}yr^{-1}$) for north and south basins of Little Rock Lake.

	Year								
	1984–’85	’85–’86	’86–’87	’87–’88	’88–’89	’89–’90	’90–’91	Mean	S.D.[c]
				SOUTH BASIN					
INPUTS:									
Wet deposition	11.0	14.4	10.8	12.0	9.6	8.6	11.0	11.1	0.6
Dry deposition	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.7
Leaf litter	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.02
Ground water	1.6	0.4	1.0	0.0	0.0	0.0	0.0	0.4	0.2
Total:	**16.5**	**18.7**	**15.7**	**15.9**	**13.5**	**12.5**	**14.9**	**15.4**	**3.76**
OUTPUTS:									
Outseepage	8.4	6.6	6.0	8.5	7.2	5.8	4.2	6.7	0.5
Basin transfer	3.2	3.1	2.5	3.5	1.8	1.6	1.3	2.4	0.3
Total:	**11.6**	**9.7**	**8.5**	**12.0**	**9.0**	**7.4**	**5.5**	**9.1**	**0.6**
Δ storage[a]:	–11.9	–1.7	–1.7	6.1	–3.2	2.9	6.3	–0.5	2.2
Sediment reaction[b]								6.7	4.4

Table 2. Continued.

	Year								
	1984–’85	’85–’86	’86–’87	’87–’88	’88–’89	’89–’90	’90–’91	Mean	S.D.[c]
				NORTH BASIN					
INPUTS:									
Wet deposition	(11.0)	14.4	10.8	12.0	9.6	8.6	11.0	11.1	0.6
Dry deposition	(3.6)	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.7
Leaf litter	(0.3)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.02
Basin transfer	(2.6)	2.6	2.1	2.8	1.6	1.4	1.1	1.9	0.2
Acid addition	(0)	68.4	27.3	75.6	45.3	91.5	66.7	62.5	0
Total:	**(19.7)**	**91.5**	**46.3**	**96.5**	**62.6**	**107.6**	**84.9**	**79.4**	**3.8**
OUTPUTS:									
Outseepage:	(13.3)	16.2	18.0	25.3	20.2	20.0	15.6	19.2	1.4
Δ storage[a]:	(–0.5)	21.0	39.8	22.2	18.4	48.2	33.9	30.6	5.6
Sediment reaction[b]	(4.7)							29.6	6.9

[a] Change in storage in the water column.

[b] Calculated by difference (reaction = $\sum$inputs – $\sum$outputs – Δstorage).

[c] For fluxes whose annual variation is much larger than experimental uncertainties, the uncertainty about the mean is calculation as S.D./$\sqrt{n}$. The estimated uncertainty for dry deposition is discussed in the text. The uncertainty about the basin transfer also is estimated by a first order analysis to be 10% of the mean value. First order analysis is used to calculate the uncertainty in total inputs, total outputs, and sediment reactions.

tion rate reported here (14.6 mmol m^{-2} yr^{-1}) is lower than that reported previously (19.3 mmol m^{-2} yr^{-1}; Baker et al. 1989) because of the different periods of measurement.

There is a very large uncertainty in the estimate of dry deposition. The estimated uncertainty (S.D. = 3.7 mmol m^{-2} yr^{-1}) in this flux is based on a first order analysis (e.g., Schnoor 1996) and indicates that the uncertainty in the deposition velocities ($\sim$0.1 cm s^{-1}) contributes more than the variability in measured concentrations. The uncertainty in the combined estimates for SO_2 and aerosol deposition (3.6 ± 3.7 mmol m^{-2} yr^{-1}) certainly encompasses the magnitude of deposition to dry buckets (3.5 mmol m^{-2} yr^{-1}). The uncertainty in the estimate of dry deposition amounts to about 20% of the total input of S to Little Rock Lake prior to acidification but only about 5% of the average annual inputs to the north basin during acidification.

Ground water constitutes a minor input of S to the lake. The regional groundwater table impinges the lake only at the southeast corner; in years of low rainfall (e.g., 1986–1990) there is no contact between the lake and the water table. Water budgets (Table 1) indicate that groundwater contributes only 0–2% of water inputs. Concentrations of SO_4^{2-} in the influent groundwater varied little, and the total S input from groundwater ranged only from 0 to 0.7 mmol m^{-2} yr^{-1} (expressed per area of lake basin) during this study (Table 2). The value reported previously (1.2 mmol m^{-2} yr^{-1}; Baker et al. 1989) was based only on the period 1984–1987, when groundwater inflow was occurring.

The majority of the lake always lies above the water table, and outseepage occurs through all sediments that are sufficiently permeable. Calculation of the output of S requires an assumption about the concentration of SO_4^{2-} in the outseeping water. For the budget presented in Table 2, concentrations in the lake water were used. It is clear, however, that this calculated efflux of S from the lake water column does not equal the S flux into the ground water. Porewater profiles in littoral regions indicate that sulfate reduction in littoral sediments attenuated sulfate concentrations to 5–20 μM. Also, SO_4^{2-} concentrations in groundwater wells down-gradient of the lake were lower than concentrations in the lake. The uncertainty in SO_4^{2-} concentrations is problematic in computing the transfer of S between the two basins of the lake after the installation of the vinyl curtain; all transfer occurred via flow through the sediments. The basin transfer reported in Table 2 is based on an average of the concentration in the south basin and the concentration in a nearby groundwater well.

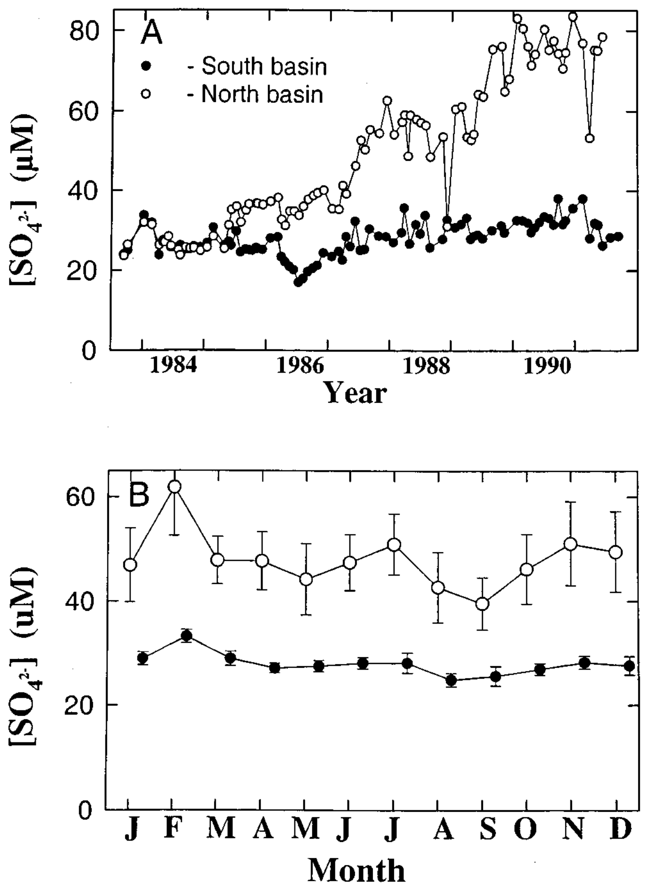

Figure 1. (A) Volume-weighted mean SO_4^{2-} concentrations in north and south basins of LRL. Experimental acid additions caused the systematic divergence of concentrations in the two basins. (B) Monthly means (8-yr mean ± S.E.) of volume-weighted mean SO_4^{2-} concentrations in north and south basins of LRL. For the north basin, the data were 'detrended' by normalizing each monthly concentration to the annual mean concentration. In both basins concentrations are higher in winter (Nov.–Mar.) than in non-winter months; the difference between winter and non-winter is statistically significant at the 10% confidence level (t-test) for the south basin, but acid additions in summer render the trend less pronounced in the north basin.

Water column

Concentrations of SO_4^{2-} in the water columns of both basins varied seasonally and annually as a result of acid additions, sulfate reduction, sulfide oxidation, algal uptake, and climatic variations (Figure 1). In the south (reference) basin, SO_4^{2-} concentrations decreased slightly in the uppermost 2 m of water during summer. In both basins, concentrations rose slightly in fall and remained elevated through winter (Figure 1(b)); concentrations in winter are significantly higher ($P < 0.10$) than during the remainder of the year in the south basin. Addition of sulfuric acid to the north basin caused a progressive increase in SO_4^{2-} concentrations from an initial value of 28 μmole L^{-1} to over 70 μmole L^{-1} (Figure 1(a)). This increase in SO_4^{2-} concentration was equal to only 62% of that which would have occurred if all added H_2SO_4 had remained in the water column; the remaining 38% was lost to outseepage and burial in the sediments. In contrast to the south basin, the deeper waters of the north basin became depleted in SO_4^{2-} relative to the surface waters in summer and winter (except in the winters of 1984, 1985 and 1986). A slight increase in concentration (from 28 to 35 μmole L^{-1}) occurred in the south basin during the drought years of 1986–1989.

Annual changes in inventories of SO_4^{2-} in the water column were large (Table 2). Variations in SO_4^{2-} inventories on consecutive sampling dates are one indication of the uncertainty in this term; during spring and fall holomixis these variations are as large as 20–30%. However, rates of SO_4^{2-} uptake by phytoplankton and mineralization, in combination with variations in rates of inputs, can account for the variations in inventories.

Plankton uptake and deposition of S

In 1986, the annual net primary production by phytoplankton was estimated (^{14}C fixation) to be 3.9–7.3 mol C m^{-2} yr^{-1}, and macrophyte production was estimated to be 0.8–1.1 mol C m^{-2} yr^{-1} (Wachtler 1987). Over the five years in which seston deposition was monitored (1985–1988, 1990), rates of organic C deposition averaged 6.4, 5.3 and 9.5 mol C m^{-2} yr^{-1} at the 5-m south basin, 5-m north basin, and 9-m north basin sites, respectively.

The sulfur content of seston ranged from 60 to 520 μmol g^{-1}, a range similar to that in other lakes (Table 3). Molar C:S ratios in seston ranged between 40 and 217 (analytical uncertainty = ± 6%); the average value (118 ± 9, mean ± S.E.) was similar to the Redfield ratio of 106:1 for C:P and to Jassby's (1975) value (133) for aquatic bacteria, but quite different than the value (500) assumed by Monheimer (1974) to apply to all plankton. Different species of algae have different S contents (Goldman et al. 1972; Healey 1973), and it is not known if the variability in LRL arose from temporal variations in algal species or from other environmental variables. Concentrations of S in seston were independent of SO_4^{2-} concentrations in the lake water; seston from the acidified basin (measured only through 1987) had concentrations no higher than those in the reference basin. Division of the average seston C:S ratio into the rate of phytoplankton production (3.9–7.3 mol C m^{-2} yr^{-1}) yields an estimated rate of algal S uptake of 33–62 mmol S m^{-2} yr^{-1}.

Table 3. S content and fluxes in seston in Little Rock and other lakes.

Lake	S conc. (μmol g^{-1})	C:S (molar)	HI-S % of S	S flux mmol m^{-2} yr^{-1}	Ref.
Little Rock	60–520	40–217	23–51	53 ± 5	this study
Wintergreen	260	77	35	266	(Smith & Klug 1981)
South	270	120	44–59	9–21	(David & Mitchell 1985)
302S				40	(Rudd et al. 1990)
302N				31	(Rudd et al. 1990)
Sudbury lakes	250–440	24–61			(Nriagu and Soon 1985)
Zurich	220–375				(Losher 1989)
Cadagno	150–1090	21–93			Urban, unpub.
Greifen	62–590	13–83		174	Urban, unpub.
Constance	55	77			(Stabel 1985)
Linsley P.	11	290			(Stuiver 1967)

Seasonal and annual variations in seston deposition rates (Figure 2) parallelled the expected patterns of primary production. Because organic matter comprised 70% of the seston, trends in organic C and total seston deposition are largely the same. Seston deposition rates were highest in summer months. Deposition increased in both basins from 1985 through 1988, although it may have been anomalously low in 1985. Increased seston deposition rates and higher chlorophyll concentrations (not shown) suggest that primary production was enhanced during drought years (1986–1988).

Sediment focusing caused variations in seston deposition rates among sites. As indicated by the monthly pattern of seston deposition at the 9-m site (Figure 2(a)), resuspension and focusing occurred primarily in spring and fall when the lake was well-mixed. As a result of focusing, annual seston deposition at the 9-m site was 1.5- to 1.8-fold higher than at the 5-m sites.

An estimate of annual seston deposition for the entire lake must account for the focusing that affected each of the measured rates. In sediments, ^{210}Pb is bound primarily to fine organic and clay particles (e.g., Edgington & Robbins 1976), and hence is focused to a similar extent as organic matter. Ratios of organic carbon deposition in sediment traps (0.68:0.56:1; south basin 5-m:north basin 5-m: north basin 9-m) are similar to the ratios of ^{210}Pb concentrations in surface sediments (0.62:0.57:1) as well as to the ^{210}Pb inventories (0.73:0.57:1) and the rates of organic matter accumulation in the sediments at each site (0.63:0.55:1) (data given in Baker et al. 1992). All of these ratios reflect the degree of focusing of organic matter, and a focusing

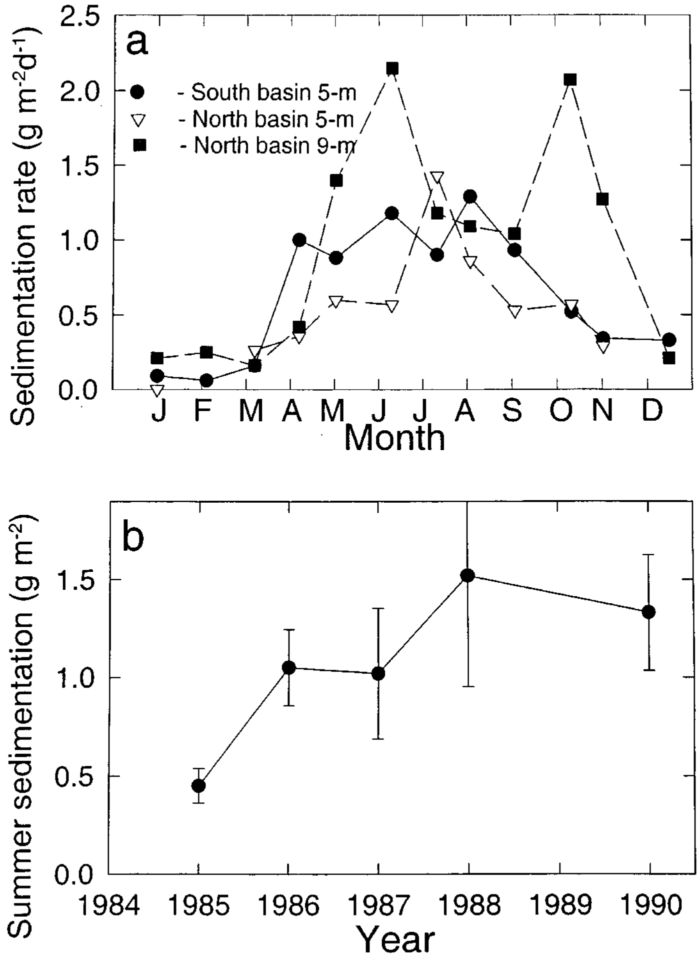

Figure 2. Seston deposition in Little Rock Lake. (a) The monthly pattern of seston deposition follows the expected pattern of primary production at the 5-m sites in both basins. At the 9-m site, a second peak in deposition occurs in fall probably as a result of sediment resuspension. Deposition is higher at the 9-m site than at either of the 5-m sites as a result of sediment focusing. (b) Time trend of summer seston deposition (mean ± S.D. for three sites).

factor (^{210}Pb accumulation rate at a site divided by the atmospheric deposition rate) may be used to correct site-specific rates to lake-wide rates of organic matter accumulation. The focusing factors for the three sites are 1.08 (south basin 5-m), 0.84 (north basin 5-m) and 1.47 (north basin 9-m; data in Baker et al. 1992). Dividing the organic matter deposition rates at each site by these focusing factors yields similar estimates (5.9, 6.3, 6.4 mol C m^{-2}yr^{-1}) for the lake-wide rate of deposition.

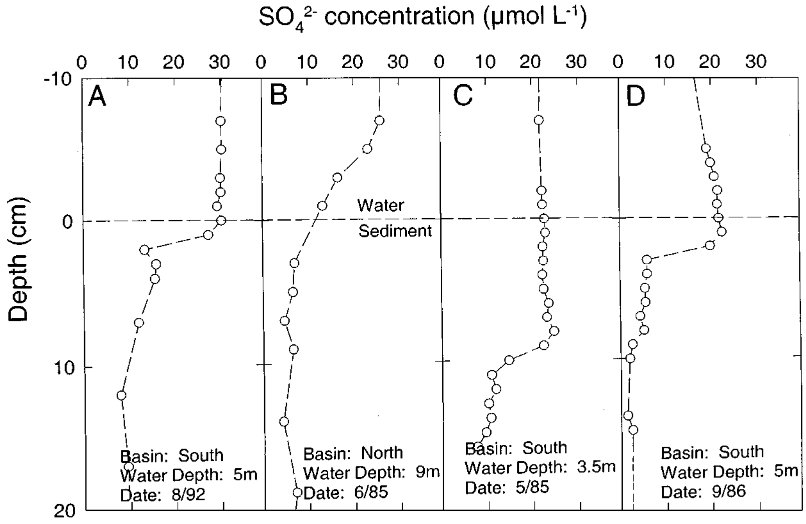

Figure 3. Porewater profiles of SO_4^{2-} exhibited several patterns. (A) The 'normal' pattern consisted of rapid attenuation of concentrations below the sediment surface in response to net SO_4^{2-} reduction. (B) In the north basin, depletion of SO_4^{2-} often occurred above the sediment surface. (C) Numerous (12 of 45) profiles exhibited SO_4^{2-} depletion beginning well below the sediment surface. (D) Relatively few profiles (3 of 45) indicated that the sediments were acting as a net source of SO_4^{2-} to the water column.

The rate of S deposition (53 ± 1 mmol m^{-2} yr^{-1}, mean ± S.E.) was estimated by dividing the mean C:S ratio (118) for 1985–1987 into the lake-wide rate of organic carbon deposition for 1985–1990. The estimate given here is larger than our previous estimate (36 mmol $m^{-2}yr^{-1}$; Baker et al. 1989) which was an average of measured fluxes for only 1.5 years with no correction for focusing. The estimated rate of S deposition is in the middle of the range of estimated phytoplankton S uptake rates (33–62 mmol m^{-2} yr^{-1}). In this shallow lake, it is possible that a large fraction of the phytoplankton production settles to the bottom rather than being decomposed in the water column. It also is possible that the phytoplankton production measured in 1985 underestimated the long-term mean just as the seston deposition rate in 1985 was much lower than the 5-year mean (Figure 2). In the discussion below, the seston S deposition rate (53 mmol m^{-2} yr^{-1}) will be used as a conservative estimate of the rate of algal S uptake.

Pore waters and diffusive fluxes

Among the 45 porewater profiles measured during the study, the majority showed the expected shape (Figure 3(a)), with nearly constant concentrations above the sediment surface that were rapidly attenuated within the first 5 cm of sediment to a low, constant value. The attenuation of SO_4^{2-} within the sediments is attributed to dissimilatory sulfate reduction (e.g., Rudd et al. 1986b). Many SO_4^{2-} profiles, however, had shapes different from that expected. Profiles from the north basin often exhibited SO_4^{2-} attenuation in the water column above the sediment surface (Figure 3(b)), an indication that bottom waters were stagnant rather than well-mixed. Because of the orientation and depth of this basin, it is not as well mixed by winds, and the water column stratifies more stably than in the south basin.

More difficult to explain are the profiles in which SO_4^{2-} attenuation began 1–10 cm below the sediment surface (Figure 3(c)). In these cases, there was no apparent diffusive flux of SO_4^{2-} across the sediment-water interface, but net consumption occurred within the sediments. Such profiles indicate either (1) that bioturbation was pumping sulfate into the sediments; (2) that non-steady state conditions existed (i.e., the location of the concentration gradient moves upward in the sediments as the pool of SO_4^{2-} in the porewaters is consumed) or (3) that SO_4^{2-} generation in the upper sediments is equal to SO_4^{2-} consumption in lower sediments, such that no flux across the sediment-water interface occurs. Such profiles were observed sporadically in the south basin and occurred in the north basin during the last three years of acidification. A few profiles (3 of 45) showed a peak in SO_4^{2-} concentrations at or below the sediment surface (Figure 3(d)), indicating that SO_4^{2-} production exceeded consumption.

Acidification of the north basin had a marked effect on porewater profiles of SO_4^{2-}. The depth at which net consumption of SO_4^{2-} began moved down as much as 10 cm into the sediments, and the minimum SO_4^{2-} concentrations at depth in the profiles were more than double the pre-acidification values. This effect was not observed until 1990–1992 when the pH of the water column was below 5. Concomitant with these changes in SO_4^{2-} were decreased production of NH_4^+, decreased release of base cations, and lowered pH in the pore waters (all determined from porewater profiles; Sampson 1992). Observed changes in macroinvertebrate populations do not suggest that the changes were caused by increased bioturbation (Brezonik et al. 1993).

Diffusive fluxes of SO_4^{2-} across the sediment surface ranged from –3 (negative values indicate flux into the water column) to 160 μmol m^{-2} d^{-1}. Diffusive fluxes at the 5-m site in the reference basin ranged from –3 to 62 μmol m^{-2} d^{-1} with a relative standard deviation of 106% (n = 17). Some of the variability may be ascribable to measurement errors; the mean deviation among fluxes calculated from three pairs of replicate profiles was 22%. There were no significant differences among diffusive fluxes from the seven sites nor among seasonal fluxes at any given site (Sherman et al. 1994; Urban et al. 1994). However, only one profile was recovered from under the ice, and hence winter fluxes were not well characterized. Contrary to expectations, diffusive fluxes as calculated from the porewater profiles did not increase in response to increased sulfate concentrations in the north basin. The mean (± S.D.) diffusive flux for all sites (n = 45) was 23 ± 28 μmol m^{-2} d^{-1}. This value differs from those reported previously (15 ± 7.4 [n = 7], Baker et al. 1989; 32 ± 24 [n = 19], Sherman et al. 1994; 36 ± 22 [n = 33], Urban et al. 1994) because of the larger number of measurements included; this paper includes measurements from 1990–1992 and from two additional sites (3.5-m south basin, 7-m north basin) that were not included in previous reports.

The calculated diffusive fluxes probably underestimate the actual fluxes of sulfate into the sediments. Even in lakes with laminated sediments (i.e., minimal bioturbation), fluxes calculated from porewater profiles underestimate fluxes measured in benthic chambers (Urban et al. 1997). Bioturbation is likely to enhance the diffusive fluxes in Little Rock Lake. The zoobenthos in Little Rock Lake is dominated by chironomid larvae at an average density of 3,200 individuals per m^2 in the north basin and 4,600 per m^2 in the south basin; oligochaetes are very few in number (Webster, unpub. data). These densities might enhance the diffusional fluxes from 2- to 12-fold (Fukuhara & Sakamoto 1987; Ullman & Aller 1989). Clearly, more accurate methods for assessing the flux of sulfate in sediment pore waters are needed.

Low sulfide concentrations were observed in the pore waters at all sites. Peak concentrations (1.5–4 μmole L^{-1}) occurred within 3 cm of the sediment surface; below these peaks, concentrations rapidly declined to 0.5–1 μmole L^{-1}. Sulfide was only measured on two occasions (June and August 1985), and it is not known if seasonal variations occur. Calculation of saturation indices indicated that all iron monosulfides were highly undersaturated (Sherman et al. 1994).

Sediment characterization

Concentrations of S in pelagic (i.e., water depths $>$4 m) sediments increase with increasing water depth and range from about 150 to 300 μmol g^{-1} (Baker et al. 1992). From 60 to 85% of the total S is organic; one third occurs as sulfate esters, and the remainder is assumed to be carbon-bonded S. Inorganic S is primarily pyrite; concentrations of acid-volatile sulfides (AVS; 2–6 μmol g^{-1}) are only 7–33% of the concentrations of chromium-reducible S (CRS; Figure 4). Elemental S represents less than 10% of CRS. Concentrations of total S are not significantly ($P > 10\%$) lower in littoral (80–300 μmol g^{-1}) sediments, but concentrations of AVS (2% of values in pelagic sediments) and CRS are markedly lower in littoral (4.5–10 μmol g^{-1}; Monte 1998) as compared to pelagic (12–125 μmol g^{-1}) sediments.

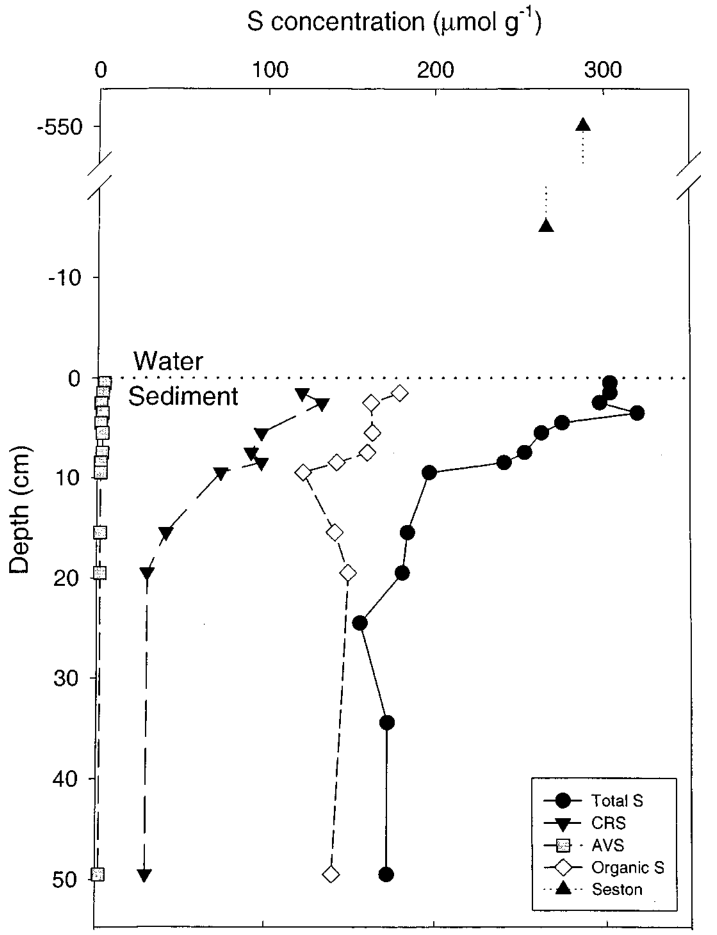

Figure 4. Speciation of S in pelagic sediments of Little Rock Lake. Sulfur is enriched in surface sediments over that collected in sediment traps (denoted as seston S); although concentrations of organic S are lower in the sediments than concentrations of total S in the traps, inorganic S formed as a result of dissimilatory SO_4^{2-} reduction increases the total S concentrations in the sediments. Concentrations of all species, most markedly inorganic S species, decrease with depth in the sediments. This core was retrieved from 9-m water depth in the north basin in 1985. The seston values represent two-year averages (1985, 1986) for sediment traps at 5- and 9-m water depths in the north basin.

Sediment accumulation rates based on ^{210}Pb dating did not increase systematically with increasing water depth in the pelagic zone. Rates range from 87 to 130 g m^{-2} yr^{-1}, and have remained relatively constant over the past 100 years (Baker et al. 1992). In contrast, accumulation rates of both organic and inorganic S increased in recent sediments of all pelagic cores. The magnitude

Table 4. Comparison of estimated lake- and basin-wide rates of S storage (mmol m^{-2} yr^{-1}) in sediments.

Model:	Surface accumulation rate[e]			Long-term accumulation rate[e]		
	1[a]	2[b]	3[c]	1[a]	2[b]	3[c]
Lakewide[d]	13.2	18.6	22.9	8.6	13.7	14.6
North basin[d]	15.7	25.6	28.3	8.4	14.5	15.2
South basin[d]	10.9	10.1	10.3	13.7	12.7	13.0

[a] Accumulation rates from each core were weighted according to the fraction of the total depositional area represented. Rate = $\sum$[(site rate)•(fraction of sedimentation area represented by site)].

[b] Accumulation rates from each core were divided by the ^{210}Pb focusing factors and then weighted according to the fraction of the basin (or lake) represented to correct for non-focusing related differences.

[c] Basin (lake) rates are calculated as the sum of accumulation rates of ‘excess’ S (weighted according to fraction of basin represented) and seston S (corrected for focusing with ^{210}Pb focusing factors).

[d] The calculations are based on three cores from the north basin and two from the south basin.

[e] Surface accumulation rates refer to the top 0.5 cm of sediment. Long-term accumulation rates are based on the entire period of ^{210}Pb dating (1800–1985).

of increases in accumulation rates of S varied with water depth and were greatest at the deepest site.

Systematic spatial variations that existed even prior to lake acidification make calculation of a lakewide rate of S storage difficult. The average rate of S accumulation (i.e., avg. S concentration times mean sedimentation rate over dated portion of cores) was similar for the two 5-m and the 7-m sites (12,14,13 mmol m^{-2} yr^{-1}), but was much higher at the 9-m site (30 mmol m^{-2} yr^{-1}). This probably results from both higher rates of organic S deposition at this site (focusing of organic matter) and less reoxidation of reduced S because of hypolimnetic anoxia. A lakewide rate of S storage may be calculated by weighting accumulation rates at each site by the fraction of total lake area represented by the site. If sediments accumulate only in 60% of the total lake area (Baker et al. 1992), the lakewide rate of S accumulation in surface sediments is 13 mmol m^{-2} yr^{-1} (Table 4, Model 1), and the long-term lakewide accumulation rate (i.e., average rate since 1800) is 8.6 mmol m^{-2} yr^{-1} (Table 4).

An alternative estimate of the lakewide accumulation rate may be calculated using ^{210}Pb inventories to correct for focusing of organic matter, as discussed above (Table 4, Model 2). Focusing corrections reveal two facts. First, focusing-corrected accumulation rates of organic C as well as of S are lower in the south ($C = 2.0 \pm 0.5$ mol m^{-2} yr^{-1}, n = 2; S = 10 mmol m^{-2} yr^{-1}) than in the north basin ($C = 3.2 \pm 0.3$, n = 3; S = 24 mmol m^{-2} yr^{-1}). This is not likely to have resulted from lower primary production in the south basin; seston deposition rates were 20% higher in the south than in the north basin 5-m sediment traps. Rather, the greater wind exposure of the south basin may facilitate aeration and decomposition; the lower organic C concentrations in surface sediments of the south (20–21 mmol g^{-1}) versus north (23–27 mmol g^{-1}) basin could result from such enhanced decomposition. Second, although dividing the organic C accumulation rates at each site by the ^{210}Pb focusing factors yields similar basinwide accumulation rates, the focusing-corrected S accumulation rate at the 9-m site (43 mmol m^{-2} yr^{-1}) is higher than at the 5- and 7-m sites (23,24 mmol m^{-2} yr^{-1}, respectively). Factors other than focusing (e.g., decreased S oxidation due to seasonal anoxia) account for the high S concentrations and accumulation rates at the deepest site.

The third model of S accumulation (Table 4) assumes that only seston-derived S and not microbially-reduced S is focused; this calculation requires distinguishing seston S from S reduced by microbial respiration. The differentiation was based on the C:S ratios discussed in Baker et al (1992). Focusing of seston-derived S is corrected with ^{210}Pb inventories, and accumulation of excess or microbially-derived S is weighted according to the fraction of lake area represented by each core. The first model result (13.2 mmol m^{-2} yr^{-1} for surface sediments) is lower than the other two (19,23 mmol m^{-2} yr^{-1}) largely because of the smaller estimated depositional area. Clearly, basin-wide S accumulation is difficult to assess accurately, and there is a large uncertainty in our estimate of S accumulation rates.

Discussion

Two sulfur cycles operate concurrently within LRL (Figure 5); one occurs primarily within the water column and the second within the sediments. The first cycle involves the uptake of SO_4^{2-} by phytoplankton and the subsequent mineralization of organic S back to SO_4^{2-}. Inputs to this cycle come primarily from outside the lake (atmospheric deposition, groundwater inflow, leaf litter), and outputs include out-seepage of lake water to ground water, diffusion of SO_4^{2-} into sediment pore waters, and long-term storage of plankton S in sediments. The second sulfur cycle occurs entirely within the sediments. Outputs from the sedimentary cycle (release of H_2S or SO_4^{2-} back into the water column from the sediments) serve as inputs to the first cycle. In this paper we consider only the water column cycle.

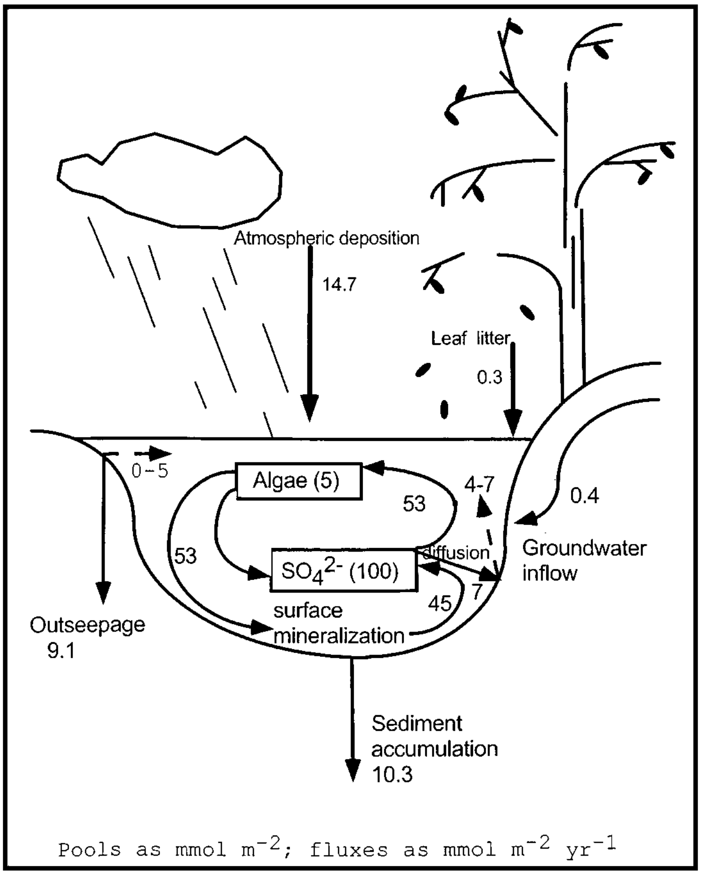

Figure 5. Sulfur cycle within the water column of the south basin of LRL. Large fluxes of SO_4^{2-} into and out of the water column result in a turnover time of about 1.5 years although the water residence time is 4–5 years. Of the total inputs (15.4 mmol m^{-2} yr^{-1}), the majority is buried in the sediment. The majority of S accumulating in the sediments was deposited as organic S in seston. However, approximately 85% of the organic S in mineralized at the sediment surface. Much of the diffusive flux and possibly some of the outseepage flux (both return fluxes shown as dotted lines) are lost from the sediments during fall and winter. Fluxes in the figure are long-term averages.

Sulfur mass balance

Mass balances provide a convenient structure that allows comparison of the relative magnitudes of fluxes, and either allows assessment of unmeasured or poorly constrained fluxes, or allows verification that all measured fluxes are correct. For the mass balances presented here, fluxes are calculated on an annual basis, but because of uncertainties in many of these fluxes, multi-year mean fluxes may be the most appropriate basis for comparison. The sulfur mass balance for the south (reference) basin of Little Rock Lake (Table 2) indicates that atmospheric deposition (14.7 mmol m^{-2} yr^{-1}) was the major source of sulfur to the lake prior to experimental manipulations. The mass balance indicates that, on average, $\sim$45% of the inputs (6.7 ± 4.4 mmol m^{-2} yr^{-1}) are buried in the sediments and the remainder is lost to groundwater outflow (including basin transfer). The major contributor to the propagated uncertainty in the sediment reaction term (Table 2) is the large uncertainty in dry deposition which provides 23% of the total S inputs. The S accumulation rates measured in sediment cores (10.1–10.9 mol m^{-2} yr^{-1}; Table 4) are higher than the estimate based on the mass balance (6.7 mmol m^{-2} yr^{-1}); this discrepancy may result from retention in the sediments of some of the sulfur in outseepage, or it may indicate that dry deposition has been underestimated. However, the accumulation rates in the cores are within the uncertainty of the estimate based on the mass balance, and therefore support the accuracy of the measured components of the mass balance.

The S budget for the north basin prior to experimental acidification has the same discrepancy as the south basin, but to a larger degree. Basin-wide rates of S accumulation estimated from sediment cores (15.7–28.3 mmol m^{-2} yr^{-1}; Table 4) are larger than the sediment reaction term (4.7 mmol m^{-2} yr^{-1}) in the mass balance for 1984 (Table 2) and some estimates even exceed the total inputs to the basin (17.5 mmol m^{-2} yr^{-1}) in 1984. Either the extrapolation from the sediment cores was incorrect, dry deposition was underestimated, or much of the outseeping S was retained in the sediments.

The experimental additions of S (27–92 mmol m^{-2} yr^{-1}) exceeded all other inputs (16.9 mmol m^{-2} yr^{-1}) to the north basin, but the mass balance does not clearly indicate the fate of this added S. The average sediment reaction rate (Table 2) for the experimental basin during acidification (1985–1990) was 29.6 ± 6.9 mmol m^{-2} yr^{-1} (mean ± propagated error (S.D.)). This estimate of S accumulation within the sediments overlaps with the basin-wide rates (15.7–28.3 mmol m^{-2} yr^{-1}) estimated from sediment cores taken prior to acidification. Sediment cores collected in 1990 had S concentrations 20% higher than those collected in 1984 (Monte & Urban 2000). Thus, the sediment reaction rates calculated from the mass balance cannot distinguish unambiguously between rates prior to acid additions and the enhanced rates that resulted from acid additions. For the mass balance to yield a definitive answer as to the fate of the added S, the uncertainty in the deposition velocity for sulfate aerosols and SO_2 would have to be refined, or the uncertainty in the estimates of S accumulation rates in sediment cores would have to be further constrained. The latter option would seem to be the easier hurdle

Table 5. Comparison of seston deposition (1984–1989) and sediment accumulation in cores from 1985.

Site	South 5-m	North 5-m	North 9-m
Seston:			
Deposition (g m^{-2} yr^{-1})	235	193	351
org-C content (mmol g^{-1})	27	27	27
S deposition[a] (mmol m^{-2} yr^{-1})	54	45	80
lakewide S deposition[b]	50	53	54
Sediment accumulation:			
Surface[c] (g m^{-2} yr^{-1})	74	123	210
Mean[c] (g m^{-2} yr^{-1})	116	90	114
Surface org-C.			
Conc. (mmol g^{-1})	21	23	25
Accum. (mmol m^{-2} yr^{-1})	1560	2810	5200
(% of deposition)	24%	53%	55%
Surface organic S			
Conc. (μmol g^{-1})	100–147	142	186
Accum. (mmol m^{-2} yr^{-1})	7.4–11	16	24
(% of deposition)	14–20%	36%	30%
^{210}Pb focusing factor[d]	1.08	0.84	1.47

[a] Based on the average S concentration in all samples (270 μmol g^{-1}).

[b] Lakewide deposition rates are calculated as the deposition rate at each site divided by the focusing factor for each site.

[c] Surface accumulation rates are based on ^{210}Pb measurements in the uppermost 0.5 cm of sediment cores. Mean sediment accumulation rates cover the entire period dated by Pb-210 (i.e., 1800–1986).

[d] ^{210}Pb focusing factor is defined as the ratio of the annual Pb-210 flux at each site to the rate of atmospheric deposition of Pb-210 (0.466 pCi cm^{-2} yr^{-1} (Urban et al. 1990).

to overcome; analysis of more sediment cores should further constrain the possible magnitude of S accumulation rates.

The S mass balances for the two basins point to one further problem in environmental measurements. Both the S mass balances and the sediment cores indicate that rates of S accumulation are higher (two- to threefold) in the north than in the south basin. Sulfur arrives in the sediments either in settling seston or by diffusion of SO_4^{2-}. The sediment traps did not indicate that seston deposition was higher in the north basin than in the south basin (Table 5). There is no particular reason to expect primary production or settling rates to be higher in the north than in the south basin. The sediment cores do indicate that there is some difference in the mineralization rates in the two basins; as shown in Table 5, organic carbon accumulation rates are 24% of deposition rates in the south basin compared to 54% in the north basin. Thus, differences in mineralization rates may cause a twofold difference in S accumulation rates between the two basins. However, the observed difference in accumulation rates between the basins is between two- and fourfold (Tables 4 and 5). It would seem that one of the net input fluxes of S to the sediments must be larger in the north than in the south basin. However, porewater equilibrators did not indicate that diffusive fluxes of SO_4^{2-} were higher in the north basin than in the south basin. These data may corroborate other recent studies (Urban et al. 1997) that indicate that diffusive fluxes calculated from porewater equilibrators underestimate the actual fluxes.

Lakewater S cycle

The S mass balances discussed above consider only the net inputs to and outputs from the water column. These net fluxes underestimate the ‘gross’ fluxes if S is returned from the sediments to the water column. Mineralization of organic matter in the sediments releases S in the form of H_2S that may be either fixed in the sediments or recycled to the water column. Similarly, SO_4^{2-} that diffuses into the sediments and is reduced to H_2S may be either fixed in the sediments or returned to the water column. In Little Rock Lake, these fluxes of S from the sediments to the water column are large relative to the S fluxes into the sediments.

Sulfate generally is not considered to be a reactive ion in lakes. Although depletion of SO_4^{2-} frequently is observed in hypolimnia due to bacterial sulfate reduction in the sediments (e.g., Hutchinson 1957; Cook & Schindler 1983; Davison & Finlay 1986), depletion in the epilimnion due to plankton uptake seldom is observed. King and Klug (1982) estimated that only 7% of the lakewater inventory of SO_4^{2-} was cycled annually through the plankton in a eutrophic, hard water lake. However, in soft water lakes, concentrations of SO_4^{2-} are much lower, and cycling of S through the plankton may be large relative to the lake inventory. In Lake Victoria with a SO_4^{2-} concentration of <5 μM, the turnover time for SO_4^{2-} is only 10–15 days (Lehman & Branstrator 1994). In extreme cases, SO_4^{2-} may be a limiting nutrient; in African lakes with SO_4^{2-} concentrations of 1–7 μM Beauchamp (1953) reported that algal growth was limited by SO_4^{2-} although recent studies indicate that phosphorus is now the limiting nutrient (Lehman & Branstrator 1994). In streams on the Canadian Shield with SO_4^{2-} concentrations of 15 μM, addition of SO_4^{2-} stimulated periphyton growth (Planas & Moreau 1986). Marine bacteria have half-saturation constants for SO_4^{2-} uptake of about 50 μM; when grown at lower concentrations such bacteria build proteins that are depleted in S (Cuhel et al. 1981). Little Rock Lake has a SO_4^{2-} concentration of only 25–30 μM; this small inventory in the water column makes SO_4^{2-} a sensitive tracer of organic matter cycling as well as of reduction and oxidation in the sediments.

A comparison of the measured fluxes reveals that uptake of S by plankton is large relative to the total inputs to the lake as well as to the inventory in the water column. Plankton uptake (53 mmol m^{-2} yr^{-1}) is more than three times greater than the annual input of S to the lake (15.6 mmol m^{-2} yr^{-1}) and represents 53% of the inventory of SO_4^{2-} in the water column (prior to experimental acidification). Because some mineralization of organic matter occurs in the water column, plankton uptake may be larger than our estimate based on sediment trap fluxes. In general, settling fluxes of organic matter in other lakes are reported to be only 20–60% of net primary production (e.g., Bloesch & Uehlinger 1990; Baines et al. 1994). In Little Rock Lake, the lakewide rate of organic C deposition (6.2 mol m^{-2} yr^{-1}) represents 74% of the upper estimate of net primary production (8.4 mol m^{-2} yr^{-1}; Wachtler 1987); hence plankton uptake of S may have been 30% higher than the estimate above or 70 mmol m^{-2} yr^{-1}. Despite this large uptake by the plankton, only small (2–10 μM) seasonal fluctuations were observed in SO_4^{2-} concentrations in the lake (Figure 1). Clearly, the large flux through plankton is possible only if mineralization regenerates the SO_4^{2-} assimilated by the plankton.

The magnitude of S mineralization may be assessed by comparing seston deposition and S accumulation in sediment cores (Table 5). Rates of organic C accumulation in surface sediments are 24–55% of the rates of organic C deposition in sediment traps. Mineralization of organic S in seston and surface sediments is faster than mineralization of organic C; rates of accumulation of organic S are only 14–36% of the rates of deposition (Table 5). The discrepancy between deposition and accumulation rates results from mineralization of 64–86% of the organic S at the sediment surface (i.e., within the first 0.5 cm of sediment), not from over-estimation of deposition due to sediment resuspension. Comparison of the ash content in surface sediments (40%) and sediment trap material (8–20%) also indicates that 60–86% of the organic material is decomposed at the sediment surface (assuming that ash is conservative). Were resuspension causing an overestimation of deposition rates, the ash content in sediment trap material would be higher, and mineralization estimates based on ash content would be lower than those based on accumulation rates. Mineralization does not necessarily stop at the sediment surface; in the north basin, organic C accumulation rates at depth are 30% lower than at the surface. However, in the south basin, organic C accumulation rates do not decrease with depth; accumulation rates at the sediment surface in the south basin are equal to those at depth in the north basin. Hence, it would appear that 80-86% of organic S deposited in the south basin is mineralized. Given these estimates of mineralization rates and the other measured fluxes of SO_4^{2-} into and out of the lake water, it is possible to estimate other fluxes of S from the sediments to the water column. Over the 9 years of this study there was no net change in SO_4^{2-} concentration in the south basin. Hence the sum of inputs must equal the sum of outputs:

$$I = \alpha' \bullet O + \alpha \bullet D + (PU - M) \tag{3}$$

where I is the sum of inputs (15.4 mmol $m^{-2}yr^{-1}$; Table 2), O is the outseepage (9.1 mmol m^{-2} yr^{-1}; Table 2), D is the diffusive flux, PU is the plankton uptake (53–70 mmol m^{-2} yr^{-1}), M is the mineralization rate, and α and α' represent the fractions of the diffusive and outseepage fluxes that are not returned to the lake. As noted above, porewater profiles in littoral areas (presumed sites of outseepage) showed SO_4^{2-} depletion in the sediments. Similarly, the mass balances for both basins suggested that some of the S outseepage may be retained in the sediments. If some of the diffusive flux to pelagic sediments ($1 - \alpha$) is returned to the lake water, it is possible that some of the outseepage flux is returned by similar mechanisms (i.e., seasonal oxidation). The average (± S.E.) of all measured diffusive fluxes in the south basin (n = 19) was 19 ± 4.6 μmol m^{-2} d^{-1} or 6.9 mmol m^{-2} yr^{-1}. Substitution of the measured values into eqn 3 indicates that the observed mineralization rates (80–86% of seston S deposition) can exist only if α is low. Specifically, if none of the outseepage flux returns to the lake (α'' = 1), then none of the diffusive flux can remain in the sediments (α = 0). If the same fractions of diffusive and outseepage fluxes return to the lake, then α lies between 30% and 50%. If diffusive fluxes were underestimated due to bioturbation, then α must be even lower than estimated above. Under all possible scenarios, less than 50% of diffusive fluxes can remain fixed in the south basin sediments if the measured fluxes (I,O,D) are accurate. A similar analysis for the north basin (accounting for SO_4^{2-} additions and the change in concentration in the basin) indicates that 50–100% of the diffusive flux remains in the sediments or is lost to groundwater recharge.

Retention in the sediments of less than 50% of the diffusive SO_4^{2-} flux is consistent with other information from LRL as well as with other reports in the literature. Only about 50% of ^{35}S originally fixed in sediments of Lake 302 was retained over a 6 month period (Rudd et al. 1986a); the loss was attributed to oxygen penetration into sediments during winter when microbial activity was reduced (Rudd et al. 1990). Kling et al. (1991) also observed release of S from sediments following overturn of the water column in fall in New England lakes. Release of S from sediments during fall and winter is consistent with the higher [SO_4^{2-}] in winter compared to summer (Figure 1(b)), with cyclic variations in SO_4^{2-} inventories in the water column

(Figure 6), and with cyclic variations in ratios of SO_4^{2-} to CI^- in LRL (Figure 7). The larger difference between winter and summer ratios of SO_4^{2-} to CI^- in the north basin compared with the south basin suggests that oxidation of reduced S (probably greater in the seasonally anoxic, deep regions of the north basin) contributes to the periodicity observed.

The discussion above focussed on annual or long-term average annual rates of S movement and transformation. However, the rapidity of S cycling can only be appreciated by examining short-term fluxes. The temporal dynamics of mineralization and return of diffusive fluxes of SO_4^{2-} to the water column are revealed by the seasonal variations in lake $[SO_4^{2-}]$ (Figure 1) or SO_4^{2-} inventories (Figure 6(a)). Because lake stage is highest in winter, seasonal variations in SO_4^{2-} inventories are larger than variations in $[SO_4^{2-}]$. The temporal variations may be simulated with a non-steady state variant of eqn 3 where B is SO_4^{2-} inventory and A is lake surface area:

$$\mathrm{d(B)/dt} = (\mathrm{I} - \alpha' \bullet \mathrm{O} - \mathrm{PU} + \mathrm{M} - \alpha \bullet \mathrm{D}) \bullet \mathrm{A} \tag{4}$$

Mineralization may be parameterized simplistically as first order with respect to the decomposable fraction (β) of seston deposition (S_D):

$$\mathrm{M(mmol\ m^{-2}yr^{-1})} = \mathrm{k(yr^{-1})} \bullet \beta \bullet \mathrm{S_D} \tag{5}$$

where k (yr^{-1}) is the rate coefficient for mineralization. As discussed above, some organic matter may be decomposed in the water column of LRL; in the following simulation this rapid mineralization is ignored, and measured fluxes of S in sediment traps (S_D) are used as a measure of phytoplankton uptake (PU). For simplicity, mineralization is assumed to proceed at the same, constant rate within the sediments and at the sediment surface. The diffusive flux can be parameterized as a function of lake $[SO_4^{2-}]$ (e.g., Baker et al. 1986); however, the small changes in $[SO_4^{2-}]$ in the south basin (Figure 1) render this unnecessary. Measured fluxes (input, outseepage, mean diffusive flux, seston deposition) were used to simulate the inventory of SO_4^{2-} in the south basin and to verify the values of α (0.3–0.5) and β (0.80–0.86) discussed above and to determine approximate values of k (Figure 6(b)).

The simulation reveals that the annual, cyclic variations in SO_4^{2-} inventories observed in both basins (Figure 6(a)) must result from the combined effects of organic matter mineralization and seasonal oxidation of S that diffuses into the sediments. The seasonal peak in simulated S inventories did not coincide with the time of the observed peak (Jan.–Feb.); there must be a seasonality in rates of mineralization due to temperature or oxygen availability that was not incorporated into this simple model. The magnitude of the seasonal variations in SO_4^{2-} inventories caused by mineralization of seston

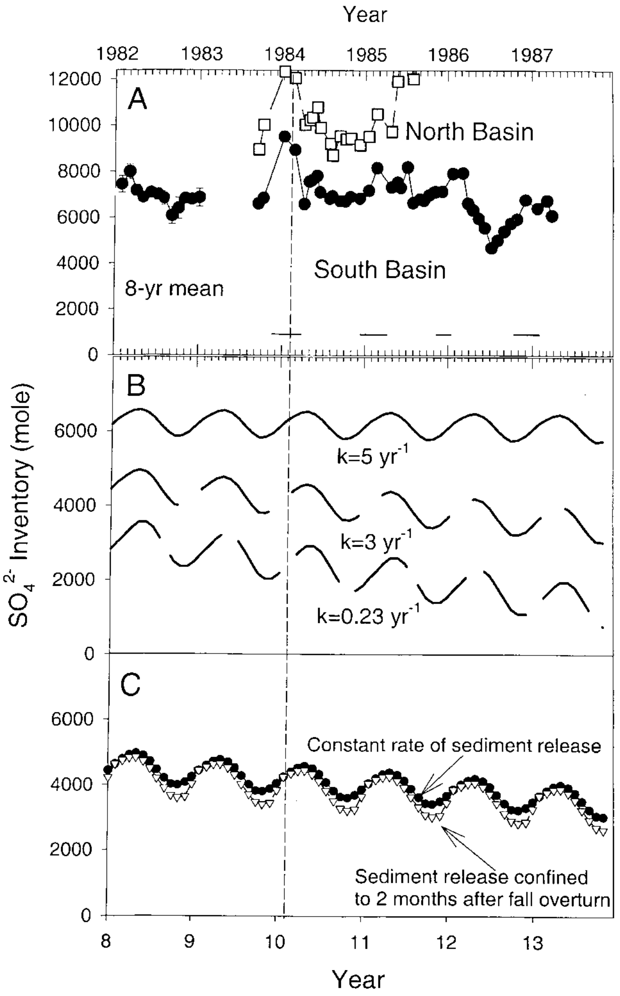

Figure 6. (A) Time course of SO_4^{2-} inventories in the south (1983–1987) and north (1983–1985) basins of LRL. Shown in the area marked 1982 are the 8-yr mean monthly inventories in the south basin. A cyclic pattern is visible in both the 8-yr mean and the north and south basin annual timecourses with lower values in summer than in winter. The vertical dashed line indicates the timing of maximum inventory (February) in the 8-yr mean record. (Short, solid, horizontal lines indicate periods of ice cover.) (B) Simulation of SO_4^{2-} inventories in south basin of LRL. The simulation (described in text) was run for 13 years at monthly time steps. Values of α, α' and β were selected as described in the text. The initial inventory was varied for the three simulations in order to separate the model lines. Changes in the rate constant (k) for mineralization result in changes in the magnitude of the annual variation in inventory; the faster the mineralization, the smaller the annual fluctuation in inventory. (C) Further simulations showing effects of seasonal oxidation of inorganic S. Both the magnitude and timing of the seasonal cycle in inventories is altered when the sediment release (i.e., return of diffusive and outseepage fluxes to the lake water) is modeled as occurring in the two months following fall overturn.

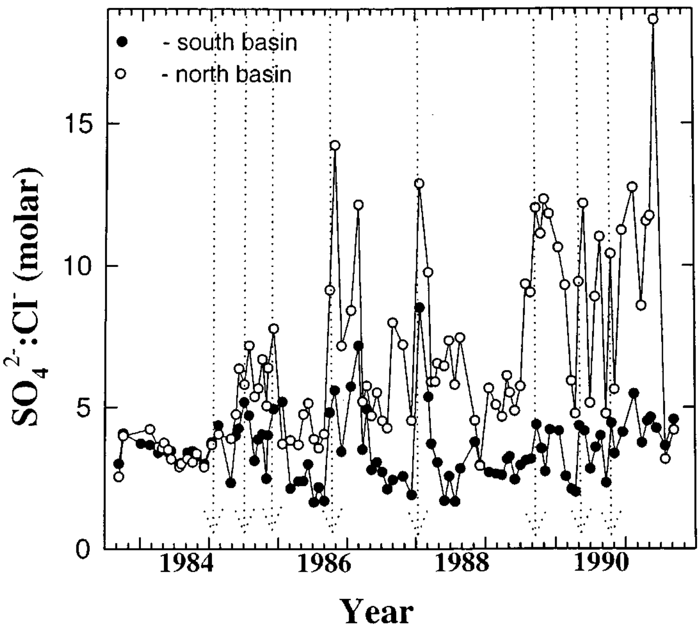

Figure 7. Ratios of [SO_4^{2-}] to [Cl^-] underwent seasonal fluctuations in both basins. Depicted here are ratios of the volume-weighted mean concentrations in both basins. Ratios in both basins were higher in winter than in summer; the increase generally occurred abruptly and simultaneously in both basins at the points indicated by the arrows. Increased ratios in the north basin also resulted from the acid additions, most notably in summers 1985 and 1989. Release of S from sediments in winters 1986–'87 and '87–'88 caused larger increases in the SO_4^{2-}:Cl^- ratio than did the acid additions in summer.

depends on the rate of mineralization; the faster the mineralization rate, the smaller are the fluctuations in lake SO_4^{2-} (Figure 6(b)). The average, observed fluctuation in the south basin (~2000 moles) was larger than any predicted by the simulations (800–1200 moles/yr) when typical rate constants for algal decomposition (half-lives of 2–36 mo; Westrich & Berner 1984; Carignan & Lean 1991; Burdige 1991) were used. Although larger fluctuations could be obtained with slower decomposition rates, such rates would imply that less than 50% of decomposition occurs in the top centimeter of sediments; sediment profiles are not consistent with such slow rates of decomposition. The magnitude of the seasonal fluctuation increases by ~300 moles yr^{-1} if it is assumed that a fraction of the diffusive (1 – α) and outseepage fluxes are returned to the water column in the two months following fall overturn (Figure 6(c)). Thus the simulation suggests that mineralization rates in Little Rock Lake lie in the range of 0.2–3 yr^{-1} (i.e., half-lives of 3–36 mo), and that seasonal oxidation of reduced, sediment S occurs. The picture that emerges from the array of measurements and mass balance analyses is one of rapid fluxes through moderate size pools of S in the lake-water S cycle. Consequently, turnover times of S within each pool are short. Total annual inputs of S to the south basin of LRL (7-yr mean = 15.4 mmol m^{-2} yr^{-1}) represent about 20% of the pool of S in the water column; hence the residence time of S in the water column (5 yr; T_R = pool/flux) about equals the water residence time (4–5 yr), but is shorter than that of conservative ions such as Cl^- ($\sim$11 yr). However, cycling within the water column renders the residence time of dissolved SO_4^{2-} shorter. Annual uptake by plankton represents 50-90% of the SO_4^{2-} pool in the water column in this soft-water lake. The organic S in the seston (half-life 90–1000 d) turns over more slowly than phosphorus (half-life $\approx$ 5–8 d) (e.g., Bloesch et al. 1977). At typical algal settling velocities (v = 0.5^{-1} m d^{-1}; e.g., Lehman et al. 1975), the rate constant for sedimentation (v/mean depth = 0.2–0.3 d^{-1}; Bannister 1974) is higher than that for mineralization of seston S (k = 0.0006–0.008 d^{-1}); accordingly, most of the organic S reaches the sediment surface. The residence time for particles in the uppermost 0.5 cm of sediments (9–48 mo; Table 5) is comparable to the half-life for mineralization of the organic S (3–36 mo), and hence most S is mineralized at the sediment surface. The residence time for S in this thin sediment layer is only $\sim$10 mo. The diffusive flux of SO_4^{2-} into the sediments represents 10–13% of the SO_4^{2-} pool in the water column; the return flux caused by reoxidation of iron sulfides is estimated to be 50–70% of the diffusive flux into the sediments. The combination of these fluxes (Figure 5) results in the SO_4^{2-} pool in the water column being turned over with a half-life of only about 12 months (T_R = 1.4 yr). Thus Little Rock Lake with a turnover time of 1.4 years is intermediate between hardwater lakes where SO_4^{2-} turnover times are many years (Stuiver 1967; King & Klug 1982) and lakes with extremely low SO_4^{2-} concentrations (e.g., 5 μM in L. Victoria) where turnover times are as rapid as 10-16 days (Lehman & Branstrator 1994).

Summary

Although S has the appearance of being a conservative substance in lakes, this study revealed that it is cycled rapidly in the water column. Because of the low SO_4^{2-} concentrations in Little Rock Lake, annual plankton S assimilation was equivalent to a large fraction of the lake S inventory, but mineralization of the plankton (turnover time 4–52 months) prevented a large depletion in lake-water SO_4^{2-} concentrations. Diffusion of SO_4^{2-} into the sediment is presumed to have increase as the SO_4^{2-} concentration was increased experimentally.

However, 50–80% of the diffusive flux was returned to the water column between fall and spring overturn as a result of oxidation of sediment S.

The mass balance, although nearly closed for the south basin of the lake, could not reveal the fate of the sulfur added to the north basin. The large uncertainty in the basin-wide accumulation rate of S in sediments and in the diffusive and outseepage fluxes must be resolved to improve the mass balance.

References

Anderson RF & Schiff SL (1987) Alkalinity generation and the fate of sulfur in lake sediments. Can. J. Fish. Aquat. Sci. 44: 188–193

Baines SB, Pace ML & Karl DM (1994) Why does the relationship between sinking flux and planktonic primary production differ between lakes and oceans? Limnol. Oceanogr. 39: 213–226

Baker LA (1991) Regional estimates of atmospheric dry deposition. In: Charles DF (Ed.) Acidic Deposition and Aquatic Ecosystems, Regional Case Studies (pp 645–652). Springer-Verlag, New York

Baker LA, Brezonik PL & Pollman CD (1986) Model of internal alkalinity generation: sulfate retention component. Water Air Soil Pollut. 31: 89–94

Baker LA, Eilers JM, Cook RB, Kaufmann PR & Herlihy AT (1991) Interregional comparison of surface water chemistry and biogeochemical processes. In: Charles DF (Ed.) Acidic Deposition and Aquatic Ecosystems: Regional Case Studies (pp 567–613). Springer-Verlag, New York

Baker LA, Engstrom DR & Brezonik PL (1992) Recent sulfur enrichment in the sediments of Little Rock Lake, Wisconsin. Limnol. Oceanogr. 37: 689–702

Baker LA, Tacconi JE & Brezonik PL (1988) Role of sedimentation in regulating major ion composition in a softwater, seepage lake in n. Wisconsin. *Verh. Int. Verein Limnol.* 23: 346–350

Baker LA, Urban NR, Sherman LA & Brezonik PL (1989) Sulfur cycling in an experimentally acidified seepage lake. In: Saltzman E & Cooper W (Eds) Biogenic Sulfur (pp 79–100). Amer. Chem. Soc., Wash. DC

Bannister TT (1974) A general theory of steady state phytoplankton growth in a nutrient-saturated mixed layer. Limnol. Oceanogr. 19: 13–30

Beauchamp, RSA (1953) Sulphates in African inland waters. Nature 171: 769–771

Bloesch J, Stadelmann P & Buhrer H (1977) Primary production, mineralization, and sedimentation in the euphotic zone of two Swiss lakes. Limnol. Oceanogr. 22: 511–526

Bloesch J & Uehlinger U (1990) Eqilimnetic carbon flux and turnover of different particle size classes in oligo-mesotrophic Lake Lucerne, Switzerland. Arch. Hydrobiol. 118: 403–419

Brezonik P, Baker L, Eaton J, Frost T, Garrison P, Krats T, Magnuson J, Perry J & Rose W (1986) Experimental acidification of Little Rock Lake, Wisconsin. Water Air Soil Poll. 30: 115–122

Brezonik P, Baker L & Perry TE (1987) Mechanisms of alkalinity generation in acid-sensitive soft water lakes. In: Hites RA & Eisenreich SJ (Eds) Sources and Fates of Aquatic Pollutants (pp 229–262). Amer. Chem. Soc., Washington, DC

Brezonik PL, Eaton JG, Frost TM, Garrison PJ, Kratz TK, Mach CE, McCormick J, Perry J, Rose W, Sampson C, et al. (1993) Experimental acidification of Little Rock Lake, Wisconsin: Chemical and biological changes over the pH range 6.1 to 4.7. Can J. Fish. Aq. Sci. 50: 1101–1121

Brezonik PL, Mach C, Downing G, Richardson N & Brigham M (1990) Effects of acidification on minor and trace metal chemistry in Little Rock Lake, Wisconsin. Envir. Toxicol. Chem. 9: 871–885

Burdige DJ (1991) The kinetics of organic matter mineralization in anoxic marine sediments. J. Mar. Res. 49: 727–761

Caldwell DE & Tiedje JM (1975) The structure of anaerobic bacterial communities in the hypolimnia of several Michigan lakes. Can. J. Microbiol. 21: 377–385

Capone DG & Kiene RP (1988) Comparison of microbial dynamics in marine and freshwater sediments: contrasts in anaerobic carbon catabolism. Limnol. Oceanogr. 33: 725–749

Carignan R & Lean DRS (1991) Regeneration of dissolved substances in a seasonally anoxic lake: the relative importance of processes occurring in the water column and in the sediments. Limnol. Oceanogr. 36: 683–707

Carignan R & Tessier A (1988) The co-diagenesis of sulfur and iron in acid lake sediments of southwestern Quebec. Geochim. Cosmochim. Acta 52: 1179–1188

Cook RB (1981) The biogeochemistry of sulfur in two small lakes. Ph.D. Thesis, Columbia University

Cook RB (1984) Distributions of ferrous iron and sulfide in an anoxic hypolimnion. Can.J. Fish. Aquat. Sci. 41: 386–293

Cook RB & Kelly CA (1992) Sulfur cycling and fluxes in temperate dimictic lakes. In: Howarth RW, Ivanov MV & Stewart JWB (Eds) Sulfur Cycling on the Continents (pp 145–188). J. Wiley & Sons, NY

Cook RB & Schindler DW (1983) The biogeochemistry of sulfur in an experimentally acidified lake. Ecol. Bull (Stockholm) 35: 115–127

Cuhel RL, Taylor CD & Jannasch HW (1981) Assimilatory sulfur metabolism in marine microorganisms: characteristics and regulation of sulfate transport in *Pseudomonas halodurans* and *Alteromonas luteo-violaceus*. J. Bacteriol. 147: 340–349

David MB & Mitchell MJ (1985) Sulfur constituents and cycling in waters, seston, and sediments of an oligotrophic lake. Limnol. Oceanogr. 30: 1196–1207

Davision W & Finlay BJ (1986) Ferrous iron and phototrophy as alternative sinks for sulphide in the anoxic hypolimnia of two adjacent lakes. J.Ecology 74: 663–673

DiToro DM, Mahony JD, Hansen DJ, Scott KJ, Carlson AR & Ankley GT (1992) Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. Environ. Sci. Technol 26: 96–101

DiToro DM, Mahony JD, Hansen DJ, Scott KJ, Mayr MB & Redmond MS (1990) Toxicity of cadmium in sediments: The role of acid volatile sulfide. Environ. Toxicol. Chem. 9: 1487–1502

Edgington DN & Robbins JA (1976) Records of lead deposition in Lake Michigan sediments since 1800. Environ. Sci. Technol. 10: 266–174

Fukuhara H & Sakamoto M (1987) Enhancement of inorganic nitrogen and phosphate release from lake sediment by tubificid worms and chironomid larvae. Oikos 48(3): 312–320

Giblin AE, Likens GE & Howarht RW (1991) A reply to the comment by Stauffer. Limnol. Oceanogr. 36: 1265–1270

Giblin AE, Likens GE, White D & Howarth RW (1990) Sulfur storage and alkalinity generation New England lake sediments. Limnol. Oceanogr. 35: 852–869

Goldman JC, Porcella DB, Middlebrooks EJ & Toerien DF (1972) The effect of carbon on algal growth – its relationship to eutrophication. Water Res. 6: 637–679

Healey FP (1973) Inorganic nutrient uptake and deficiency in algae. Crit. Rev. Microbiol. 3: 69–113

Hesslein RH (1976) An in-situ sampler for close interval pore water studies. Limnol. Oceanogr. 21: 912–914

Hicks BB (1986) Measuring dry deposition: a re-assessment of the state of the art. Water Air Soil Pollution 30: 75–90

Hicks BB, Wesely ML & Durham JL (1980) Critique of methods to measure dry deposition. U.S. EPA, Washington, DC

Hutchinson GE (1957) A Treatise on Limnology. I. Geography, Physics, Chemistry. J. Wiley & Sons, NY

Ingvorsen K, Zehnder A & Jorgensen BB(1984) Kinetics of sulfate and acetate uptake by *Desulfobacter postgatei*. Appl. Environ. Microbiol. 47: 403–408

Jassby AD (1975) Dark sulfate uptake and bacterial productivity in a subalpine lake. Ecology 56: 627–636

Johnson CM & Nishita H (1952) Microestimation of sulfur in plant materials, soils, and irrigation waters. Anal. Chem. 24: 736–742

Jorgensen BB (1990) A thiosulfate shunt in the sulfur cycle of marine sediments. Science 249: 152–154

Kelly CA, Rudd JW, Hesslein RH, Schindler DW, Dillon PJ, Driscoll CT & Gherini SA (1987) Prediction of biological acid neutralization in acid-sensitive lakes. Biogeochemistry 3: 129–140

King GM & Klug MJ (1982) Comparative aspects of sulfur mineralization in sediments of a eutrophic lake basin. Appl. Envir. Microbiol. 43: 1406–1412

Kling GW, Giblin AE, Fry B & Peterson BJ (1991) The role of seasonal turnover in lake alkalinity dynamics. Limnol. Oceanogr. 36: 106–122

Lehman JT, Botkin DB & Likens GE (1975) The assumptions and rationales of a computer model of phytoplankton population dynamics. Limnol. Oceanogr. 20: 343–364

Lehman JT & Branstrator DK (1994) Nutrient dynamics and turnover rates of phosphate and sulfate in Lake Victoria, East Africa. Limnol. Oceanogr. 39(2): 227–233

Li YH & Gregory S (1974) Diffusion of ions in sea water and in deep-sea sediments. Geochim. Cosmochim. Acta 38: 703–714

Losher A (1989) The sulfur cycle in freshwater lake sediments and implications for the use of C/S ratios as indicators of past environmental change. Ph.D. Diss., Swiss Federal Institute of Technology, Zurich

Lovley DR, Dwyer DF & Klug MJ (1982) Kinetic analysis of competition between sulfate reducers and methanogens for hydrogen in sediments. Appl. Environ. Microbiol. 43: 1373–1379

Mach CE (1992) The aquatic chemistry of aluminum, iron, manganese, cadmium, copper, lead, and zinc in an experimentally-acidified seepage lake. Ph.D. thesis, University of Minnesota

Mitchell MJ, David MB & Uutala AJ (1985) Sulfur distribution in lake sediment profiles as an index of historical depositional patterns. Hydrobiol. 121: 121–127

Mitchell MJ, Landers DH, Brodowski F, Lawrence GB & David MB (1984) Organic and inorganic sulfur constituents of the sediments in three New York lakes: effect of site, sediment depth, and season. Water Air Soil Poll. 21: 231–245

Monheimer RH (1974) Sulfate uptake as a measure of planktonic microbial production in freshwater ecosystems. Can. J. Microbiol. 20: 825–831

Monheimer RH (1975) Sulfate uptake by microplankton communities in western Lake St. Clair. Limnol. Oceanogr. 20: 183–190

Monte AE & Urban NR (2000) Transfer of sulfur between lake water and sediments of Little Rock Lake, Wisconsin. Can.J. Fish. Aquat. Sci. in prep

Newsome M (1987) Decomposition of leaf litter and elemental accumulation in microbial populations of an experimentally acidified lake. M.S. Thesis, University of Minnesota

Norton SA, Kahl JS, Mitchell MJ & Owen FS (1991) Another reply to the comment by Stauffer. Limnol. Oceanogr. 36: 1271–1274

Nriagu JO (1968) Sulfur metabolism and sedimentary environment: Lake Mendota. Wisconsin. Limnol. Oceanogr. 13: 430–439

Nriagu JO & Coker RD (1983) Sulphur in sediments chronicles past changes in lake acidification. Nature 303: 692–694

Nriagu JO & Soon YK (1985) Distribution and isotopic composition of sulfur in lake sediments of northern Ontario. Geochim. Cosmochim. Acta 49: 823–834

Ohle W (1934) Chemische und physikalische Untersuchungen norddeutscher Seen. Arch. Hydrobiol. 26: 386–658

Perry JA & Troelstrup NH (1989) Whole ecosystem manipulation: a productive avenue for test system research? Environ. Toxicol. Chem. 7: 941–951

Perry JA, Troelstrup NH, Newsom M & Shelley B (1987) Whole ecosystem manipulation experiments: the search for generality. Wat. Sci. Tech. 19: 55–71

Perry TE (1987) Acid neutralization in soft-water lakes. M.S. Thesis, Univ. Minnesota, Minneapolis

Planas D & Moreau G (1986) Reaction of lotic periphyton to experimental acidification. Water Air Soil Pollut. 30: 681–686

Rose WJ (1993) Hydrology of Little Rock Lake in Vilas County, north-central Wisconsin. U.S. Geological Survey, Madison, Wisconsin

Rudd JW, Kelly CA & Furutani A (1986a) The role of sulfate reduction in long-term accumulation of organic and inorganic sulfur in lake sediments. Limnol. Oceanogr. 31: 1281–1291

Rudd JW, Kelly CA, Schindler DW & Turner MA (1990) A comparison of the acidification efficiencies of nitric and sulfuric acids by two whole-lake addition experiments. Limnol. Oceanogr. 35: 663–679

Rudd JW, Kelly CA, St. Louis V, Hesslein RH, Furutani A & Holoka MH (1986b) Microbial consumption of nitric and sulfuric acids in acidified north temperate lakes. Limnol. Oceanogr. 31: 1267–1280

Sampson CJ (1992) Chemical responses in experimentally-acidified Little Rock Lake, Wisconsin. M.S. Thesis, University of Minnesota, Minneapolis

Sampson CJ, Brezonik PL & Weir EP (1994) Effects of acidification on chemical composition and chemical cycles in a seepage lake: mechanistic inferences from a whole-lake experimetn,. In: Baker LA (Ed.) Environmental Chemistry of Lakes and Reservoirs (pp 121–160). Amer. Chem. Soc., Washington, DC

Schindler DW (1986) The significance of in-lake production of alkalinity. Water Air Soil Pollut. 31: 931–944

Schindler DW, Turner MA, Stainton MP & Linsey GA (1986) Natural sources of acid-neutralizing capacity in low alkalinity lakes of the PreCambrian shield. Science 232: 844–847

Schnoor JL (1996) Environmental Modeling: Fate and Transport of Pollutants in Water, Air and Soil. Wiley-Interscience, NYC

Schoenheit P, Kristhansson JK & Thauer RK (1982) Kinetic mechanism for the ability of sulfate reducers to out-compete methanogens for acetate. Arch. Microbiol. 132: 285–288

Sherman LA, Brezonik PL, Baker LA & Weir EP (1994) Sediment porewater dynamics of Little Rock Lake, Wisconsin. Limnol. Oceanogr. 39: 1155–1171

Smith RL & Klug MJ (1981) Reduction of sulfur compounds in the sediments of a eutrophic lake basin. Appl. Envir. Microbiol. 41: 1230–1237

Sorokin JI (1975) Sulfide formation and chemical composition of bottom sediments of some Italian lakes. Hydrobiol. 47: 231–240

Stabel H (1985) Mechanisms controlling the sedimentation sequence of various elements in prealpine lakes. In: Stumm W (Ed.) Chemical Processes in Lakes (pp 143–168). Wiley, NY

Stauffer RE (1991) A comment on Sulfur storage and alkalinity generation in New England lake sediments. Limnol. Oceanogr. 36: 1263–1265

Strohl WR & Larkin JM (1978) Enumeration, isolation and characterization of Beggiatoa from freshwater sediments, Appl. Environment. Microbiol. 36: 755–770

Stuiver M (1967) The sulfur cycle in lake waters during thermal stratification. Geochim. Cosmochim. Acta 31: 2151–2167

Sweerts JP, De Beer D, Nielsin LP, Verdouw H, Van Den Heuvel JC, Cohen Y & Cappenberg TE (1990) Denitrification by sulphur oxidizing *Beggiatoa* spp. Mats on freshwater sediments. Nature 344: 762–763

Tacconi JE (1988) Ion Budgets and Cycling Processes in an acid-sensitive Seepage Lake. M.S. Thesis, University of Minnesota, Minneapolis

Ullman WJ & Aller RC (1989) Nutrient release rates from the sediments of Saginaw Bay, Lake Huron. Hydrobiologia 171: 127–140

Urban NR & Baker LA (1989) Alkalinity generation associated with the formation of ester sulfates. Limnol. Oceanogr. 34: 1144–1146

Urban NR, Baker LA, Sherman LA & Brezonik PL (1994) Sulfate reduction and diffusion in Little Rock Lake, Wisconsin. Limnol. Oceanogr. 39: 797–815

Urban NR, Dinkel C & Wehrli B (1997) Solute transfer across the sediment surface of a eutrophic lake: I. Porewater profiles from dialysis samplers. Aquatic Sci. 59(1): 1–25

Urban NR, Gorham E, Underwood JK, Martin FB & Ogden JG (1990) Geochemical processes controlling concentrations of Al, Fe, and Mn in Nova Scotian lakes. Limnol. Oceanogr. 35: 1516–1534

Wachtler JN (1987) The effect of acidification on primary production in Little Rock Lake, Wisconsin, M.S. Thesis, University of Minnesota, Minneapolis

Weir E (1989) Acidification of Little Rock Lake, M.S. thesis, Univ. Minnesota, Minneapolis

Westrich JT & Berner RA (1984) The role of sedimentary organic carbon and bacterial sulfate reduction: the G-theory revisited. Limnol. Oceanogr. 29: 236–249

Zaback DA & Pratt LM (1992) Isotopic composition and speciation of sulfur in the Miocene Monterey Formation: Reevaluation of sulfur reactions during early diagenesis in marine environments. Geochim. Cosmochim. Acta 56: 763–774

Zhabina NN & Volkov II (1978) A method of determination of various sulfur compounds in sea sediments and rocks. In: Krumbein G (Ed.) Environmental Biogeochemistry and Geomicrobiology (pp. 735–745). Ann Arbor Sci., Ann Arbor

Zobrist J, Wersin P, Jaques C, Sigg L & Stumm W (1993) Dry deposition measurements using water as a receptor: a chemical approach. Water Air Soil Pollut. 71: 111–130