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Author(s): Leslie A. Sherman, Lawrence A. Baker, Edward P. Weir, Patrick L. Brezonik

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Sediment pore-water dynamics of Little Rock Lake, Wisconsin: Geochemical processes and seasonal and spatial variability

Leslie A. Sherman

Department of Soil Science, 1525 Observatory Dr., University of Wisconsin, Madison 53706

Lawrence A. Baker

Department of Civil Engineering, Arizona State University, Tempe 85287

Edward P. Weir

Minnesota Pollution Control Agency, Rochester 55904

Patrick L. Brezonik

Department of Civil & Mineral Engineering, 500 Pillsbury Dr. SE, University of Minnesota, Minneapolis 55455

Abstract

The nature of sediment alkalinity generation processes and the temporal and spatial variability of the pore-water chemistry of an experimentally acidified seepage lake (Little Rock Lake, Wisconsin) were determined. Analysis of vertical gradients of solutes near the sediment–water interface indicates that sulfate reduction and base cation production were the major mechanisms of alkalinity generation. A comparison of surficial accumulation rates and burial rates indicates that the major source of cations to the pore water occurred by release of organically bound and exchangeable cations through decomposition. Pore-water measurements also reveal significant seasonal changes in solute fluxes, including a sudden change in sediment metabolism following a springtime algal bloom. Spatial differences in particle deposition caused pore-water fluxes of ammonium and alkalinity to be almost an order of magnitude higher at a hypolimnetic site than at epilimnetic sites. After 2 yr of acidification, pore-water gradients of sulfate, calcium, and alkalinity showed only minor changes, and the pore-water pH in the acidified basin remained within 0.5 pH units of preacidification pH.

Sediments are major sites of alkalinity generation for the water columns of soft-water lakes (Cook et al. 1986; Brezonik et al. 1987; Rudd et al. 1986). This process is important in lakes with small watershed-to-lake-area ratios (Schindler 1986) and especially for precipitation-dominated seepage lakes (Brezonik et al. 1987). The latter constitute a major fraction of the low alkalinity lakes in the United States and are especially prevalent in the upper midwest and in Florida (Baker et al. 1991).

Acknowledgments

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Sediment pore-water dynamics have been studied as a means of understanding alkalinity generation in lake sediments (Kuivila and Murray 1984; Schiff and Anderson 1986; Rudd et al. 1986). However, detailed investigations of these dynamics have not been conducted. Although some investigators have noted differences in pore-water chemistry in soft-water lakes between sites and across seasons (Cook et al. 1987; Rudd et al. 1990; Carignan and Lean 1991), studies have not been specifically designed to evaluate the spatial and temporal variability of the pore-water chemistry in soft-water lakes. Pore-water data most often have been collected at low temporal and spatial resolution, which may conceal significant temporal variability in response to temperature, sedimentation, and lake mixing patterns or may mask spatial trends resulting from different sedimentation rates or overlaying water-column concentrations. In addition, although cation production (as well as SO_4^{2-} reduction) contributes significantly to sediment alkalinity generation (Schiff and Anderson 1986), de-

tailed studies of the mechanisms of cation production in lake sediments have not been made.

This paper examines the sediment pore-water chemistry of Little Rock Lake, a precipitation-dominated seepage lake that is the site of an experimental acidification study. Pore-water concentrations of alkalinity, major ions, and nutrients were measured seven times during the first 2 yr of acidification at five different sites in the lake. Results reveal a spatially and temporally dynamic sediment pore-water environment controlled by multiple related factors. Coupled with solid-phase carbon and cation measurements, the profiles provide insights into the mechanisms of sediment alkalinity generation in a seepage lake. This study demonstrates the importance and dynamics of calcium release from organic matter in the sediments of such lakes.

Study site

Little Rock Lake (Vilas Co., northeastern Wisconsin, 49°60'N 89°50'W) is an oligotrophic seepage system. Precipitation comprises 98–100% of the total water input to the lake (W. Rose unpubl. data). The lake has two basins connected by a narrow (70 m) constriction. The total surface area is 18 ha, and the maximum depths are 10.5 m in the north basin and 5 m in the south basin. The north basin stratifies thermally, creating an oxygen-depleted hypolimnion that constitutes ~8% of the total basin volume. Before experimental acidification, the lake had a low ionic content (sp cond. = 11 $\mu\text{S cm}^{-1}$ at 25°C), low nutrient and chlorophyll concentrations (total P = 11 $\mu\text{g liter}^{-1}$; Chl *a* = 2–5 $\mu\text{g liter}^{-1}$), and low color (~15 PCU) and turbidity (<1 NTU); alkalinity was ~25 $\mu\text{eq liter}^{-1}$, and pH was 6.1 (Brezonik et al. 1993).

The sediments of Little Rock Lake are primarily soft, organic-rich gyttja and fine-grained sand. About 60% of the lake area is gyttja with a water content >90% and organic content >40%. The lakewide gross sedimentation rate (calculated from sediment traps) is 120 $\text{g m}^{-2} \text{yr}^{-1}$, and the sedimenting material was ~36% organic C (Baker et al. 1989). Sediments in most of the littoral regions are >90% sand and have a water content of ~70%. The organic content is variable, ranging from 5 to 20%. The littoral sediments are often overlain with a thin

layer of flocculent organic matter or macrophytes.

In the acidification experiment, the north basin was acidified with electrolyte-grade H_2SO_4 , and the south basin provided a reference (see Brezonik et al. 1993). The pore-water study reported here was conducted in the first 2 yr of acidification (April 1985–April 1987), during which the pH of the north basin was lowered from its preacidification value of 6.1 to a level of 5.6.

Methods

Field—Pore-water equilibrators were deployed for seven sampling periods: April, June, and August 1985, 10 and 30 May 1986, September 1986, and January 1987. The equilibrators were installed at five sites in the lake: at 1-m and 5-m depths in the south basin and 1-, 5-, and 9-m depths in the north basin. The 1-m depths were sampled only in 1985 and the 9-m depth only in 1985 and May 1986.

The design of the equilibrators closely resembled that of Hesslein (1976); each consisted of a $2.0 \times 10 \times 79$ -cm Plexiglas bar into which were milled 7-ml cells at 1-cm intervals. A Nuclepore polycarbonate membrane with a 2.0- μm pore size covered the cells, which were filled with distilled deionized water (DDW). A Plexiglas face plate with holes cut to match the equilibrator cells was used to hold the membrane filter in place. A DDW-soaked, 0.5-cm-thick polyurethane foam filter rested between the membrane and the top plate, protecting the membrane from puncture during installation. The face plate was fastened to the equilibrator body with nylon screws. Before installation, a 1×1 -m plastic grating with a 2-cm grid was attached to each pelagic equilibrator at the center to prevent it from sinking into the flocculent sediment. In this way, half the equilibrator stayed above the sediment–water interface and half below.

The equilibrators remained in the sediment for a 3-week equilibration period. Hypodermic syringes or Eppendorf pipettes were used to withdraw samples through the exposed membrane covering the cells. Redox-sensitive species ($\Sigma\text{H}_2\text{S}$, Fe^{2+} , total Mn) were sampled first and preserved as described below. Samples were withdrawn from each cell in the region extending from 5 cm above to 10 cm below

the interface, with sampling at wider intervals outside this range. Analyses of the pore water for all desired chemical constituents required >7 ml (the volume of one cell). In 1985, two neighboring equilibrators cells were sampled (but not combined) to collect a sufficient volume: one cell was sampled for major ions and the next for the remaining species. Therefore, a resolution in depth of only 2 cm was obtained for each chemical constituent in the region of the interface. In the two May 1986 sampling periods, fewer species were measured (only Ca^{2+} , Mg^{2+} , SO_4^{2-} , and Fe^{2+}), and a 1-cm resolution was achieved. In September 1986 and January 1987, two or three equilibrators were deployed at each site to measure many species and obtain a 1-cm resolution. The average time required to remove samples from an equilibrator was ~0.75–1 h.

Analytical—The pore water was analyzed for SO_4^{2-} , Ca^{2+} , Mg^{2+} , and Fe^{2+} on all the sampling dates and for alkalinity and NH_4^+ on all dates except the May periods; pH, DIC (dissolved inorganic C), DOC (dissolved organic C), NO_3^- , SiO_2 , $\Sigma\text{H}_2\text{S}$, Mn_T (total Mn), and Al_T (total Al) were measured on one or two occasions. All samples, except those for pH and DIC, were placed in small plastic vials and refrigerated. The following were also preserved: $\Sigma\text{H}_2\text{S}$ (0.09 N ZnAc and 0.18 N NaOH), Fe^{2+} (0.3 N HCl), and Mn_T and Al_T (0.04 N Ultrex HNO_3). Analyses for these parameters were performed in a laboratory at the University of Minnesota: SO_4^{2-} by ion chromatography; major cations by flame atomic absorption spectrophotometry (AAS); Mn_T and Al_T by graphite furnace AAS; and NH_4^+ , SiO_2 , Fe^{2+} , $\Sigma\text{H}_2\text{S}$, and NO_3^- by colorimetric methods (Brezonik et al. 1993). Alkalinity was determined by Gran alkalinity titration. Holding times for preserved Fe^{2+} and $\Sigma\text{H}_2\text{S}$ samples were <2 d.

DIC and pH were measured at the Trout Lake Field Station (University of Wisconsin) to minimize holding time. Samples for these parameters were withdrawn by hypodermic syringe and stored briefly by inserting the needle into a rubber stopper. Closed-cell pH measurements were made with a 3-ml cylindrical glass chamber with three ports. One port allowed injection of the sample into the chamber, the second drained the cell, and the third

Table 1. Precision and accuracy of Little Rock Lake pore-water analyses.

Constituent	Avg	Bias* (%)	C.V. (%)	n†
A. Precision of replicate analyses of pore-water samples				
pH	6.11		0.49	4
Alkalinity ($\mu\text{eq liter}^{-1}$)	549		4.28	18
Ca^{2+} (mg liter^{-1})	3.08		3.90	24
Mg^{2+} (mg liter^{-1})	0.77		3.90	24
SO_4^{2-} (mg liter^{-1})	0.89		10.1	26
H_2S (μM)	0.58		5.17	15
NH_4^+ (mg liter^{-1})	3.34		5.69	13
SiO_2 ($\mu\text{g liter}^{-1}$)	15.3		7.97	2
Fe^{2+} (mg liter^{-1})	2.18		6.88	10
DIC (mg liter^{-1})	12.6		4.59	4
DOC (mg liter^{-1})	3.48		6.03	3
B. Accuracy of analyses of EPA QC sample				
Ca^{2+}		+3.26		56
Mg^{2+}		+2.67		54
SO_4^{2-}		+8.97		22
NH_4^+		-6.46		12

* Bias = (measured value - true value)/true value \times 100. True values are published values for EPA QC sample.

† n is the number of pairs of replicates (part A) or analyses (part B).

contained the pH electrode, which was sealed by an O-ring. DIC samples were injected into a nitrogen-stripping column and acidified with 0.03 N HCl. The purged CO_2 was analyzed on a Beckman model 865 infrared gas analyzer.

Accuracy of the pore-water measurements was evaluated by analyzing an EPA quality control (QC) sample during each instrument run for Ca^{2+} , Mg^{2+} , SO_4^{2-} , and NH_4^+ ; bias was calculated as the difference between the nominal concentration and the measured concentration. Precision, expressed as a coefficient of variation, was determined for each chemical constituent by analyzing split samples obtained from a single equilibrator cell for 5% of the total cells sampled. Table 1 gives a summary of the calculated bias and the C.V. of the pore-water analyses for 1985–1987.

Flux calculations—Sediment–water fluxes were calculated from Fick's first law of diffusion. Diffusion coefficients were taken from Li and Gregory (1974), using a linear interpolation to adjust coefficients to ambient temperature and correcting for sediment porosity (Baker et al. 1989). Bioturbation is negligible in Little Rock Lake because the benthic invertebrate population is low (Brezonik et al. 1993), and advective flow of pore water into the lake also is negligible except for a small area in the

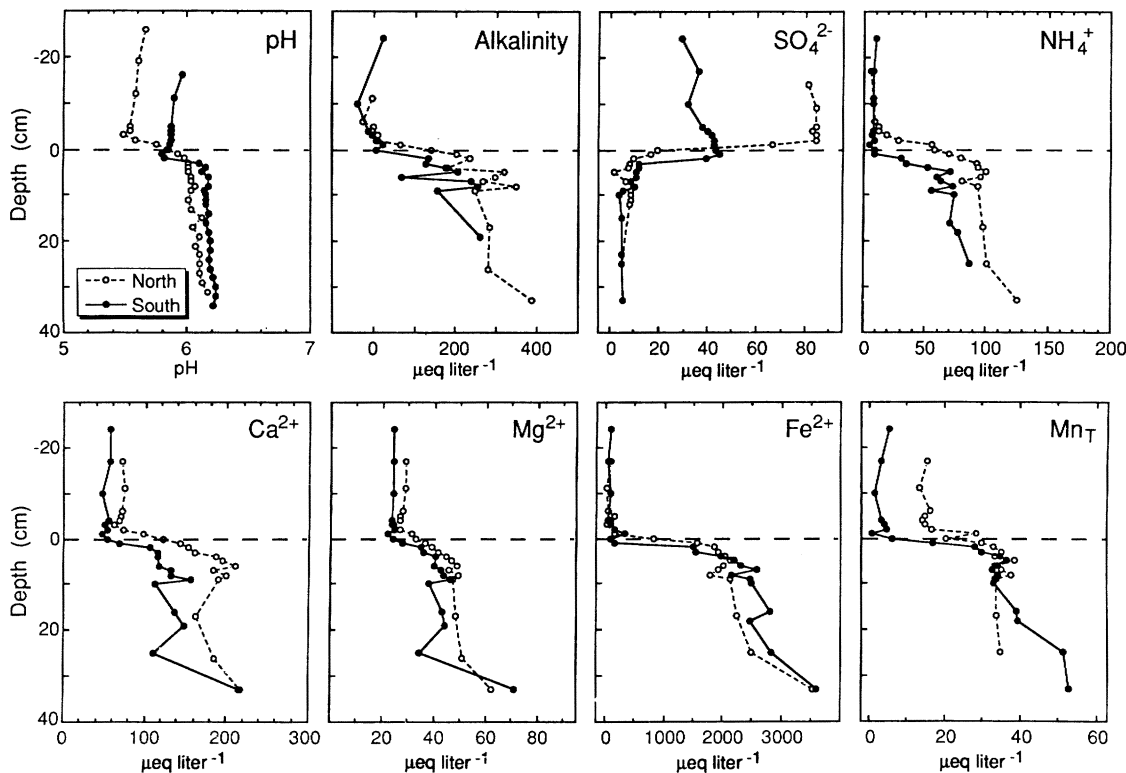


Fig. 1. Pore-water profiles of pH, alkalinity, SO_4^{2-} , NH_4^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , and Mn_T at 5-m depth in Little Rock Lake (September 1986).

littoral region in the south basin where in-seepage occurs periodically. In general, points in the top few centimeters of sediment, beginning at the interface (or the closest point above it when the interface was not sampled), were included in the calculation of the gradient. When a flocculent layer of organic matter was present above consolidated sediments (*see results and discussion*), points in the few centimeters directly above and including the interface were chosen. To measure the full extent of the linear portion of the gradient, we selected the greatest number of points (averaging 3–4 points) to calculate the gradient. The criteria for selecting the points was that the regression coefficient (r^2) of the gradient from these points must be >0.9 . Even if fewer points gave a higher r^2 , the greater number was used for statistical purposes. About 85% of the gradients had an $r^2 > 0.93$.

Solid-phase analyses—The methods for collecting and analyzing sediment trap data and sediment cores in Little Rock Lake were sum-

marized by Baker et al. (1988, 1992). Sediment cation fractions were analyzed by a sequential extraction. The exchangeable fraction was determined by the ammonia saturation method (Thomas 1982), the organic fraction was measured by peroxide oxidation (Tessier et al. 1979), and the residual (mineral) fraction was determined by lithium metaborate fusion (Suhr and Ingamells 1966). Digestates for the first two fractions were analyzed by flame AAS. Cations in the residual fraction were analyzed by direct-current plasma spectroscopy. In addition, the sediments were analyzed by X-ray diffraction to identify mineral species.

Results and discussion

Examples of concentration profiles of the major species in pore water of Little Rock Lake for September 1986 are given in Fig. 1. Pore-water concentrations of all the chemical constituents increased below the region of the sediment–water interface, except SO_4^{2-} , which decreased. DOC and $\Sigma\text{H}_2\text{S}$ (not shown) both

increased slightly in the pore water but remained at low concentrations; NO_3^- was not detectable ($<10 \mu\text{g liter}^{-1}$) in the pore water or the overlying water column.

The depth in the sediment at which pore-water concentration changes rapidly differed in the two basins of the lake. In the south basin, concentration gradients most often began at or just below the sediment–water interface, whereas in the north basin, they most often began 2–3 cm above the interface (*see Figs. 1, 2, 5, 6, and 7*). We conclude that the difference between the basins reflects the presence of a flocculent layer of fine suspended organic particles above the sediment–water interface in the north basin, which has a shorter fetch and is deeper than the south basin. A layer of flocculent material 2–3 cm thick was regularly recovered above sediment cores from the north basin but not from the south basin (N. Urban pers. comm.). Sweerts et al. (1986) found a similar flocculent layer covering littoral sediments of a Precambrian Shield lake, and this also caused the zone of SO_4^{2-} reduction to shift upward.

Sulfate reduction—Profiles of redox-sensitive species [Fe(II) , Mn_T , and SO_4^{2-}] indicate that aerobic decomposition was confined to the upper 1 cm of surficial sediments or flocculent layer. This finding is consistent with microelectrode oxygen measurements, which indicate that oxygen penetration is confined to the upper 2 cm of the sediment column even in highly oligotrophic systems (Carleton et al. 1989). Fe(II) increased rapidly within 1 cm of the interface (Fig. 3), and $\Sigma\text{H}_2\text{S}$ was present in the pore water in this region, though at low concentrations ($<2 \mu\text{M}$). The profiles indicate that organic matter decomposition proceeded anaerobically below the surficial sediments. Nitrate was not detectable in the pore water or the water column 30 cm above the sediment–water interface, indicating no significant denitrification in the sediments. In contrast, in many lakes investigated by Rudd et al. (1986), NO_3^- derived from atmospheric deposition is high enough to support significant denitrification.

Sulfate concentrations decreased with depth in the pore water, reflecting consumption by SO_4^{2-} reduction; concentrations were reduced from lake-water values of 30–50 $\mu\text{eq liter}^{-1}$ in the south basin and 50–70 $\mu\text{eq liter}^{-1}$ in the

north basin to $<10 \mu\text{eq liter}^{-1}$ 5–10 cm below the sediment–water interface (Fig. 2). The minimum pore-water SO_4^{2-} concentration is comparable to minimum concentrations found in other lakes (Schiff and Anderson 1986; Rudd et al. 1986). This concentration is lower than Lovley and Klug's (1986) estimate of the level below which bacterial growth of SO_4^{2-} reducers cannot be maintained (30 μM), which suggests that natural populations of SO_4^{2-} reducers may decrease SO_4^{2-} concentrations below the experimentally determined threshold value. The presence of methane in the pore water (300–500 μM at 10 cm) suggests that methanogenesis supplants SO_4^{2-} reduction at depths >10 cm below the interface. This shift in decomposition processes with depth in the sediment has been observed in many aquatic systems (e.g. Kelly and Rudd 1984; Lovley and Klug 1986). Ammonium concentrations, produced from organic matter decomposition, typically increased throughout this region (from 10 to $>100 \mu\text{eq liter}^{-1}$).

The amount of $\Sigma\text{H}_2\text{S}$ produced did not equal the amount of SO_4^{2-} reduced, suggesting that $\Sigma\text{H}_2\text{S}$ was not the final product of SO_4^{2-} reduction. Saturation indices (the ratio of the product of measured ion activities to the solubility constant) were calculated for amorphous FeS , mackinawite, greigite, and pyrite from the measured pH and concentrations of pore-water Fe^{2+} and $\Sigma\text{H}_2\text{S}$ concentrations with K_{s0} values from Giblin and Howarth (1984). The pore water was highly undersaturated with respect to the first three minerals, suggesting that the fixation of sulfide into these forms did not occur within the sediments. Pyrite, on the other hand, was highly oversaturated in the pore water. Chromium-reducible sulfur (CRS) (composed primarily of FeS_2 and S in Little Rock Lake; Baker et al. 1992) represented 20% of the total S in sediment cores at the two 5-m sites (Baker et al. 1989). Rudd et al. (1986) observed rapid formation of CRS in $^{35}\text{SO}_4^{2-}$ enrichment studies of sediments of several lakes. In Little Rock Lake sediments, CRS is formed from $^{35}\text{SO}_4^{2-}$ within 24 h (Baker et al. 1989). We conclude that the oversaturation of pyrite in the pore water of Little Rock Lake, along with the presence of CRS in the sediments, indicates the formation of pyrite.

The SO_4^{2-} pore-water profiles show moderate but revealing seasonal changes (Fig. 2).

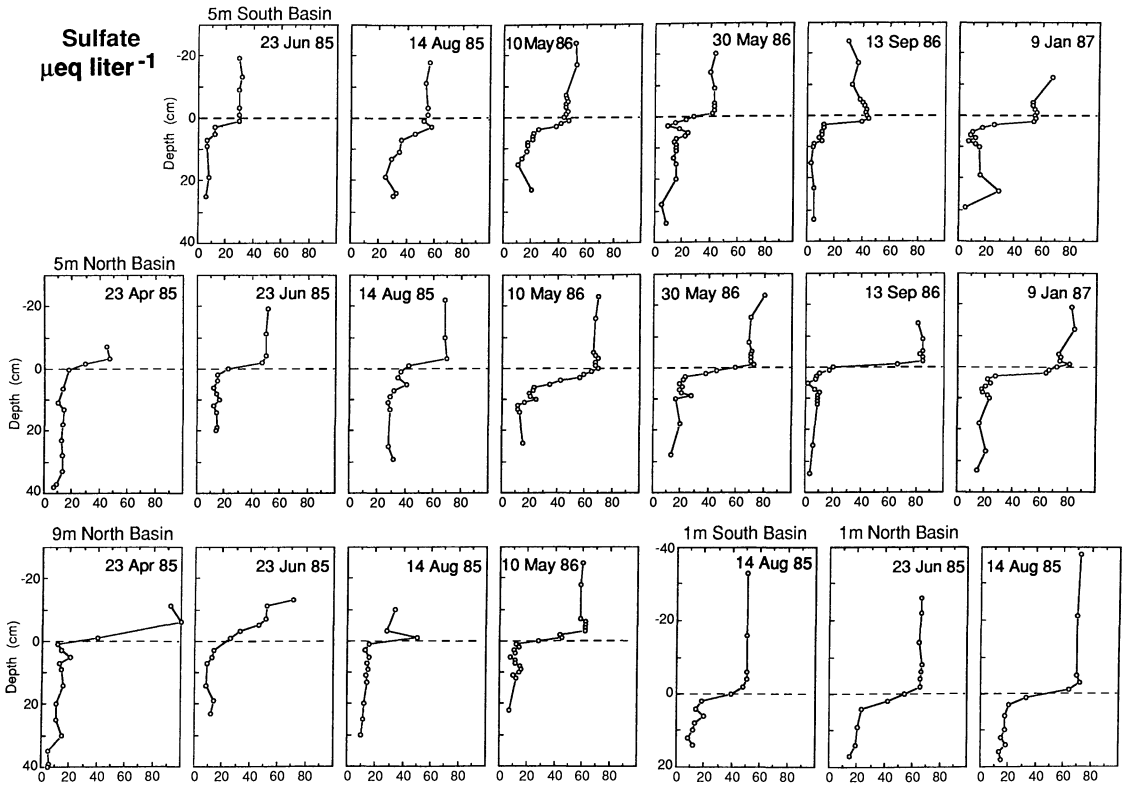


Fig. 2. Pore-water profiles of SO_4^{2-} concentrations in the two basins of Little Rock Lake at the depths indicated.

The shapes of the profiles were comparable among all dates, with SO_4^{2-} consumed rapidly in the region of the sediment–water interface. There was, however, a small seasonal progression of the depth and magnitude of the SO_4^{2-} gradient. For example, in late summer (September 1986), the magnitude of the diffusive flux of SO_4^{2-} in the region of the interface in both basins was 10 times the flux in midwinter under ice (January 1987). Bottom-water temperatures were 21°C in summer and 4°C in winter. A comparison of the early and late May 1986 profiles reveals that seasonal changes may be quite rapid. In early May, the SO_4^{2-} concentration gradients were shallow, began low in the sediment column, and extended to as much as 10 cm below the interface. In late May, the gradients began several centimeters higher (toward their summertime positions) and were steeper. The change in temperature was from 6°C to 13°C. Reduced Fe profiles also show a major change between these dates (Fig. 3). Peak Fe^{2+} concentrations

increased two–three times and were ~5 cm closer to the interface in late May than in early May. Overall, SO_4^{2-} fluxes ranged from 20 $\mu\text{eq m}^{-2} \text{d}^{-1}$ in colder months to 230 in warmer months (Table 2; Fig. 4).

The seasonal changes in SO_4^{2-} profiles reflect changes in temperature and productivity. Bottom-water temperatures varied from 4 to 24°C, and gross sedimentation rates were <0.2 $\text{g m}^{-2} \text{d}^{-1}$ in winter, peaked after ice-out in early May at 1.0–2.0 $\text{g m}^{-2} \text{d}^{-1}$, and declined to a constant level of 0.3–0.7 $\text{g m}^{-2} \text{d}^{-1}$ in summer (Baker et al. 1988). In warmer, more productive months, higher temperatures and higher organic loadings to the sediment resulted in increased microbial activity and hence steeper SO_4^{2-} gradients. In winter months, low microbial activity resulted in greater oxygen penetration into the sediments, thus reoxidizing some of the previously reduced SO_4^{2-} and shifting the SO_4^{2-} reducing zone downward. The large change between early- and late-May profiles primarily reflects the sudden pulse in

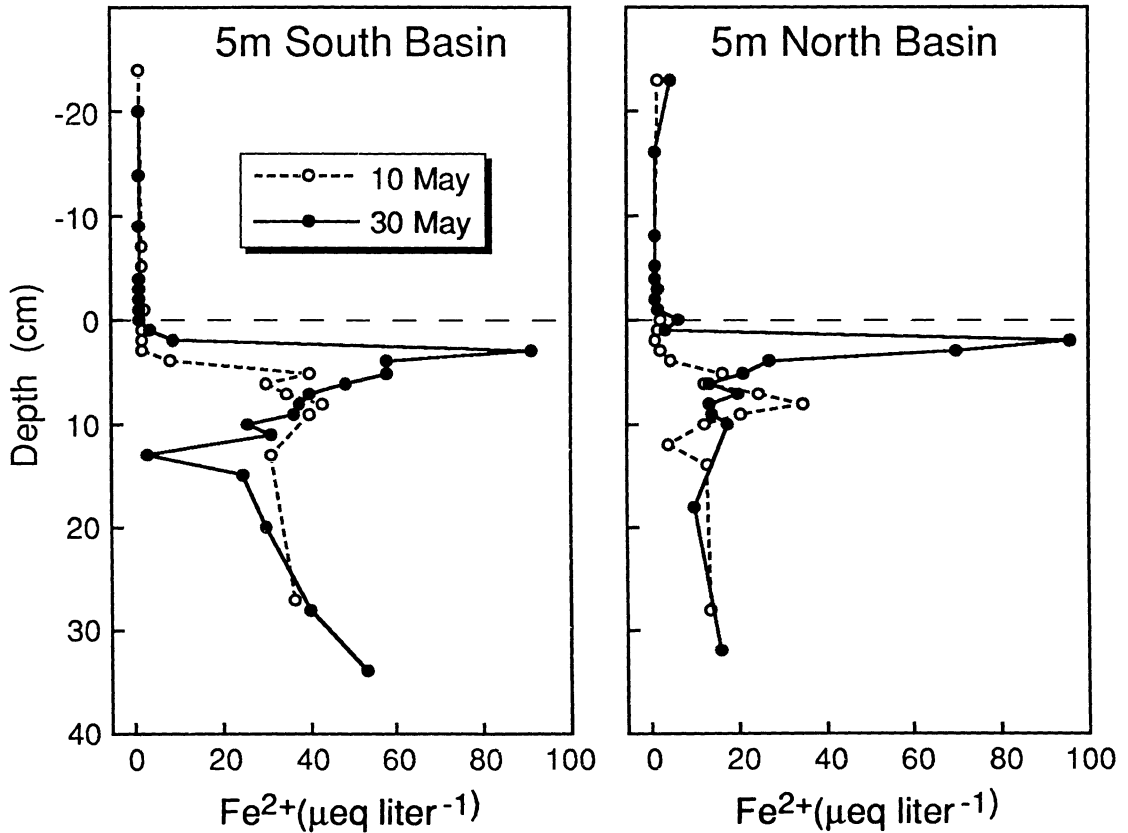


Fig. 3. Pore-water profiles of reduced Fe in epilimnetic sediments of Little Rock Lake at 5-m depth (May 1986).

organic deposition after ice-out. Rudd et al. (1990) also observed that the depth of penetration of SO_4^{2-} varied seasonally in response to seasonal changes in sediment microbial activity in a Canadian Shield lake.

Spatial patterns in pore-water SO_4^{2-} concentrations were not evident. The littoral and 5-m pelagic site concentrations were comparable, even though the littoral sediment had less organic content. This finding suggests that metabolizable organic matter was of sufficient magnitude to support SO_4^{2-} reduction in the littoral region. Rudd et al. (1986) also found comparable littoral and pelagic SO_4^{2-} profiles in lakes in the Experimental Lakes Area in northwestern Ontario. In contrast, Cook et al. (1987) found differences in pore-water fluxes between three sites sampled in Little Rock Lake and attributed the differences to seepage patterns. Seepage was not a major factor in controlling pore-water concentrations at our sam-

pling sites. The concentrations of SO_4^{2-} were also similar at the 5-m sites and the hypolimnetic 9-m site. However, in warmer months at the 9-m site, the gradients began much higher in the water column (up to 10 cm above the sediment–water interface), suggesting the presence of a thick flocculent layer in which anaerobic decomposition was active.

Ammonium production—One might expect to find seasonal changes in pore-water NH_4^+ concentrations, corresponding to those of SO_4^{2-} , which reflect changes in sediment decomposition rates. However, seasonal trends were not readily apparent in the pore-water NH_4^+ at the 5-m sites (Fig. 5), although calculated fluxes were lower in colder months. In the north basin, fluxes were 30–40% lower in January than in September, and those in April were slightly lower (5–10%) than those in June (Table 2). Concentrations at a given depth varied from 50 to 250 $\mu\text{eq liter}^{-1}$ between seasons

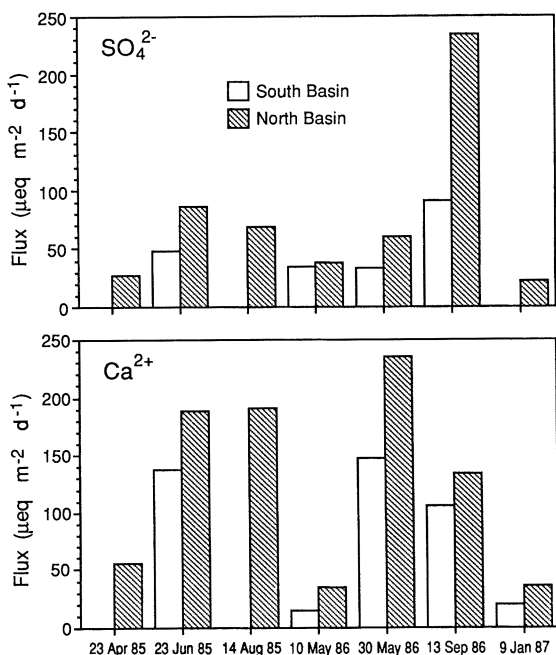


Fig. 4. Pore-water fluxes of SO_4^{2-} and Ca^{2+} across the sediment-water interface in epilimnetic sediments of Little Rock Lake at 5-m depth. Fluxes were calculated with Fick's first law, using diffusion coefficients from Li and Gregory (1974) that are corrected for temperature and sediment porosity.

at the same site, but the changes did not follow a clear pattern. No spatial differences in NH_4^+ concentrations were found between the littoral and the 5-m pelagic sites, as was the case for SO_4^{2-} . On the other hand, NH_4^+ concentrations were always nearly an order of magnitude higher at the 9-m sites than at other sites. The maximum NH_4^+ flux was $1,150 \mu\text{eq m}^{-2} \text{d}^{-1}$ at the 9-m site, compared to a maximum of $113 \mu\text{eq m}^{-2} \text{d}^{-1}$ at the 5-m site.

The high concentrations of NH_4^+ at the 9-m site were likely due to the location of the site in the hypolimnion. The site is in a region of sediment focusing caused by sloughing of sediment from the sides of the deep hole, and thus it receives a greater supply of fine-grain organic-rich particles. The site has a focusing factor of 1.8 (Baker et al. 1992) (measured as the sedimentation rate at a site divided by the lakewide sedimentation rate, Robbins 1980). Moreover, low oxygen influx and low light penetration into the hypolimnion result in the buildup of NH_4^+ , which impedes the diffusion

of additional NH_4^+ out of the sediment by reducing the pore-water gradient. CH_4 concentrations were 2–3 times higher at the 9-m site. Carignan and Lean (1991) also found higher pore-water fluxes of NH_4^+ and CH_4 in deeper locations of a small shield lake in response to greater deposition rates of fine labile organic matter.

Cation production—Pore-water profiles of Ca^{2+} and Mg^{2+} indicate that the sediments were a source of cations to the pore water and to the overlying water column (Fig. 6). Ca^{2+} and Mg^{2+} concentrations increased from ~ 50 and $\sim 25 \mu\text{eq liter}^{-1}$, respectively, in the water column 20 cm above the sediment surface to ~ 200 and $\sim 50 \mu\text{eq liter}^{-1}$ within the top 10 cm of the pore water. The locations of the concentration gradients were comparable to those of the SO_4^{2-} gradients. Pore-water Ca^{2+} fluxes ranged from 36 to $236 \mu\text{eq m}^{-2} \text{d}^{-1}$ at the 5-m north basin site and from 14 to $148 \mu\text{eq m}^{-2} \text{d}^{-1}$ at the 5-m south basin site (Table 2, Fig. 4). Pore-water Ca^{2+} fluxes measured in other soft-water lakes in North America and Scandinavia have a similar range, varying from 16 to $148 \mu\text{eq m}^{-2} \text{d}^{-1}$ (Cook et al. 1987); however, the temporal variability of the fluxes in these lakes is not known.

Several mechanisms may control pore-water cation concentrations in Little Rock Lake sediments; these mechanisms include mineral weathering, ion exchange, and organic matter decomposition. X-ray diffraction of the sediment indicated the presence of plagioclase and orthoclase feldspars, mica, quartz, smectite, and vermiculite. No carbonate minerals were present. A sequential extraction revealed that exchangeable and organically bound cations, particularly Ca, were also present in significant proportions (Table 3). In the top 2 cm of sediment at the south basin 5-m site, the exchangeable fraction was 45% and the organic fraction was $\sim 15\%$ of the total sediment Ca. Of the total sediment Mg, the exchangeable fraction was only $\sim 6\%$ and the organic fraction was $\sim 2\%$.

The concentration of Ca and Mg in the mineral phase did not decrease with depth in the sediment, whereas both the exchangeable and organic fractions decreased rapidly with depth in the surficial sediments of the south basin. Similar trends were observed in the north basin, although surficial sediment concentrations

Table 2. Little Rock Lake pore-water fluxes across the sediment-water interface. (N—north basin; S—south basin.)

	Apr 85	Jun 85	Aug 85	10 May 86	30 May 86	Sep 86	Jan 87
SO₄²⁻ ($\mu\text{eq m}^{-2} \text{d}^{-1}$)							
5-m N	26.9	86.6	69.1	38.2	60.7	234	22.2
5-m S	—	47.8	—	34.3	33.4	90.6	0.0
1-m N	—	46.7	69.9	—	—	—	—
1-m S	—	—	69.4	—	—	—	—
9-m N	75.5	28.4	80.8	92.3	—	—	—
Ca²⁺ ($\mu\text{eq m}^{-2} \text{d}^{-1}$)							
5-m N	56.4	188	191	34.5	236	134	35.7
5-m S	—	138	—	14.5	148	106	19.9
1-m N	—	167	210	—	—	—	—
1-m S	—	—	148	—	—	—	—
9-m N	86.4	63.3	97.1	173	—	—	—
Mg²⁺ ($\mu\text{eq m}^{-2} \text{d}^{-1}$)							
5-m N	25.7	23.5	19.6	0.0	20.6	14.0	3.3
5-m S	—	22.3	—	4.2	17.7	20.5	2.0
1-m N	—	14.0	33.0	—	—	—	—
1-m S	—	—	40.8	—	—	—	—
9-m N	25.2	11.9	39.5	55.5	—	—	—
NH₄⁺ ($\mu\text{eq m}^{-2} \text{d}^{-1}$)							
5-m N	113	185	80.1	—	—	174	104
5-m S	—	96.4	—	—	—	130	106
1-m N	—	57.1	79.8	—	—	—	—
1-m S	—	—	113	—	—	—	—
9-m N	1,150	662	781	—	—	—	—
Alkalinity ($\mu\text{eq m}^{-2} \text{d}^{-1}$)							
5-m N	200	431	383	—	—	443	170
5-m S	—	284	—	—	—	428	121
1-m N	—	369	495	—	—	—	—
1-m S	—	—	274	—	—	—	—
9-m N	651	298	722	—	—	—	—

of exchangeable and organic cations were 30–55% lower than those in the south basin. The lower concentrations in the north basin could reflect a decrease in the sediment accumulation of the labile fraction as a result of the acidification; this possibility is supported by measured increases in Ca and Mg concentrations in the water column during north basin acidification (Brezonik et al. 1993). Alternatively, the flocculent layer may not have been captured in the core in which the solid-phase analyses were done.

The decrease in exchangeable and organically bound cations with depth in Little Rock Lake sediments corresponds with increasing pore-water cations with depth; this correspondence suggests that pore-water fluxes are supported by these two phases. Further evidence for this conclusion is derived from accumulation rates of the various cation phases in the upper 2 cm and at depths >10 cm in the sed-

iment. We assume that the top segment (2 cm) of the core represents the most recently deposited sediment and that most cation diagenesis occurred within the top 10 cm (because pore-water cation concentrations become near constant below this depth). Accumulation rates of cations in the three fractions in the top segment and the sediment below 10 cm were calculated for the south basin 5-m site from the mass sediment accumulation rate (11.6 mg cm⁻² yr⁻¹; Baker et al. 1992) (Table 4). The difference in accumulation rates between the layers (i.e. the difference between the deposition rate and burial rate) gives an estimate of the recycling rates. Recycling rates for Ca and Mg were 53 and 9 $\mu\text{eq m}^{-2} \text{d}^{-1}$, respectively. These rates are similar to the Ca²⁺ and Mg²⁺ pore-water fluxes—15–150 and 4–22 $\mu\text{eq m}^{-2} \text{d}^{-1}$, respectively. Two-thirds of the exchangeable Ca and one-third of the organically bound Ca deposited to the sediment surface were re-

**Ammonium
μeq liter⁻¹**

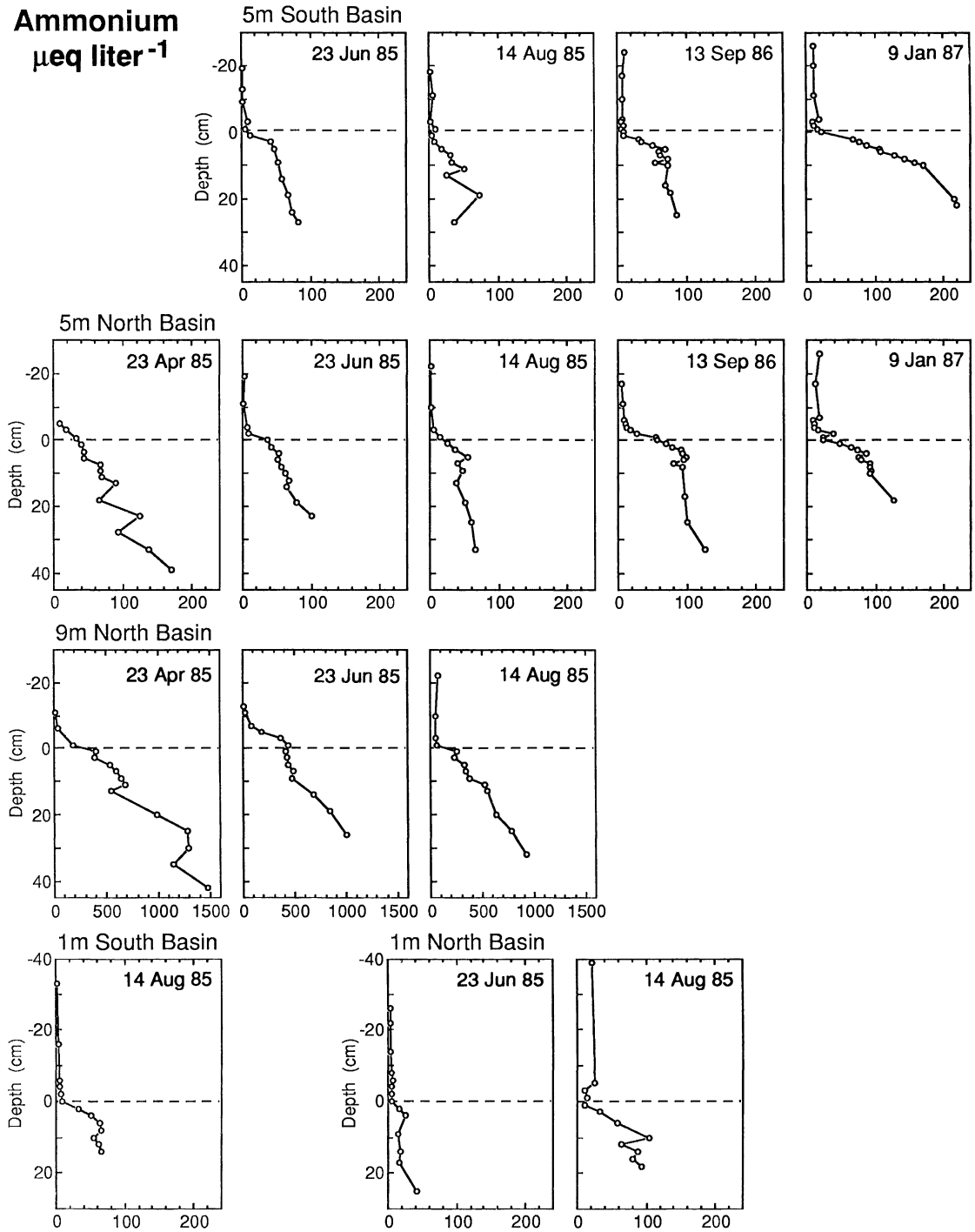


Fig. 5. As Fig. 2, but of NH₄⁺ concentrations in sediments of Little Rock Lake.

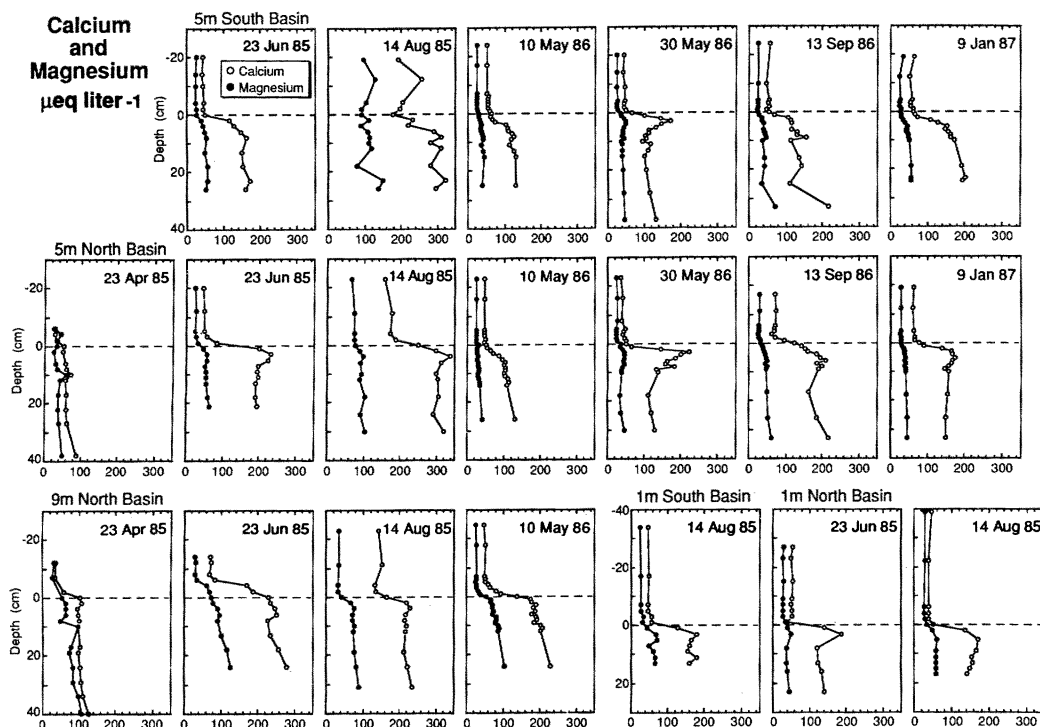


Fig. 6. As Fig. 2, but of Ca^{2+} and Mg^{2+} concentrations.

cycled; recycling from the mineral fraction was minimal. Of the total sediment Ca recycled (38%, based on the sum of the fractions), the exchangeable fraction accounts for 81% and the organically bound fraction accounts for 14%. Although Mg shows the same pattern, the total recycling was low (5%) because most Mg was in the mineral fraction.

Although the solid-phase cation data indicate that the mineral phases were not a major source of cations to the pore water, the mineral phases may provide a minor source. Equilibrium calculations indicate several minerals are dissolving. The chemical equilibrium program PCWATEQ was used to characterize the pore water with respect to controlling mineral phases. Data from the comprehensive January 1987 sampling period at the two 5-m sites were used for these calculations (at 30 cm, $\text{SiO}_2 = 200 \mu\text{M}$, $\text{Mn}_T = 0.8 \mu\text{M}$, and $\text{Al}_T = 2 \mu\text{M}$). Of the clay minerals present, halloysite, illite, and pyrophyllite remained undersaturated throughout the profiles, indicating that they could be undergoing dissolution in the sediments. Kaolinite, gibbsite, and mica were undersaturated

in the top 10–15 cm but were supersaturated below this depth, indicating that these minerals could be formed in the deeper older sediments from weathering of feldspars. Quartz and the montmorillonites became supersaturated below 30 cm, indicating that these minerals could be formed at such depths.

The pore-water cation profiles exhibit temporal variability that parallels changes in pore-water SO_4^{2-} concentrations. In the warmer, more biologically active months, cation gradients were steep (e.g. Fig. 6, June and August 1985, September 1986 profiles), while in colder, less productive months, gradients were smaller and concentrations were low (e.g. Fig. 6, April 1985 and January 1987 profiles). Ca^{2+} concentrations ranged from 100 to 200 $\mu\text{eq liter}^{-1}$ at depths >20 cm, and Mg^{2+} ranged from 30 to 60 $\mu\text{eq liter}^{-1}$ (Fig. 6). The changes from early to late May were more pronounced than for SO_4^{2-} . The peaks in both Ca^{2+} and Mg^{2+} concentrations below the sediment–water interface in late May were 3–4 times larger than those of early May. Between these dates, the calculated Ca^{2+} flux increased from ~35 to

Table 3. Little Rock Lake solid-phase Ca and Mg concentrations. (S—south basin; N—north basin.)

Depth (cm)	Ca, meq (100 g) ⁻¹		Mg, meq (100 g) ⁻¹	
	S	N	S	N
Exchangeable fraction				
0–2	19.8	9.9	3.2	1.0
2–4	11.7	11.2	2.4	1.6
4–6	6.1	12.8	1.0	1.4
6–8	8.3	16.7	1.3	1.7
8–10	7.2	7.8	1.0	0.8
10–12	5.8	12.0	0.7	1.2
12–14	6.9	6.8	0.8	0.9
14–16	6.2	7.2	0.9	1.0
16–18	6.8	7.3	1.2	0.9
Organic fraction				
0–2	6.8	3.2	1.1	0.6
2–4	4.6	5.0	1.1	0.6
4–6	5.6		0.6	
6–8	6.1	8.3	0.5	0.8
8–10	5.1		0.4	
10–12	3.1	6.0	0.2	0.4
12–14	4.3	5.4	0.3	0.3
14–16	5.8	5.5	0.8	0.8
16–18	4.4	4.3	0.4	0.3
Mineral fraction				
0–2	17.2	16.8	51.8	50.0
2–4	16.8		51.8	
4–6	17.4	15.0	53.5	43.0
8–10	17.1	16.9	54.9	49.2
12–14	16.3	15.1	52.1	51.5

~236 $\mu\text{eq m}^{-2} \text{d}^{-1}$ in the north basin and from 14 to ~148 $\mu\text{eq m}^{-2} \text{d}^{-1}$ in the south basin.

The temporal trends in cation profiles support the inference that organic decomposition, with a concomitant loss of exchange sites and release of organically bound cations into the

pore water, was the primary source of cations to the pore water. The trends result from seasonal changes in temperature, organic matter deposition rates, and seston concentrations of Ca and Mg. Seston concentrations at the 5-m site in the south basin ranged from an average of 0.059 mmol g⁻¹ of Ca and 0.048 mmol g⁻¹ of Mg in winter to 0.114 mmol g⁻¹ of Ca and 0.075 mmol g⁻¹ of Mg in summer (Baker et al. 1988). Depositional fluxes of Ca were 0.24–0.48 mg m⁻² d⁻¹ (12–24 $\mu\text{eq m}^{-2} \text{d}^{-1}$) in winter and 1.36–3.21 mg m⁻² d⁻¹ (68–160 $\mu\text{eq m}^{-2} \text{d}^{-1}$) in summer; Mg fluxes were 0.12–0.23 mg m⁻² d⁻¹ (10–19 $\mu\text{eq m}^{-2} \text{d}^{-1}$) in winter and 0.55–1.27 mg m⁻² d⁻¹ (45–105 $\mu\text{eq m}^{-2} \text{d}^{-1}$) in summer. These depositional fluxes support the seasonal pore-water fluxes of the two cations, which ranged from 15 to 150 $\mu\text{eq m}^{-2} \text{d}^{-1}$ for Ca²⁺ and from 4 to 22 $\mu\text{eq m}^{-2} \text{d}^{-1}$ for Mg²⁺ at the 5-m south basin site.

Alkalinity generation—The net effect of the diagenetic reactions in the anoxic sediment of the lake is to increase alkalinity from <50 $\mu\text{eq liter}^{-1}$ in the water column to 200–2,000 in the pore water (Fig. 7). Alkalinity increased most in the region of the sediment–water interface, where biogeochemical processes were most active. As a consequence, the pH increased in the south basin from ~5.9 in the water column to 6.3 at 3 cm below the interface; in the acidified north basin, the pH increased from ~5.5 in the water column to 6.1 at 4 cm below the top of the flocculent layer. Measurements of total DOC and DIC in the pore water indicate that the alkalinity is primarily carbonate alkalinity. Pore-water DOC

Table 4. Little Rock Lake solid-phase Ca and Mg accumulation in the surface 10 cm at 5-m south basin site.

Fraction	Concn, meq (100 g) ⁻¹		Accumulation, $\mu\text{eq m}^{-2} \text{d}^{-1}$			Recycle (%)
	Top*	Bottom†	Top	Bottom	Recycle	
Ca						
Exchangeable	19.8	6.4	63.0	20.3	42.5	67.6
Organic	6.8	4.6	21.6	14.5	7.1	32.5
Mineral	17.2	16.3	54.8	51.8	2.7	5.2
Total	43.8	27.3	139.2	86.8	52.6	37.7
Mg						
Exchangeable	3.2	0.9	10.1	2.7	7.4	71.9
Organic	1.1	0.4	3.6	1.4	2.2	62.8
Mineral	51.8	52.1	164.7	165.5	-0.8	-0.6
Total	56.1	53.4	178.4	169.9	8.5	4.8

* Top is the surface 2 cm below the sediment–water interface.

† Bottom is an average below 10 cm of the sediment–water interface.

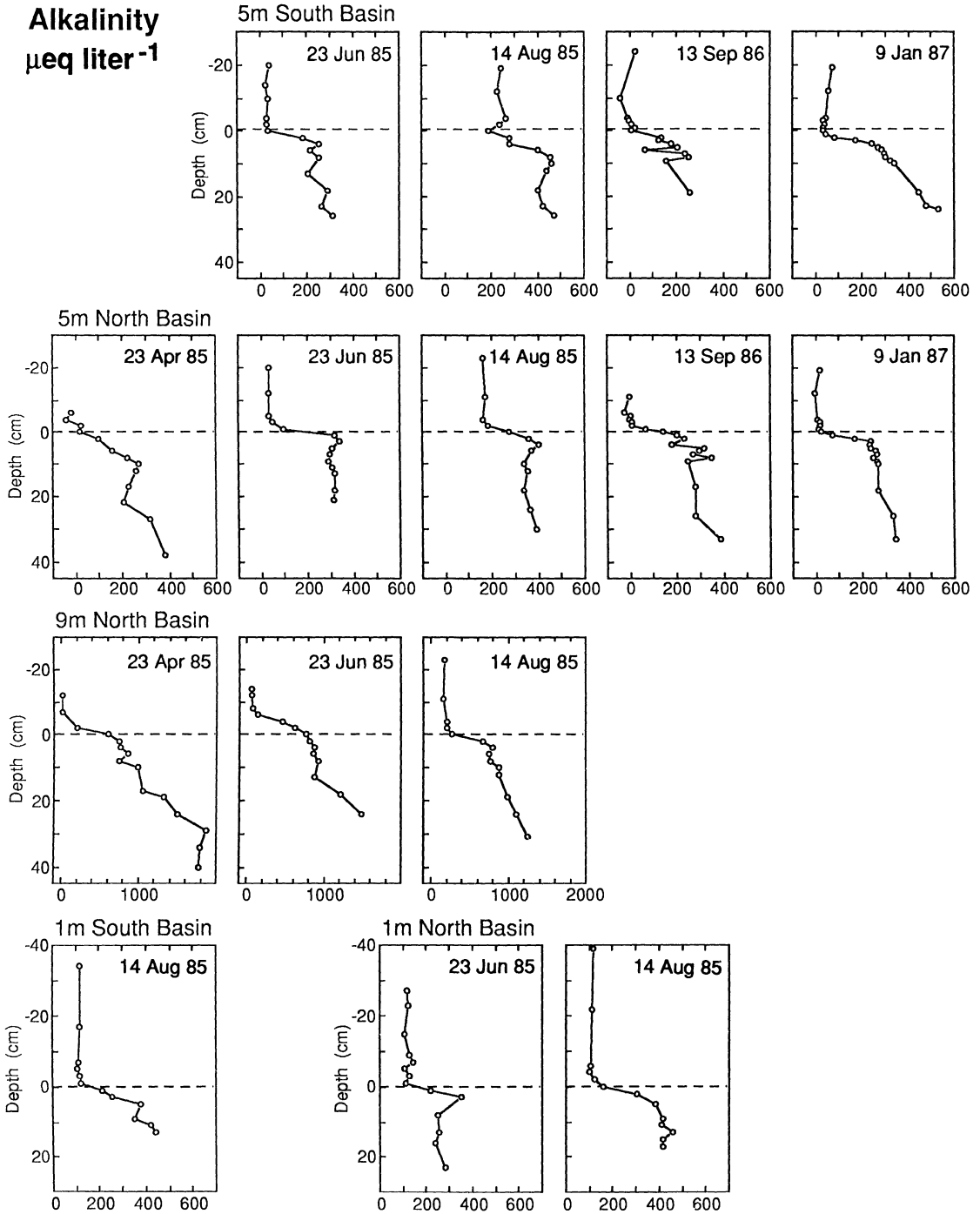


Fig. 7. As Fig. 2, but of alkalinity concentrations in sediments of Little Rock Lake.

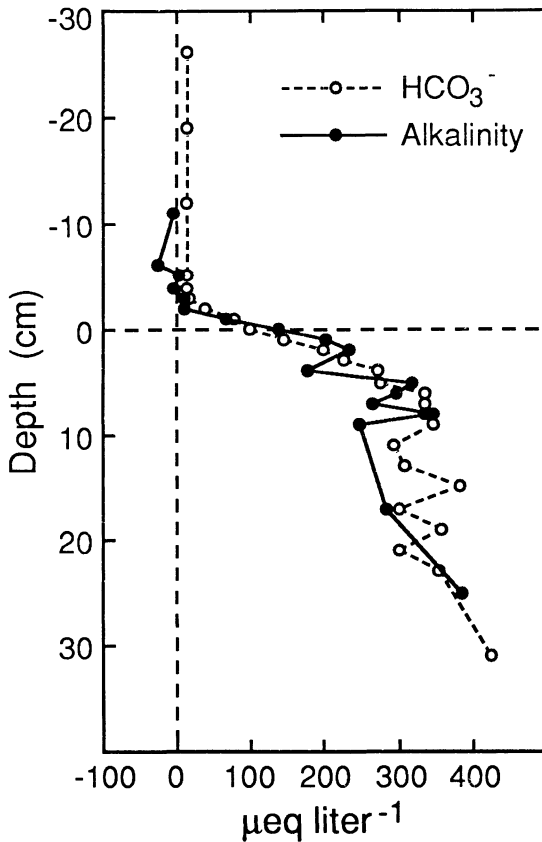


Fig. 8. Pore-water profiles of inorganic C and Gran alkalinity in epilimnetic sediments at 5-m depth in the north basin of Little Rock Lake (September 1986).

concentrations ($\sim 3 \text{ mg liter}^{-1}$) were about the same as the lake-water concentrations ($\sim 3.5 \text{ mg liter}^{-1}$) and increased little with depth. Moreover, the concentrations of HCO_3^- (calculated from carbonate equilibria equations) and total alkalinity (measured by Gran titration) were nearly equal (Fig. 8), indicating that the contribution of organic acid anions to alkalinity was small.

Contributions to pore-water alkalinity generation from changes in SO_4^{2-} , Ca^{2+} , Mg^{2+} , NH_4^+ , Fe^{2+} , and Mn_T concentrations were calculated by the method of Kuivila and Murray (1984). In this method, changes in ion concentrations at each depth are calculated relative to a reference concentration at depth = 0 (i.e. the oxic-anoxic boundary). The change in the concentration (on an equivalent basis) of each ion at a particular depth is assumed to

represent an increase in HCO_3^- . Ion contributions to alkalinity were calculated in the top 10 cm for the most complete set of profiles measured—those taken in January 1987 (Fig. 9). Concentrations at each 1-cm depth interval were subtracted from the concentration at depth 0. Changes in concentration with depth were then plotted cumulatively for the various chemical constituents. The area between the curves gives the magnitude of change in concentration of a particular species from its concentration at the sediment–water interface.

At both 5-m sites, the major contributors to alkalinity production in the top 10 cm of sediment were reactions involving Ca^{2+} , SO_4^{2-} , and NH_4^+ . In the north basin, Ca^{2+} release was the major contributor to pore-water alkalinity, but in the south basin, Ca^{2+} and NH_4^+ production made comparable contributions. Mg^{2+} and Fe^{2+} (from reduction of Fe oxides) were small contributors in both basins. Schiff and Anderson (1986) used the same method of calculation on small lakes of pH >6.0 in Ontario and New York and found that Ca^{2+} release into the pore water is a major component of alkalinity production in the pore water, whereas Mg^{2+} and NH_4^+ are minor contributors. In lakes with pH <6.0, they found that Fe and Mn reduction are the major contributors, because Ca had apparently been leached from the sediments. Continued acidification of the north basin of Little Rock Lake caused a similar phenomenon (Sampson et al. 1994; Brezonik et al. 1993). Based on mass balance calculations, Cook et al. (1986) determined that Ca^{2+} release in Lake 223 (Experimental Lakes Area, northwestern Ontario) is a major component of alkalinity generation, accounting for 19% of total lake alkalinity production. They attributed the Ca^{2+} release to exchange with H^+ ion in the sediments in response to early acidification. Our more detailed study in Little Rock Lake suggests that Ca^{2+} production results from interrelated organic decomposition and ion-exchange processes.

The fate of the reaction products that diffuse into the water column determines whether the production or consumption of each ion provides a permanent source of alkalinity to the lake. Net SO_4^{2-} consumption and net Ca^{2+} release generate bicarbonate alkalinity (or consume acidity, i.e. hydrogen ion). Production of

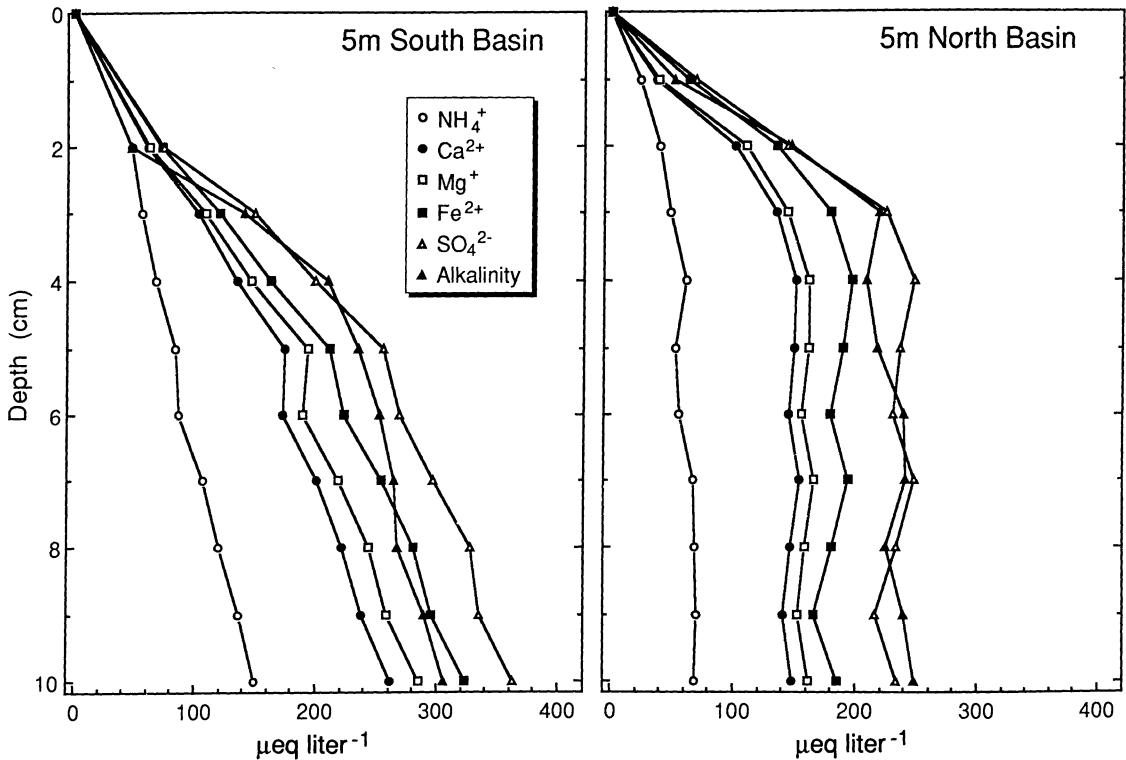


Fig. 9. Pore-water ion contributions of SO_4^{2-} reduction, Ca^{2+} and Mg^{2+} release, NH_4^+ production, and Fe reduction to alkalinity production in epilimnetic sediments of Little Rock Lake (January 1987). Contributions were calculated for each ion by subtracting concentrations at each 1-cm depth interval from the concentration at depth 0 (the oxic-anoxic boundary). Changes in concentration with depth were then plotted cumulatively for the various chemical constituents. The area between the curves gives the magnitude change in concentration of a particular species from its concentration at the sediment-water interface.

reduced Fe and NH_4^+ results in no net source of alkalinity to the lake if these end-products are oxidized in the overlying water. A fraction of the dissolved NH_4^+ , however, adsorbs to exchange sites on the organic matter and metal oxide surfaces in Little Rock Lake sediments. Thus, organic matter decomposition can yield permanent alkalinity increases through NH_4^+ production, if assimilation or adsorption with displacement of Ca^{2+} and Mg^{2+} occurs, thereby fixing the NH_4^+ in the sediments and so preventing reoxidation. Reduced Fe also could compete for exchange sites with these cations and in this way contribute to permanent alkalinity, if it exchanges with Ca^{2+} and Mg^{2+} . In contrast, if there is significant biological or chemical uptake of Ca in the water column, a portion of the pore-water flux of Ca^{2+} will be recycled to the sediments and will not represent a permanent source of alkalinity.

Seasonal changes in Ca^{2+} production and SO_4^{2-} reduction result in changes in the magnitude of permanent alkalinity generated in the sediment pore water and in the relative contributions of the two. Alkalinity fluxes were greater in warmer, more productive months than in colder months (Table 2). This pattern corresponds to the seasonal trends in Ca^{2+} and SO_4^{2-} fluxes. Ca^{2+} fluxes were almost always greater than SO_4^{2-} fluxes, revealing that Ca^{2+} production contributes more to alkalinity fluxes than does SO_4^{2-} reduction in the pore water; however, the relative contributions vary seasonally (Fig. 4). In the less productive months, the fluxes were more comparable, while in more productive months, especially after ice-out, Ca^{2+} fluxes were 2–4 times greater than SO_4^{2-} fluxes because of increases in seston Ca concentrations at these times. There was an exception to this general trend in September 1986

when SO_4^{2-} fluxes were higher than Ca^{2+} fluxes due to higher lake water (acidified) concentrations of SO_4^{2-} . The only spatial trend observed was a large difference in alkalinity concentrations between the 5- and 9-m north basin sites; this difference is attributable to the large difference in NH_4^+ concentrations. However, the higher alkalinity flux at the 9-m site, resulting from NH_4^+ production, would not represent a higher flux of permanent alkalinity unless the NH_4^+ is fixed.

Only small differences between the concentrations and fluxes of the major pore-water species were observed in the first 2 yr of acidification. Pore-water SO_4^{2-} concentrations increased in the region of the sediment-water interface by 20–30%, and Ca^{2+} fluxes were 20–40% higher in the north basin in response to higher water-column SO_4^{2-} concentrations and higher acidity. However, changes in pore-water alkalinity or alkalinity fluxes were not major. Correspondingly, the pore-water pH did not change as a result of 2 yr of acidification, as indicated by a comparison of pH profiles at the 5-m sites in the acidified and control basins after this period (Fig. 1). The similarity in pH between the basins also suggests there was no acidification of the surficial sediment. However, pore-water profiles measured during the later years of the acidification experiment—in particular in 1989 and 1990 when the north basin pH was lowered to 4.7–4.9—showed strong evidence of sediment acidification (Sampson et al. 1994; Brezonik et al. 1993). In experimentally acidified Lake 302 (ELA), Rudd et al. (1990) also observed a decrease in pore-water pH of 0.5 units in 3 yr of acidification.

Current models of in-lake alkalinity generation should be revised to include the major contribution of pore-water cation fluxes resulting from active cation release from the sediments. The potential depletion of this cation pool with continued acidification must, however, be accounted for. Moreover, the observation of significant spatial and temporal trends of pore-water constituents in Little Rock Lake, reflecting variations in temperature and the nature and rate of organic matter sedimentation, indicates that high spatial and temporal resolution sampling is essential to characterizing the dynamic pore-water environment. Extrapolations from one site and one sampling

period are not adequate for calculating annual pore-water concentrations or sediment-water fluxes. Finally, the relative contributions of the various diagenetic mechanisms to sediment alkalinity generation cannot be fully ascertained without taking spatial and temporal variability into account.

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