

Chemical limnology of soft water lakes in the Upper Midwest

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Abstract. Water samples from 36 lakes in northern Minnesota, Wisconsin, and Michigan were collected and analyzed during 1983–84. All study lakes were dilute and had total alkalinities of less than $150 \mu\text{eq} \cdot \text{L}^{-1}$. Minnesota lakes have hydrologic inputs from the watershed and inputs of base cations derived from the watershed. Study lakes in Minnesota had higher total alkalinities, dissolved organic carbon, and noncarbonate alkalinity as a result of watershed inputs. Lakes in Michigan and Wisconsin were precipitation-dominated seepage lakes that have lower concentrations of base cations than lakes in Minnesota. All of the study lakes have lower sulfate concentrations than expected, based on atmospheric wet deposition and evapotranspiration.

Pore water samples collected from one of the study lakes — Little Rock Lake — in Wisconsin were used to calculate diffusive fluxes between the sediment and water column. According to these calculations, the sediments were a source of total alkalinity and Ca^{2+} and a sink for SO_4^{2-} . The sediment-water exchange of total alkalinity, Ca^{2+} , and SO_4^{2-} appears to be important in the whole-lake budgets of these ions for Little Rock Lake.

Introduction

The acquisition of solutes by headwater lakes and streams is the result of a complex interaction of atmospheric deposition, hydrologic flowpaths, bedrock and soil geochemistry, and biological activity. As a consequence, even for lakes within a small geographic region ($< 500 \text{ km}$) having a uniform geologic substrate, the lake water chemistry resulting from these interacting processes may be distinctly different (Gorham et al. 1983; Driscoll and Newton, 1985; Melack et al. 1985; Eilers et al. 1983; Rapp et al. 1985). Where the concentration of solutes due to these processes is dilute, surface waters are particularly sensitive to atmospheric deposition of strong acids and acid precursors. The chemical parameter that determines the sensitivity of surface waters to acidic deposition is acid-neutralizing capacity or total alkalinity (TAlk), which for most surface waters is defined as:

$$\text{TAlk} = \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+ - \text{Cl}^- - \text{SO}_4^{2-} - \text{NO}_3^-, \quad (1)$$

where all terms are in $\mu\text{eq} \cdot \text{L}^{-1}$. Because TAlk is a function of all nonprotolytic cations and anions, the sensitivity of natural waters to acidic inputs will be

determined by the various processes controlling the concentration of the ions in Eq. 1.

The objectives of this paper are to examine the differences in water chemistry among a suite of lakes in northern Minnesota, northern Wisconsin, and the Upper Peninsula of Michigan and to evaluate the processes responsible for the acquisition of solutes by these waters. We also investigated the pore water chemistry of one of the study lakes—Little Rock Lake (Wisconsin)—to appraise the importance of transport of solutes between the sediment and the water column in controlling water-column chemistry. The water-column data examined here were collected as part of the 'Paleoecological Investigation of Recent Lake Acidification' project (Charles et al. 1986) to determine the present-day relationship between water chemistry and diatom populations. Reconstructions of the pH history for one of the lakes in the upper Midwest are presented in Kreis et al. (in press).

Description of the study lakes

The entire northern Great Lakes study area is underlain by bedrock or till that provides little acid-neutralizing capacity. Lakes in northern Minnesota have bedrock basins in crystalline igneous and metamorphic rocks. The glacial till and outwash are typically thin (< 5 m) and bedrock outcrops are frequent (Rapp et al. 1985). In northern Wisconsin, glacial drift ranges from 30 to 60 m thickness over metamorphosed igneous and sedimentary rocks (Eilers et al. 1983). In northern Michigan, sandstone and limestone bedrock are covered by greater than 20 m of deposits of quartz-rich glacial drift (Rapp et al. in press). The bedrock and till in the study area provide few solutes to lake water; rates of geochemical weathering in this area are extremely low (Schnoor et al. 1986).

The majority of the study lakes in northern Michigan and Wisconsin are seepage lakes; nearly all of the water entering the lakes comes from precipitation and most of the water leaves via evaporation or groundwater seepage. Seepage lakes have no surface inflow or stream outlet. Except for Dunnigan Lake, the lakes in Minnesota are drainage lakes; they receive water from direct runoff, precipitation, and a stream, and lose water via a stream outlet.

The study area is covered by a second-growth mixed deciduous-coniferous forest that is 50 to 100 years old. The area was extensively logged in the late 1800s and early 1900s, except for the Hustler Lake watershed, which was burned by forest fires in 1864 and 1894, and the small Dunnigan Lake watershed.

Annual average precipitation for the study area ranges from 69 to 84 cm and evapotranspiration averages between 31 and 49 cm (Geraghty et al. 1973). Annual water evaporation ranges between 55 and 66 cm (Geraghty et al. 1973).

The region receives a gradient of acidic and ionic atmospheric deposition. The Upper Peninsula of Michigan receives precipitation with an annual average pH of 4.4, northern Wisconsin with a pH of 4.6, and northern Minnesota with a pH

of 4.9 to 5.0 (Glass and Loucks 1986). Sulfate in precipitation exhibits a similar gradient, from $50 \mu\text{eq} \cdot \text{L}^{-1}$ in Michigan to $30 \mu\text{eq} \cdot \text{L}^{-1}$ in Minnesota (Munger and Eisenreich 1983; Glass and Loucks 1986). Average concentrations of ions from precipitation in the study area are collected in Table 1. Data for dry deposition to the study area are limited, but generally indicate an increasing dry deposition of SO_4^{2-} to the east (Barrie et al. 1984) and an increasing dry deposition of base cations to the east (Gorham et al. 1984; Cadle et al. 1984; Linsey et al. in press). Estimates of the ratio of dry deposition to total deposition, based on accumulation in snowpack, wet vs bulk collectors, and dry deposition of measured gas and particle concentrations, range from 10 to 30% for SO_4^{2-} (Cadle et al. 1984; Barrie et al. 1984; Linsey et al. in press) and 25 to 56% for base cations (Cadle et al. 1984; Linsey et al. in press).

The 36 lakes sampled in this study were chosen from a 636-lake data set (Eilers et al. 1983; Rapp et al. 1985; Rapp et al. in press) to represent lakes that have low alkalinities and are susceptible to acidification from atmospheric deposition of strong acids and acid precursors. The lake selection criteria were: undisturbed watershed or a watershed with a known disturbance history; maximum water depth greater than 8 m; size between 10 and 100 ha, with lake surface occupying greater than 4% of total watershed; and a range of pH and TAlk values (Whitehead and Charles 1986). Lake location and morphometric data are collected in Table 2. The lakes are all oligotrophic, having low concentrations of total phosphorus, nitrate, ammonium, and chlorophyll-*a* (Cook et al. in press).

Materials and methods

Water samples were collected from a depth of 1 m at a station located over the deepest point of each lake. Each lake was sampled in July 1983 and in May, June, August, and October 1984.

Pore water samples were collected at several sites in one of the study lakes (Little Rock Lake) in July 1984, using close-interval membrane equilibrators (Hesslein 1976; Cook 1984). The samplers consist of a series of 60 compartments milled into a sheet of 2-cm (0.75-in.) thick Plexiglas at 1-cm intervals. Approximately 6 mL of distilled water was poured into each compartment, and polycarbonate membrane (0.2- μm pore size) was placed over the compartments. The samplers were inserted vertically into the sediments by SCUBA divers, who noted the compartment just above the sediment-water interface. The samplers were deployed on 27–28 June 1984 and retrieved three weeks later. pH, total alkalinity, ferrous iron, and total hydrogen sulfide were measured within 8 h of collection.

pH was measured in lake water samples before and after air equilibration with an Orion Ross electrode calibrated with high-ionic strength pH 4 and pH 7 buffers and a strong-acid low-ionic strength solution of sulfuric acid (pH 3.80). TAlk was measured by titration with strong acid while the solution was being

aerated with air from inside the laboratory in 1983 and from outside the laboratory in 1984; the end point was determined from a Gran plot, using titration data between pH 4.5 and 3.5. TAlk was fractionated according to the procedure of Schofield (1986). Briefly, this method is based on the following definitions:

$$\text{TAlk} = \text{carb-Alk} + \text{noncarb-Alk}, \quad (2)$$

$$\text{carb-Alk} = \text{HCO}_3^- + 2\text{CO}_3^{2-} + \text{OH}^- - \text{H}^+, \quad (3)$$

where carb-Alk represents alkalinity derived from carbonate species, hydrogen ion, and hydroxide ion (Butler 1982; Stumm and Morgan 1981), and noncarb-Alk represents alkalinity derived from protolytic species other than the ions in carbonate-alkalinity (Eq. 3). Noncarbonate alkalinity comprises primarily weak-acid organic anions, but may include small contributions from protolytic metal complexes, and particulate aluminosilicates and metal oxides (National Research Council 1986). Carbonate alkalinity was calculated using equilibrium constants (Stumm and Morgan 1981) and the pH and pCO_2 of an air-equilibrated sample of known temperature; the pCO_2 of the air was calculated from the pH and TAlk of a standard NaOH solution in equilibrium with air. Noncarbonate alkalinity is the difference between TAlk and carbonate alkalinity.

Dissolved organic carbon (DOC) was measured using an Ionics organic carbon analyzer on filtered samples. Base cations (Mg^{2+} , Ca^{2+} , Na^+ , K^+) were determined by atomic absorption spectrophotometry; a 1% lanthanum chloride solution was added to samples before Mg^{2+} and Ca^{2+} analysis to prevent chemical interference. Major acid anions (SO_4^{2-} , Cl^-) were measured by ion chromatography. NO_3^- was measured by azo dye and NH_4^+ by phenolhypochlorite (Stainton et al. 1977). Details of the above methods for water-column analyses are presented elsewhere (Cook 1986). For pore water samples: TAlk samples were not equilibrated with air; ferrous iron was measured colorimetrically after complexation with 1,10-phenanthroline; ammonium was measured using phenolhypochlorite colorimetry; and total hydrogen sulfide (the sum of H_2S , HS^- , and S^{2-}) was measured using the Lauth's violet method (Stainton et al. 1977).

Results

Lake water chemistry

A summary of the chemistry data from the study lakes is presented in Table 2. The lakes exhibit a continuum of acid-base chemistry from pH 4.4 to 7.6 that agrees well with a theoretical titration curve for waters in equilibrium with atmospheric CO_2 (Fig. 1) (cf. Eilers et al. 1983). Many of the study lakes have carbonate alkalinity in the range 0 to $50 \mu\text{eq} \cdot \text{L}^{-1}$, yet have relatively high pH. Small changes in the carbonate alkalinity for these lakes from, for example,

Table 1. Volume-weighted annual average precipitation chemistry for the study area (in $\mu\text{eq} \cdot \text{L}^{-1}$, except for precipitation which is in cm).

Ion	ELA, ^a Ontario	Fernberg, ^b Minnesota	Trout Lake, ^b Wisconsin	Douglas Lake, ^b Michigan
Annual precipitation	70.0	70.0	83.0	72.0
H ⁺	12.2	12.4	16.3	36.7
NH ₄ ⁺	20.3	17.8	20.8	18.0
SO ₄ ²⁻	33.6	31.1	37.7	51.0
NO ₃ ⁻	17.6	16.4	16.3	27.0
Cl ⁻	12.6	2.8	2.5	3.3
Ca ²⁺	24.2	10.6	10.5	13.8
Mg ²⁺	9.0	4.6	3.4	5.2
K ⁺	2.1	0.8	0.7	1.1
Na ⁺	8.6	3.3	1.6	2.5

^a Experiment Lakes Area. Bulk precipitation average for 1970–1982 (Linsey et al., in press).

^b Precipitation average for December 1980 through November 1982 (Glass and Loucks, 1986).

additions of strong acids will yield large changes in pH. Conversely, for lakes outside the vertical portion of the titration curve, changes in carbonate alkalinity will yield smaller changes in pH.

Uncertainties in pH measurements caused by DOC interactions with pH electrodes (Herczeg and Hesslein 1984) may produce a systematic error in carbonate alkalinity and in noncarbonate alkalinity, especially for the Minnesota study lakes, which have high DOC (Table 2). This source of uncertainty was not investigated in this study, although the close agreement between the

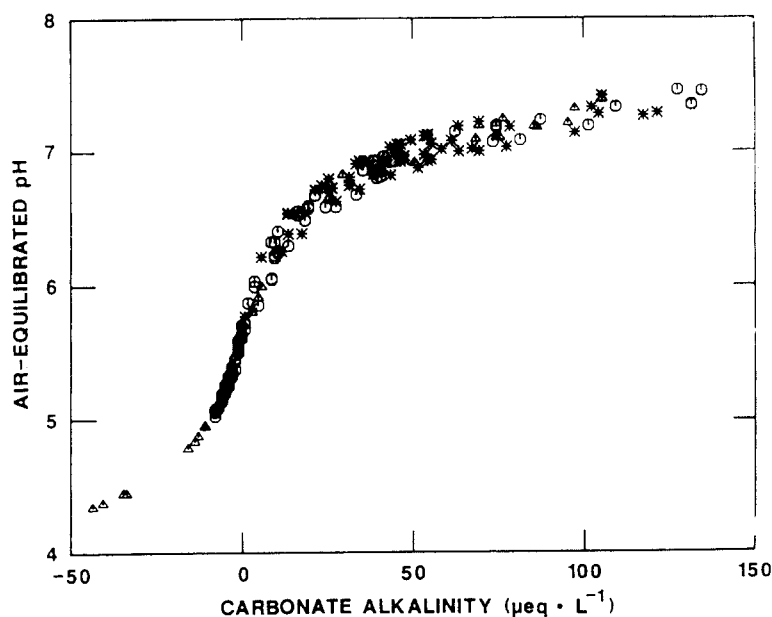


Fig. 1. Carbonate alkalinity as a function of pH for the study lakes. Asterisks are for Minnesota lakes, circles are for Wisconsin lakes, and triangles are for Michigan lakes.

Table 2. Hydrologic type and mean values for selected chemical parameters of the study lakes. Average values are for 5 samples collected in July 1983, and May, June, August and October 1984.

Lake	Location	Hydro- logic type ^a	pH	Total alkalinity ($\mu\text{eq}\cdot\text{L}^{-1}$)	Non- carbonate alkalinity ($\mu\text{eq}\cdot\text{L}^{-1}$)	DOC ($\mu\text{mol}\cdot\text{L}^{-1}$)	Cl ⁻ ($\mu\text{eq}\cdot\text{L}^{-1}$)	CF ^b	SBC ^c ($\mu\text{eq}\cdot\text{L}^{-1}$)	NH ₄ ⁺ ($\mu\text{eq}\cdot\text{L}^{-1}$)	SO ₄ ²⁻ ($\mu\text{eq}\cdot\text{L}^{-1}$)	NO ₃ ⁻ ($\mu\text{eq}\cdot\text{L}^{-1}$)
Minnesota												
Agawato	48°12'N, 92°10'W	Spring	6.4	57	28	470	7.1	2.54	163	0.5	63	0.3
Dunnigan	47°42'N, 91°38'W	Seepage	6.7	50	19	403	9.4	3.36	134	0.5	55	0.2
Grassy	48°00'N, 91°52'W	Inflow	6.7	95	37	645	9.2	3.28	219	0.6	64	0.5
Hustler	48°14'N, 92°09'W	Drainage	6.8	80	27	426	9.2	3.28	186	0.5	68	0.4
Nels	48°02'N, 91°54'W	Drainage	6.4	59	38	616	11.4	4.07	184	0.7	63	1.2
Regenbogen	48°02'N, 91°55'W	Drainage	6.8	112	33	526	8.9	3.18	213	0.3	57	1.3
Ruby	48°14'N, 92°10'W	Spring	7.0	123	26	330	6.6	2.36	217	0.5	76	0.3
Sletten	47°59'N, 91°53'W	Drainage	6.7	89	22	554	7.4	2.57	169	0.3	39	0.3
Slim	48°00'N, 91°57'W	Drainage	6.8	69	22	394	7.2	2.64	190	0.4	60	0.4
Tee	48°00'N, 91°53'W	Drainage	5.9	47	39	899	7.4	3.00	58	53	94	49
Model ^d							7					
Wisconsin												
Big Carr	45°47'N, 89°37'W	Seepage	6.5	26	7	204	26.1	10.44	139	0.3	87	0.2
Bird	45°47'N, 89°40'W	Seepage	6.8	46	8	252	7.3	2.92	107	0.3	46	0.3
Bolger	45°51'N, 89°43'W	Seepage	7.0	82	5	177	16.6	6.64	151	0.6	47	2.2
Brown	45°47'N, 89°29'W	Seepage	5.7	8	8	293	9.0	3.60	106	1.0	80	2.3
Camp 12	45°59'N, 89°22'W	Seepage	5.4	1	6	213	7.1	2.84	77	0.6	62	0.5
Crystal	45°43'N, 89°25'W	Seepage	6.1	12	6	156	13.6	5.44	119	0.3	95	0.3
Denton	45°51'N, 89°19'W	Seepage	5.2	3	8	417	8.9	3.56	86	0.6	53	0.3
Diamond	46°02'N, 89°43'W	Seepage	6.2	15	8	147	11.9	4.76	107	0.3	84	0.3
Dorothy	45°49'N, 89°34'W	Seepage	6.8	46	6	205	8.3	3.32	114	0.5	54	0.7
Franklin	45°52'N, 89°51'W	Seepage	5.8	3	5	141	12.4	4.96	114	0.3	101	0.4
Little John Jr	46°00'N, 89°37'W	Seepage	5.3	-1	4	169	7.3	2.92	80	0.3	72	0.4
Little Rock	46°00'N, 89°42'W	Seepage	6.3	24	9	207	7.0	2.80	85	0.3	49	0.3
Luna	45°54'N, 88°57'W	Seepage	5.9	8	6	197	11.0	4.40	121	0.3	103	0.2
McGrath	45°47'N, 89°38'W	Seepage	5.4	0	4	218	7.8	3.12	102	1.2	92	0.7
Otto Mielke	45°56'N, 89°45'W	Seepage	5.3	-3	3	200	6.4	2.56	72	0.6	67	0.4
Palette	46°03'N, 89°36'W	Seepage	7.6	121	0	382	8.1	3.24	193	0.3	58	0.4
Model ^d							6	3.00	48	62	113	49

pH-carbonate alkalinity plot (Fig. 1) and the theoretical titration curve, even at high pH values, suggests that the effect of DOC interaction with the pH electrode is small.

The study lakes in Minnesota had the highest noncarbonate alkalinity and the highest DOC; between 21 and 83% (average of 41%) of the TAlk could be attributed to noncarbonate alkalinity in Minnesota (Table 2). In study lakes with low DOC (i.e., lakes in Wisconsin and Michigan; Table 2), the noncarbonate alkalinity was generally less than $10 \mu\text{eq} \cdot \text{L}^{-1}$ and the TAlk was primarily comprised of carbonate alkalinity.

The noncarbonate alkalinity was significantly correlated with DOC for data from all the study lakes ($P < 0.001$; Fig 2), with a slope of $0.048 \mu\text{eq} \cdot \mu\text{mol C}^{-1}$. Other workers found similar values for the relationship between noncarbonate alkalinity and DOC (Table 3). The agreement is especially good for dilute lake and stream water in the Adirondacks [Driscoll and Bisogni 1984], in Norway (Johannessen 1980), and at the Experimental Lakes Area, Ontario (Herczeg and Hesslein 1984) (Table 3). Soils and organic-rich bog water have organic acid contents that are in general greater than values from dilute waters (Table 3).

To illustrate what the chemistry of the study lakes would be if solutes were derived solely from precipitation, we calculated the chemical composition of a model lake for each of the three states. This calculation provides a reference value of chemistry from which we can qualitatively evaluate the influence of dry

Table 3. The weak acid, strong acid, and total acid content of dissolved organic matter for water and soils from North America and Europe.

Material	Organic acid content ($\mu\text{eq} \cdot \mu\text{mol C}^{-1}$)	Reference
<i>Weak acid</i>		
Lake water	0.048	This paper
Surface water	0.031	Driscoll and Bisogni (1984)
Lake water	0.038	Herczeg and Hesslein (1984)
Lake water	0.066	Henriksen and Seip (1980)
Lake water	0.038	Johannessen (1980)
Lake water	0.025	Driscoll and Schafran (1984)
<i>Strong acid</i>		
Groundwater and surface water	0.090	Eshleman and Hemond (1985)
Bog water	0.101	McKnight et al. (1985)
Bog water	0.057	Gorham et al. (1985)
<i>Total acid</i>		
Lake sediment	0.144	Davis (1982)
Soil water	0.078	Cronan and Aiken (1985)
Groundwater and surface water	0.120	Oliver et al. (1983)
Surface water-humic acid	0.100	Weber and Wilson (1975)
Surface water-fulvic acid	0.160	Weber and Wilson (1975)
Soils-humic acid	0.077	Schnitzer (1980)
Soils-fulvic acid	0.214	Schnitzer (1980)

deposition and watershed and in-lake processes in modifying lake water chemistry. The concentrations of solutes in the model lakes were estimated from the chemistry of precipitation in the three states (Table 1) and a concentration factor, which is the total hydrologic input to the lake derived from precipitation divided by the outflow from the lake. Concentration factors for two of the study lakes have been reported: 2.67 for McNearney Lake (Schnoor et al. 1986) and 2.05 for Little Rock Lake (W. Rose, U.S. Geological Survey, Madison, Wisconsin, pers. comm.).

Concentration factors can also be calculated from the ratio of Cl^- in precipitation to the concentration of Cl^- in lake water, assuming that Cl^- is geochemically conservative and is only derived from precipitation. For the study lakes the values of concentration factors determined from Cl^- range from 2 to 4 (Table 2), except for Big Carr, Bolger, Crystal, Diamond, and Franklin lakes, whose watersheds have paved roads that receive applications of road deicing salts in winter. The concentration factors calculated from Cl^- agree well with the values determined from hydrologic data for Little Rock and McNearney, even though some Cl^- is probably supplied by dry deposition and Cl^- may not behave conservatively in some soft water lakes, as determined from whole-lake input-output mass balances (Cook et al. 1986; Schindler et al. 1986; R.F. Anderson, Columbia University, New York, pers. comm.).

Because hydrologic data are not available for most of the study lakes, we will use a concentration factor of 3 in Minnesota and Wisconsin and 2.5 in Michigan, based on the range of concentration factors determined from Cl^- . Although this calculation will not allow a quantitative evaluation of the watershed and in-lake processes responsible for the chemistry, it will allow a qualitative

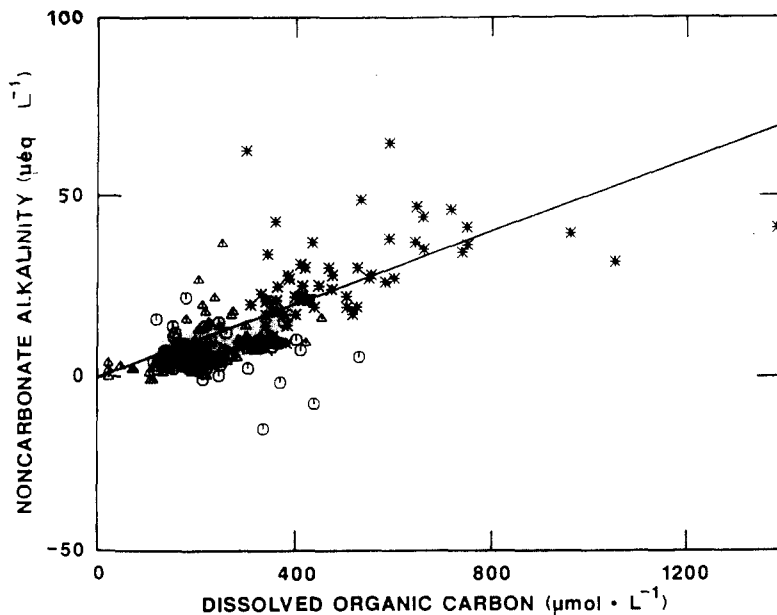


Fig. 2. Noncarbonate alkalinity vs DOC for the study lakes. Symbols as in Fig. 1.

appraisal of key differences between precipitation chemistry and lakewater chemistry. The solute concentrations for the three model lakes are presented in Table 2. The model lakes have a sum of the base cation (Ca^{2+} , Mg^{2+} , K^+ , Na^+) (SBC) concentration that is less than those of the study lakes, indicating that SBC may be supplied by dry deposition or by reactions occurring in the watershed or in the lake. The model lakes have SO_4^{2-} , NO_3^- , and NH_4^+ concentrations that are greater than those of the study lakes, except for SO_4^{2-} in McNearney, Luna, Franklin, and Camp 12 lakes; dry deposition of SO_4^{2-} , which was not included in the model calculation and for which estimates ranged from 10 to 30% (Cadle et al. 1984; Barrie et al. 1984; Linsey et al. in press), will cause a greater SO_4^{2-} loading for these four lakes than that assumed for the model lakes.

Pore water chemistry

Pore water profiles for pH, TALK, Ca^{2+} , Fe^{2+} , NH_4^+ , and SO_4^{2-} from Little Rock Lake reveal steep concentration gradients near the sediment-water interface (Fig. 3). These gradients cause diffusive flux of SO_4^{2-} and H^+ into the sediments and TALK, Ca^{2+} , Fe^{2+} , and NH_4^+ out of the sediments, resulting in a loss or gain, respectively, of these solutes in the water column. The functional relationship between the flux (J) and the gradient (dC/dz) is given by Fick's First Law [Berner 1980]:

$$J = -D \cdot \Phi \cdot dC/dz, \quad (4)$$

where D is the whole-sediment diffusion coefficient and Φ is the porosity of the sediment. Fluxes calculated using this technique are presented in Table 4.

Uncertainties in the calculated pore water fluxes originate from a number of sources. The sampling resolution is 1 cm at best, and larger when samples are not collected from each sampler compartment near the sediment-water interface (Table 4). Measurements of pH in surficial sediments using microelectrodes with

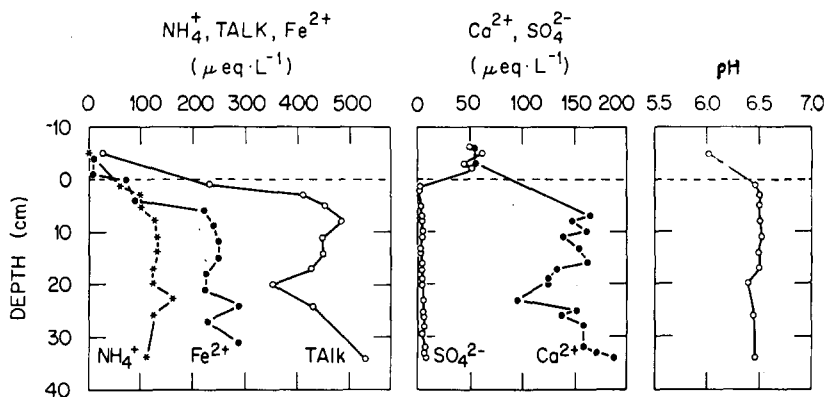


Fig. 3. Pore water profiles for samples collected from 2 m in the east basin of Little Rock Lake.

a 1-mm sampling resolution showed that the gradient may be nonlinear and steeper than predicted from equilibrator samples (Rudd et al. 1986a, b). Therefore, the observed pore water gradients in Little Rock Lake may be greater (Table 4), resulting in an underestimate of the calculated pore water flux. Bioturbation of sediments may also result in an enhanced flux of material across the sediment-water interface. This problem is most likely to take place for gyttja (East Basin 6 m; Table 4), but is not as likely in sandy littoral sediments. Another source of uncertainty stems from the hydrologic characteristics of Little Rock Lake. The two shallow pore water samplers in the East Basin were deployed in an area of periodic in seepage (W. Rose, USGS, Madison, WI, pers. comm.) in which the water flux through the sediments into the lake acts in

Table 4. Gradients and calculated fluxes for pore water samples collected in Little Rock Lake in July 1984.

Site-sample depth/ion	Sample interval (cm)	Concentration gradient ^a ($\mu\text{eq}\cdot\text{cm}^{-4}$)	Flux ^b ($\text{meq}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)
East Basin—2 m			
TAlk-e ^c	-1 to 1	0.122	241
Ca ²⁺	-1 to 7	0.015	22
Fe ²⁺	-1 to 0	0.073	93
NH ₄ ⁺	-1 to 1	0.029	107
SO ₄ ²⁻	-1 to 1	-0.025	-49
TAlk			41
East Basin—3 m			
TAlk-e	0 to 2	0.082	162
Fe ²⁺	-1 to 5	0.032	41
NH ₄ ⁺	0 to 2	0.016	59
SO ₄ ²⁻	0 to 1	-0.023	-45
TAlk			62
East Basin—6 m			
TAlk-e	0 to 2	0.056	143
Ca ²⁺	0 to 2	0.027	51
Fe ²⁺	-1 to 2	0.018	29
NH ₄ ⁺	0 to 2	0.011	52
SO ₄ ²⁻	0 to 5	-0.010	-25
TAlk			62
North Basin—2.5 m			
TAlk-e	-1 to 3	0.034	67
Ca ²⁺	-1 to 8	0.008	12
Fe ²⁺	-1 to 4	0.019	24
NH ₄ ⁺	-1 to 3	0.005	18
SO ₄ ²⁻	-1 to 3	-0.014	-27
TAlk			25

^a A positive gradient indicates higher pore water concentrations at depth in the sediments and a flux of solutes from the sediments to the water column.

^b Calculated using whole-sediment diffusion coefficients of (units $10^6\text{cm}^2\cdot\text{s}^{-1}$): HCO₃⁻ = 9.0; Ca²⁺ = 6.7; Fe²⁺ = 5.8; NH₄⁺ = 16.8; SO₄²⁻ = 8.9 (Li and Gregory 1974), and porosity of 0.7 for sandy sediments and 0.9 for gyttja (East Basin, 6 m).

^c TAlk-e (ephemeral alkalinity) is the sum of TAlk, Fe²⁺, and NH₄⁺.

concert with the chemical potential for solutes diffusing out of the sediments. The sampler deployed in the North Basin was in an area of outseepage in which water flux out of the lake acts against the diffusive flux of solutes out of the sediments into the water column. The calculated fluxes of solutes at the North Basin site were all smaller than those for the East Basin sites (Table 4), which may be due to outseepage. Carignan (1985) conjectured that the profiles of solutes from a hypolimnion site that were changing more gradually could be caused by advective outseepage, although outseepage decreases as distance from shore and depth of water increase (Frape and Patterson 1981).

To determine whether sediments influence the TALK of the water column, we examined the definition of TALK (Eq. 1). For the flux of solutes between the water column and sediments to increase TALK in the lake, the water-column concentrations of nonprotolytic cations must increase, or the concentration of anions must decrease, or both. Only those cations and anions stable in oxic water will be net contributors to permanent TALK in the water column. Cations such as Fe^{2+} , NH_4^+ , and Mn^{2+} are produced in anoxic environments by catabolic reactions and contribute to this environment's TALK (ephemeral total alkalinity: TALK-e) according to:

$$\text{TALK-e} = \text{TALK} + \text{Fe}^{2+} + \text{NH}_4^+ + \text{Mn}^{2+}. \quad (5)$$

Fe^{2+} , NH_4^+ , and Mn^{2+} are not stable in oxic environments and are rapidly converted by biological and chemical reactions to forms that do not contribute to TALK (Eq. 1). However, when anoxic waters are sampled and analyzed for TALK (TALK-e), Fe^{2+} , NH_4^+ , and, to a lesser extent, Mn^{2+} contribute to TALK-e (Cook et al. 1986; Carignan 1985; Schiff and Anderson in press-a). Therefore, TALK-e, measured on anoxic waters, must be corrected for this ephemeral contribution to TALK using measured concentrations of Fe^{2+} and NH_4^+ and Eq. (5); Mn^{2+} was not measured on these pore water samples. Fluxes of permanent TALK calculated from the fluxes of TALK-e, Fe^{2+} , and NH_4^+ are presented in Table 4.

The values of the flux of permanent TALK are all smaller than the sum of the fluxes of Ca^{2+} into the sediments and SO_4^{2-} out of the sediments. This difference implies either that the uncertainties on the flux estimates are large, or that the flux of some unmeasured ion is consuming alkalinity. The uncertainties of the flux estimates, discussed above, are propagated when fluxes of ions are summed. An additional uncertainty arises in the flux calculation because the depth interval over which the gradient of the nonlinear profile was estimated was different for each ion. Consumption of TALK may be possible if anions (e.g. Cl^-) (Schiff and Anderson in press-a) are conveyed from the sediments into the water column, or if base cations are transported into the sediments. Consumption of TALK would also result from the flux of Mn^{2+} into the water column and its subsequent oxidation. Analysis of all major ions in the pore water would allow the determination of all fluxes that consume and produce TALK (Cook et al. 1986; Schindler et al. 1986; Schiff and Anderson in press-a).

Discussion

Base cations

The study lakes from the northern Great Lakes are dilute and have a chemistry that suggests domination by wet and dry atmospheric deposition with few additional inputs. In all study lakes except Big Carr, the concentration of SBC is greater than that for the model lakes (Table 2). This finding implies that SBCs are somewhat enriched from a watershed or lake source or from dry deposition. Dry deposition of SBC, which is estimated to range from 24 to 56% of total atmospheric deposition in the study area (Cadle et al. 1984; Linsey et al. in press), may account for some of the difference between the SBC of the model lakes and that of the study lakes. Reactions that would enrich the lake in SBCs are geochemical weathering, cation exchange, and decomposition of organic matter containing base cations. These reactions occur in the terrestrial watershed (Schnoor and Stumm 1984) and in lake sediments (Lerman and Brunskill 1971; Carignan 1985; Cook et al. 1986), and the ions are conveyed into the water column by stream flow, direct drainage, seepage, or diffusion.

The drainage lakes in Minnesota, which have a large hydrologic input from the terrestrial catchment, have a larger concentration of SBCs than seepage lakes in Minnesota, Wisconsin, and Michigan. The difference between seepage lakes and drainage lakes is greater than expected from differences in dry deposition alone. Although the seepage lakes do receive most of their water from precipitation, a small seepage inflow (probably less than 10% of total annual water input to the lakes) of groundwater containing high concentrations of base cations may account for as much as 30 to 40% of the base cations in the study lakes (e.g. Hurley et al. 1985). In a doline (sink hole) seepage lake in Florida, which receives 90% of its water from precipitation, Baker et al. (1986) found little enrichment of base cations over those in precipitation, indicating low rates of base cation input from groundwater seepage.

In Little Rock Lake, diffusive flux of Ca^{2+} from the sediments to the water column was about $25 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ (Table 4). This value is comparable to the input of Ca^{2+} from precipitation of $9 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ at Trout Lake (Table 1), suggesting that diffusive flux from the sediments may be an important component of the Ca^{2+} budget for Little Rock Lake. Fluxes of Ca^{2+} from sediments to the water column for a number of soft water lakes are collected in Table 5. In two natural lakes at the Experimental Lakes Area (ELA), northwestern Ontario, Lerman and Brunskill (1971) observed a Ca^{2+} pore water flux of 12 and $28 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$, which amounted to one-third of the total import of Ca^{2+} to the lakes. More recent work at the former of the two ELA lakes studied by Brunskill and Lerman (1971) showed that the Ca^{2+} flux from input-output mass balance data was $29 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ (Schindler et al. 1986). Carignan (1985) used pore water gradients to calculate a Ca^{2+} flux of $6 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ for a lake in the Sudbury basin. In an experimentally acidified lake at ELA, Cook et al. (1986) calculated an in-lake production of Ca^{2+} of $54 \text{ meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ over 8 years and attributed this to sediment-water exchange. In the latter study, other

cations (e.g. Mg^{2+}) were apparently conveyed into the sediments, complicating the influence of sediment-water exchange on the overall SBC budget.

Sulfate

For nearly all of study lakes, the SO_4^{2-} concentration was smaller than the model lake concentration, indicating that reactions in the watersheds or lakes were causing the retention of SO_4^{2-} (Table 2). Because the model lakes did not include an input of sulfate from dry deposition, the concentration of sulfate in the model lakes is a lower limit and the actual retention of sulfate by the lake-watershed system is greater than that indicated by the difference in sulfate concentration between the lake data and the model lakes.

Sulfate retention in the watershed may possibly be caused by assimilatory sulfate reduction, dissimilatory sulfate reduction, or adsorption onto soils. Adsorption of SO_4^{2-} onto mineral soil in the catchments of the study lakes was not investigated in this study, but is likely to be limited for soils derived from glacial till [Johnson et al. 1980]. Assimilatory sulfate reduction should also be minimal, given the large supply of sulfur in precipitation relative to the small sulfur requirements of terrestrial (Likens et al. 1977) as well as aquatic (Wetzel 1975) plants. In a survey of sulfate yields from soft water lakes in eastern Canada, Thompson and Hutton (1985) concluded that sulfate was not appreciably retained by terrestrial watersheds.

Sulfate retention in lake sediments in the form of sulfide minerals or organic sulfur (ester sulfate or carbon-bonded sulfur) may be the predominant means of retention. The Little Rock Lake pore water profiles (Figure 2) and calculated pore water fluxes (Table 4) suggest that dissimilatory sulfate reduction was occurring in the sediments. Because total hydrogen sulfide concentrations in the pore water in Little Rock Lake were below the detection limit, despite the large amounts of sulfate reduced, and because of the high Fe^{2+} concentrations in the pore water, an iron sulfide phase appears to be forming (cf. Cook 1984). However, preliminary measurements of various sulfur phases (acid-volatile sulfide, pyrite sulfur, total sulfur) in the sediments of Little Rock Lake revealed that the iron sulfide phases were a small fraction of the total sulfur and could not be the end product of the sulfate-consuming reaction (L. W. Baker, University of Minnesota, pers. comm.). A more likely fate of the sulfur in Little Rock Lake is an organic sulfur phase, produced by reaction of H_2S with organic matter in the sediments (Nriagu and Soon 1985; Rudd et al. 1986a).

The flux of SO_4^{2-} from the water column to the sediments in Little Rock Lake is similar to reported values from lakes at ELA (Ontario), Florida, the Adirondack Mountains (NY), and Norway (Table 5). Lakes with high SO_4^{2-} loading (L223, Ontario, which is experimentally acidified with H_2SO_4 , and Clearwater, which is near Sudbury, Ontario) have higher rates of SO_4^{2-} retention. This trend is expected because rates of SO_4^{2-} reduction are first order with respect to SO_4^{2-} at these relatively low SO_4^{2-} concentrations (e.g. Cook and Schindler 1983; Kelly and Rudd 1984; Lovley and Klug 1986).

Table 5. Sediment-water exchange of Ca^{2+} , SO_4^{2-} , and TALK for soft water lakes from North America and Scandanavia.

Ion/lake	Flux ^a ($\text{meq} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$)	Method	Reference
Ca^{2+}			
Little Rock	25	Pore water	This paper
239	12	Pore water	Lerman and Brunskill (1971)
	29	Budget	Schindler et al. (1986)
240	28	Pore water	Lerman and Brunskill (1971)
223	54	Budget	Cook et al. (1986)
Clearwater	6	Pore water	Carignan (1985)
Langtjern	44	Budget	Wright (1983)
SO_4^{2-}			
Little Rock	-36	Pore water	This paper
239	-39	Budget	Schindler et al. (1986)
223	-245	Budget	Cook et al. (1986)
	-79	Pore water	Rudd et al. (1986b)
Lowry	-38 to -49	Budget	Baker et al. (1986)
Magnolia	-41 to -54	Budget	Baker et al. (1986)
McCloud	-27 to -35	Budget	Baker et al. (1986)
Clearwater	-119	Pore water	Carignan (1985)
Gaardsjon	-80	Budget	Hultberg et al. (1983)
Dart's	-48	Pore water	Rudd et al. (1986b)
Langtjern	-56	Budget	Wright (1983)
TALK			
Little Rock	50	Pore water	This paper
239	74	Budget	Schindler et al. (1986)
	220	Pore water	Schiff and Anderson (in press-a)
223	300-367	Budget	Cook et al. (1986)
	35	Pore water	Schiff and Anderson (in press-a)
Langtjern	118	Budget	Wright (1983)
Dart's	48	Budget	Schiff and Anderson (in review)
Clearwater	207	Pore water	Carignan (1985)
114	70	Pore water	Schiff and Anderson (in press-a)
Batchewana	60	Pore water	Schiff and Anderson (in press-a)
Mohonk	200	Pore water	Schiff and Anderson (in press-a)
Awosting	-30 to 5	Pore water	Schiff and Anderson (in press-a)

^a A positive value indicates a flux from the pore water into the lake and a negative value indicates a flux from the water column into the sediments.

Analysis of sediment cores from four of the study lakes also shows that sulfur is being retained in the lake sediments (Table 6) (Mitchell et al. in press) at rates similar to the diffusive flux of SO_4^{2-} to lake sediments (Tables 4 and 5). These sediment core data are for total sulfur and therefore do not indicate the phase containing sulfur.

Other major ions

The other major ions in lake water are Cl^- , NO_3^- , and NH_4^+ . Cl^- in the lakes was derived from atmospheric deposition. The majority of lakes have NO_3^-

Table 6. Sulfur retention by lake sediments.

Lake	Observed retention ^a
Dunnigan	46
Hustler	120
Andrus	50
McNearney	12
Little Rock	50 ^b

^a For surface (0–5 cm) sediments (Mitchell et al. (1986)).

^b From Table 4.

concentrations below $1 \mu\text{eq} \cdot \text{L}^{-1}$, and the highest NO_3^- is $6 \mu\text{eq} \cdot \text{L}^{-1}$ in McNearney Lake (Table 2). Because the concentration of NO_3^- is 15 to $30 \mu\text{eq} \cdot \text{L}^{-1}$ in precipitation (Table 1) and the concentration factors for the lakes are 2 to 3 (Table 2), one would expect NO_3^- concentrations of 30 to $90 \mu\text{eq} \cdot \text{L}^{-1}$ in these lakes if NO_3^- behave conservatively. Therefore, the low NO_3^- values strongly suggest that the terrestrial watersheds and the lakes are extremely efficient in retaining NO_3^- , either by biological assimilation or denitrification. NO_3^- is efficiently retained in nitrogen-limited terrestrial ecosystems (Bormann et al. 1977). In aquatic ecosystems, NO_3^- supplied in excess of that required for photosynthesis is effectively taken up by denitrifying communities (Schindler et al. 1985). Experimental additions of nitric acid to limnocorrals revealed that NO_3^- was efficiently removed from the watercolumn by denitrification in the sediments (Schiff and Anderson in press-b). The low NO_3^- concentrations in the study lakes are in contrast to high values observed in the Adirondacks (e.g., 5 to $30 \mu\text{eq} \cdot \text{L}^{-1}$) (Driscoll and Newton 1985) and are similar to values at other sites in the upper Midwest (Rapp et al. 1985) and in northwestern Ontario (Kelly et al. 1982). NH_4^+ concentrations are all less than or equal to $1 \mu\text{eq} \cdot \text{L}^{-1}$ in the study lakes (Table 2), despite precipitation concentrations of about $20 \mu\text{eq} \cdot \text{L}^{-1}$ (Table 1). NH_4^+ , too, was efficiently retained by the watersheds or lakes.

TAlk

For the study lakes in Wisconsin and Michigan, carbonic acid produced by biological activity in the watershed and in the lake caused base cation release through geochemical weathering and exchange reactions and thereby generated carbonate alkalinity (Table 2). The trend of a large portion of the TAlk derived from organic acids in the Minnesota study lakes (Table 2) indicates that organic acids, presumably generated in the terrestrial environment, along with carbonic acid were the source of hydrogen ions driving the weathering reactions. The relative importance of each type of weathering for the Minnesota study lakes cannot be determined because the product anions—carbonate alkalinity and noncarbonate alkalinity—are highly reactive and have a distinctly different acid-base character.

The pore water flux of TALK to the water column of Little Rock Lake is similar to that observed at Dart's Lake and Lake 239 (Table 5). Higher fluxes have been reported for acid-stressed lakes in Ontario and Norway. The fluxes demonstrate the importance of TALK-producing reactions that occur in the lake in modifying water-column chemistry.

The TALK in the water column is a function of SBC, SO_4^{2-} , Cl^- , NO_3^- , and NH_4^+ (Eq. 1) and, thus, is the result of the integration of the processes affecting the individual ions. SO_4^{2-} and NO_3^- retention by the lakes and watersheds produced TALK, as determined by the difference in SO_4^{2-} and NO_3^- concentrations between the study lakes and the model lakes (Table 2). The flux of SO_4^{2-} to the sediments of Little Rock Lake (Table 4) and the sedimentation of sulfur for Hustler, Dunnigan, Andrus, and McNearney lakes (Table 6) indicate that TALK is produced by these processes. However, the amount of TALK produced for each equivalent of SO_4^{2-} retained cannot be determined because the form of sulfur in the sediments—an iron sulfide phase, an ester sulfate phase, a carbon-bonded sulfur phase, or a combination of these phases—is not known (Rudd et al. 1986a).

Because much of the NH_4^+ in atmospheric deposition was consumed, as determined by comparison of the model lakes and study lakes (Table 2), the TALK associated with NH_4^+ (Eq. 1) was also consumed.

The range in TALK of the study lakes (Table 2) is caused primarily by variations in processes affecting SBC and SO_4^{2-} among lakes and among regions. The contribution of SBC to TALK was greater in the drainage lakes in Minnesota than in the seepage lakes in Minnesota, Wisconsin, and Michigan, apparently as a result of greater weathering inputs of SBC in the watersheds of the drainage lakes. For example, the SBC of the drainage lake Hustler ($186 \mu\text{eq} \cdot \text{L}^{-1}$) is greater than that for the seepage lakes Little Rock ($85 \mu\text{eq} \cdot \text{L}^{-1}$) and McNearney ($94 \mu\text{eq} \cdot \text{L}^{-1}$) (Table 2). The relatively high SO_4^{2-} concentration for McNearney (Table 2), coupled with the relatively low SBC concentration, cause this lake to have the lowest pH and TALK of the study lakes (pH 4.4; TALK = $-38 \mu\text{eq} \cdot \text{L}^{-1}$). The rate of sulfur sedimentation in McNearney is the lowest of those for the four lakes analyzed (Table 6) and is low compared to values from several other lake districts with soft water lakes (Table 5). Apparently, the low rates of primary productivity (total phosphorus of $3.4 \mu\text{g} \cdot \text{L}^{-1}$ and Chl-*a* of $0.2 \mu\text{g} \cdot \text{L}^{-1}$) (Kreis et al. in press) are responsible for low rates of microbial catabolism in McNearney Lake.

In contrast, Little Rock Lake (pH 6.26; TALK = $24 \mu\text{eq} \cdot \text{L}^{-1}$), which has an SBC similar to that of McNearney Lake, has a smaller SO_4^{2-} concentration (49 vs $151 \mu\text{eq} \cdot \text{L}^{-1}$), apparently due in part to a larger rate of sulfur retention by lake sediments (Tables 4 and 6). Hustler Lake (pH 6.8; TALK = $80 \mu\text{eq} \cdot \text{L}^{-1}$) has a SO_4^{2-} concentration that is slightly greater than that for Little Rock (68 vs $49 \mu\text{eq} \cdot \text{L}^{-1}$), but because of a much larger SBC (186 vs $85 \mu\text{eq} \cdot \text{L}^{-1}$) it has a greater pH and TALK than Little Rock. The differences in TALK and pH among Hustler, Little Rock, and McNearney lakes are due to the larger retention of SO_4^{2-} in the Little Rock and Hustler sediments and watersheds and the greater production of SBC in the Hustler Lake watershed and sediments.

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