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Ion Budgets and Sediment−Water Interactions during the Experimental Acidification and Recovery of Little Rock Lake, Wisconsin

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Ion budgets for the two basins of experimentally acidified Little Rock Lake (Vilas County, WI, U.S.A.) indicate that Ca^{2+}, Mg^{2+}, and K^+ were released from the bottom sediments to the water column during 1984−1994, and NH_4^+, NO_3^-, and SO_4^{2-} were removed for a net internal alkalinity generation (IAG). Sulfate removal contributed ~50% of the IAG in the reference basin, and cation production generated ~40%. In-lake processes in the reference basin removed ~38% of the sulfate input; 58% was lost to outflow, and 4% remained in the water column. As a result of acid additions that stimulated sulfate reduction and lower pH that enhanced ion exchange, sulfate removal and Ca^{2+} production were more important for IAG in the treatment basin. During 1984−1994, sulfate removal contributed about 61% of the IAG, and Ca^{2+} production contributed about half of the IAG from cation production. In the treatment basin, in-lake processes removed about 46% of the total input of sulfate (including acid additions); 36% was lost to outflow and 18% remained in the water column (representing ~25% of the added acid). In both basins of LRL, NH_4^+ consumption roughly balanced NO_3^- consumption, and net N transformations provided only 3−12% of the IAG. Overall, Na^+ and Cl^- were conservative in both basins during 1984−1994. Most ion budget components, including calculated internal reaction terms, showed fairly large interannual variations; e.g., ion inputs (dominated by atmospheric deposition) varied by a factor of about two. Over the 10-year period, ANC terms calculated from the budgets as the difference between base cation and acid anion terms agreed well with measured ANC terms for the budget components, indicating that the budgets accounted for all important IAG constituents.

Introduction

Prior to the early 1980s, microbial reduction of sulfate was not considered to be an important process in freshwater lakes. Atmospheric inputs of sulfuric acid thus were not expected to be neutralized within lakes (reduction of sulfate to sulfide consumes H^+, thus neutralizing acidity). Early models of acid impacts on lakes assumed that inputs of alkalinity to lakes were derived from terrestrial weathering (*1*). Studies during the experimental acidification of ELA Lake 223 in Ontario showed that adding sulfuric acid stimulated microbial sulfate reduction (*2*) and that this process contributed significantly to the lake's alkalinity. This finding led to further investigations of the in-lake processes that contribute to alkalinity (i.e., internal alkalinity generation or IAG).

Studies in the 1980s confirmed the importance of IAG in lake responses to acidification and elucidated the processes contributing to IAG. For example, IAG neutralized 66−81% of the acid added to Lake 223 (*3*), and IAG was 4.5 times more important than terrestrial processes in providing alkalinity to ELA Lake 239 (*4*). IAG is not important in lakes with large watersheds and short hydraulic retention times; terrestrial processes are more important for these lakes. However, IAG is usually important in regulating pH and alkalinity in seepage lakes, which have long water residence times and receive most of their water as direct precipitation (*5*−*7*).

Various methods, from laboratory experiments to whole-ecosystem manipulations, have been used to study IAG and define its contributing processes (*4*, *8*−*10*). These methods provide insights into IAG on a range of spatial and temporal scales depending on the manner of investigation. This paper evaluates IAG in Little Rock Lake, WI, based on annual whole-basin ion budgets for 1984 to 1994. During that time, the lake's north basin was acidified experimentally from pH 6.1 to 4.7 in three 2-year steps (*11*), and recovery from acidification was followed for 4 years (*12*). Site description, experimental design, and methods of sample collection and analysis were discussed elsewhere (*13*). The budgets we developed used data from several sources, but except where we modified data or quality was an issue, methods used by others are not described here.

Little Rock Lake Hydrology and Water Budgets

Overview. Little Rock Lake (LRL), Vilas County, WI, is a softwater, oligotrophic lake in an uninhabited, forested watershed with highly permeable sandy soil. The lake has two basins: north (treatment, symbolized by TB): 9.8 ha; south (reference, symbolized by RB) 8.1 ha, but the north is deeper: $z_{max,TB} = 10.3$ m; $z_{max,RB} = 6.5$ m. LRL has no surface inlets or outlets and is a groundwater recharge lake (Figure 1). It receives almost all its water from direct precipitation. Groundwater inflow occurs intermittently but is <2% of total annual inflow (*14*). Installation of a PVC barrier in 1984 to separate the basins (*15*, *16*) caused slight differences in their hydrology. The regional water table slopes down from SE to NW, and groundwater flows only into the SE corner of the reference basin. The resulting head difference caused water to leak around the barrier as transfer outflow (TO) from the reference basin and inflow (TI) to the treatment basin.

Precipitation, Evaporation, and Lake Level. Precipitation (P), evaporation (E), and lake stage were measured by the USGS (*14*). Monthly P and E data show seasonal cycles typical of north temperate regions and a drought from 1986 to 1990 (Figure 2). For annual budgets, P and E were summed over a treatment year (April−March). From 1986 to 1989, annual P decreased from 91% of the average for 1951−1980 to 69%, and E increased so that E exceeded P during 1989 (*14*). Above normal rainfall and cooler temperatures ended the drought in 1990. The level of LRL varied during the study period, causing significant changes in basin volumes and area. The highest value (April 7−9, 1986) was 0.93 m higher than the lowest value (August 8, 1990). Because LRL has virtually no watershed, its level responds quickly to rainfall events. For example, the second highest monthly rainfall in the record

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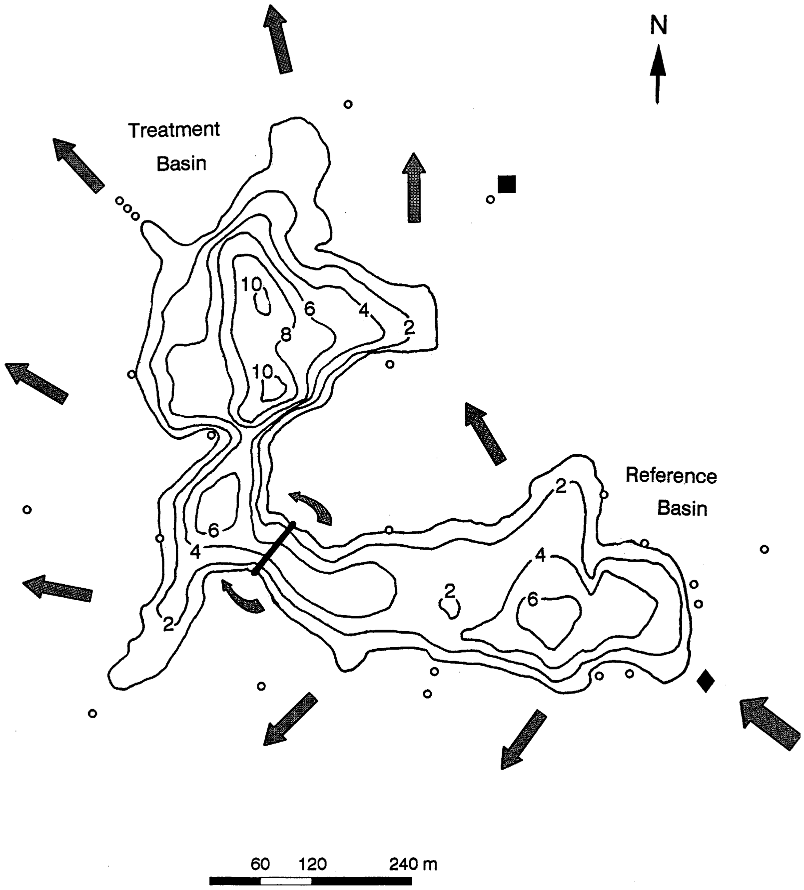

FIGURE 1. Bathymetric map of Little Rock Lake, Vilas County, WI, showing direction of shallow groundwater flow (arrows) and locations of piezometers (small circles).

(16.9 cm, August 1990) led to a lake-level increase of 11.3 cm within days.

Groundwater and Transfer Flow. Water budgets for the acidification phase (*14*) (Figure 2) yielded estimates of groundwater inflows (GI) and outflows (GO) from monthly water-table data on 59 piezometers in and around the lake, including a recording nested piezometer at the SE corner of the reference basin (referred to as well 1), where groundwater inflow occurs. During 1991–1994, the only hydrologic data collected was P, E, lake stage, and water level in the well 1. As a result, we needed to estimate unmeasured components of the water budgets (i.e., groundwater flows).

As noted above, GI occurs only to the reference basin (near well 1) and only when the water table at that location is higher than the lake level. Such inflows occurred intermittently from October 1983 to July 1986 and June 1991 to August 1993. A regression equation ($r^2 = 0.89$) developed from data for 1983–1986 (*13*) was used to predict monthly GI for 1991–1993 from GI for the preceding month and the difference between lake stage and the water table (from well 1).

Total annual outflow (O_T) from the reference basin during 1991–1994 was estimated by mass balance, $O_T = GO_{RB} + TO = P + GI - E - \Delta S$, but when this was done on a monthly basis, many values were unreasonably high (compared with ref *14*) or negative (indicating inflow when none was expected). A mass balance ($GO = P + TI - E - \Delta S$) cannot be used to calculate GO for the treatment basin because transfer inflow (TI) can be determined only by mass balance (*14*).

To calculate the water budget components needed for ion budgets, we developed empirical relationships for O_T from the reference basin and GO for the treatment basin (*13*). Lake stage, water level in well 1 (a surrogate for the water table), and surface area (related to outflow area) were used as predictor variables. Strong correlations between these variables and GO likely reflect rapid flow through highly permeable sand and gravel underlying the lake's littoral zone. The best relationship (lowest budget residual for O_T) for the reference basin had $R^2 = 0.92$. A similar relationship for GO from the treatment basin had $R^2 = 0.95$ (*13*).

The observation that water levels in the two basins stayed identical during study facilitated calculation of water flows around the barrier (*14*). Water balances for the two basins are $\Delta S_{RB} = P + GI_{RB} - E - O_{T,RB}$ and $\Delta S_{TB} = P + TI_{TB} - E - GO_{TB}$. Because budget components were expressed in terms of lake surface water level changes (mm), $\Delta S_{RB} = \Delta S_{TB} = \Delta S$. Setting the water balance equations equal and simplifying (P and E are the same for both basins) yields

$$TI_{TB} = GI_{RB} - O_{T,RB} + GO_{TB}$$

This relationship was used to calculate monthly TI for the treatment basin over the study period. The driving force for TI is the head difference caused by the greater outflow from the treatment basin relative to the reference basin. The former basin has greater outflow because it is further above the water table and has greater surface area. Although a head difference must exist for flow to occur, no difference in water level was observed between basins, which implies that flow around the barrier was rapid. Transfer outflow (TO) from the reference basin was calculated by adjusting transfer inflow (TI) by the ratio of the basin surface areas: $TO = TI \times A_{NB}/A_{SB}$. This is the only water budget component needing adjustment for surface area (e.g., 3 mm of outflow from the smaller reference basin does not equal 3 mm of inflow to the larger treatment basin).

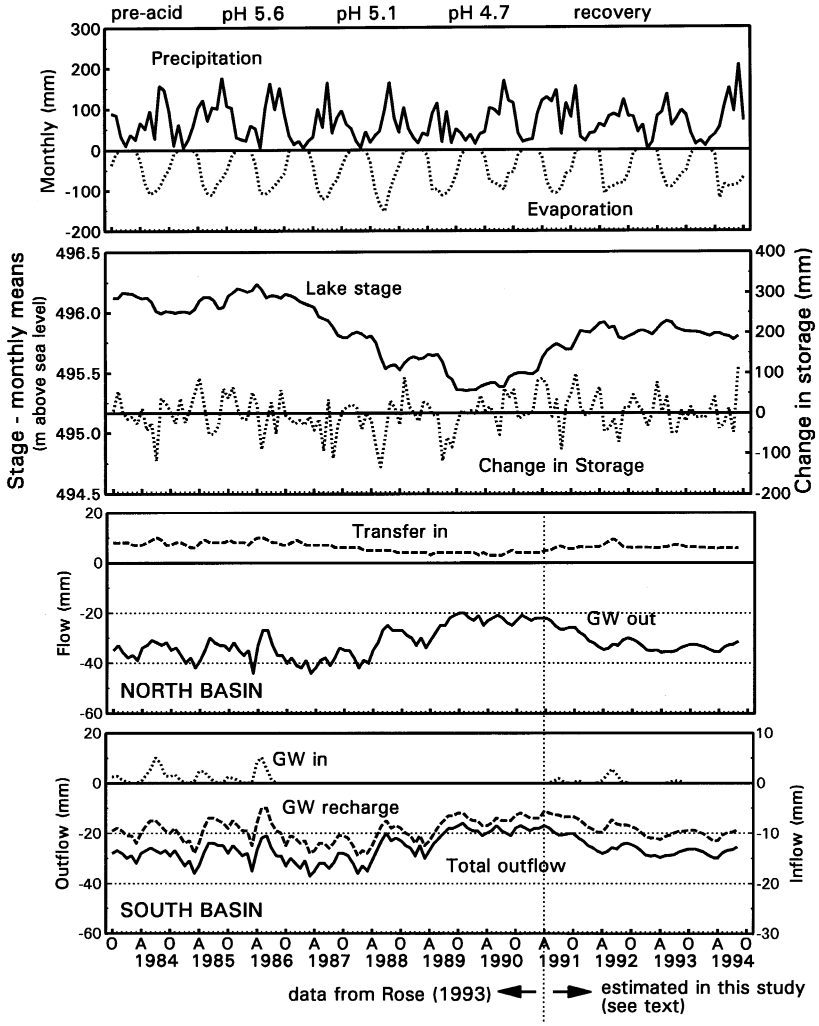

FIGURE 2. Temporal changes in water budget components for Little Rock Lake, 1984−1994.

Water Budgets. Water budgets for the basins for 1984−1994 are summarized in Figure 2 and Table S1 (Supporting Information). The approximate error in the annual budgets was determined by comparing two estimates of ΔS: (1) ΔS_{obs}, obtained from observed lake stage, and (2) ΔS_{calc}, obtained from mass balances as ΣInputs − ΣOutputs. The budget residual, R, is the difference between observed and calculated ΔS. For years 1984−1990, residuals were low: $|R| < 54$ mm. Residuals for 1991−1994 were minimized by choice of a relationship to calculate outflow from the reference basin. Resulting residuals $|R|$ were < 50 mm.

Hydraulic residence time (HRT) was calculated as the average annual basin volume divided by the total annual outflow, including evaporation. Chemical residence time (CRT), the average time a conservative chemical spends in a basin, was calculated as average annual basin volume divided by annual outflow, excluding evaporation. Treatment basin HRT was higher than reference basin HRT; 10-year averages were 4.1 and 3.4 yr, respectively. This reflects the fact that the treatment basin has a larger volume than the reference basin, but both have similar surface areas. CRT values also were higher for the treatment basin (10-year average = 10.3) than for the reference basin (10-year average = 9.6). CRT increased with decreasing stage; GO and TO, the two components of annual outflow are both functions of lake stage. CRT was highest during 1988−1991 (treatment basin, 10.5−13.6 yr; reference basin, 9.2−12.0 yr), when some constituents increased not obviously as a result of acidification. The increases were attributed to the drought.

Ion Budgets

Calculation of Budget Components. Wet Deposition. Monthly volume-weighted precipitation chemistry data from the National Acid Deposition Program/National Trends Network (NADP/NTN) for the Trout Lake site ~5 km NE of LRL (*17*) were reviewed for reliability using outlier tests and cation:anion (C:A) ratios. All but two of the 120 months of data were used as received. Outlier values of some ions for 1 week of data were deleted from each of the 2 months, and monthly values were recalculated. The mean C:A for the corrected 10-year record was 0.994 (range = 0.71−1.56; n = 120). Most values were between 0.85 and 1.15. Fluctuations in basin surface areas were taken into account in calculating wet deposition of ions to each basin.

Dry Deposition. Dry deposition constitutes a substantial portion of major ion total deposition (0.2−2.2 × mass deposition by wet precipitation (*18*)), but, as the range implies, uncertainties associated with its measurement are considerable. Collection efficiencies of various dryfall collectors are not closely related to the collection characteristics of natural surfaces, especially water (*19*). A paucity of data for the LRL region during 1988−1994 also makes estimation of dryfall difficult.

Ion budgets calculated by earlier LRL researchers used various dry deposition values. Weir (*20*) used fluxes estimated from 1980 to 1984 NADP dry-bucket data (Trout Lake site) and APIOS (Air Pollution in Ontario Study) air quality data. Tacconi (*21*) measured dry deposition and air quality at LRL

TABLE 1. Dry:Wet Flux Ratios for Upper Midwest and Dry Deposition Flux Estimates for Little Rock Lake

		dry flux estimates (meq m^{-2} yr^{-1})				
				1985–1987[c]		
ion	dry:wet (D:W) flux ratio[a]	based on D:W ratio	1980–1984[b] NADP & APIOS	DB	HV	1980–1987[d] average
Ca^{2+}	0.54 ± 0.10	4.1	4.3	5.3	6.2	4.9
Mg^{2+}	0.65 ± 0.14	1.3	1.6	3.1	3.4	2.1
K^{+}	1.64 ± 0.18	0.6	1.1	3.1	1.0	1.5
Na^{+}	0.22 ± 0.09	0.4	0.4	4.6[e]	3.4[e]	0.4
NH_4^{+}	0.19 ± 0.10	2.6	3.5	nm[f]	nm	3.5
SO_4^{2-}	0.37 ± 0.09	8.1	11.5	6.5	6.0	9.3
Cl^{-}	0.19 ± 0.03	0.3	0.5	1.8	nm	1.0
NO_3^{-}	0.30	4.4	5.1	nm	nm	5.1

[a] Mean and standard deviation for Upper Midwest region, as summarized by Baker (*18*). [b] Average fluxes estimated by Weir (*20*) from NADP dry bucket and air quality data from APIOS (Air Pollution in Ontario Study). [c] Average fluxes for ice-free period extrapolated by Tacconi (*21*) from dry bucket (DB) and high-volume air sampler (HV). [d] Weighted averages of fluxes reported in refs *20* and *21*. [e] Not used to calculate 1980–1987 average (see text). [f] Not measured.

TABLE 2. Elemental Composition (mg/g [dry wt]) of Leaf Litter near Little Rock Lake

element	ref *21*	ref *24*	element	ref *21*	ref *24*
Ca	11.7	12.2	S		0.76
Mg	3.0	3.5	N		9.4
K	7.4	6.1	C		455
Na	0.12		P		2.1

during ice-free periods of 1985–1987 and estimated annual deposition rates based on these data. The fluxes used by these workers (Table 1) illustrate the variability resulting from differences in methods as well as year-to-year fluctuations.

Baker (*18*) estimated the ratio of ion fluxes from dry and wet precipitation (D:W) based on 1980–1987 data from several sites in the Upper Midwest (Table 1). The range of sites helps to minimize site-specific errors but also minimizes the influence of local sources, which may be important. Data used by Baker are from years of normal-to-high precipitation, and D:W ratios likely were higher during drought years. Although data for the LRL region are not available to confirm this, drought results in decreased vegetative cover and increased dry deposition of particles, which is especially important for K^{+}, Ca^{2+}, and Mg^{2+}. Despite potential problems with Baker's ratios, their application to 1985–1987 wet deposition data for LRL agreed within 1.2 meq^{-2} y^{-1} of measured results (*21*) for all ions except Na^{+}, for which measured values likely are incorrect (they are much higher than values typically reported for the region). Dry deposition inputs in our budgets (Table 1) are based on monthly wet deposition and the D:W ratios in Table 1, but we also evaluated the effect of using the average measured dryfall for 1980–1987 on computed in-lake reaction terms.

Leaf Litter. Inputs from tree leaves can be a significant source of carbon, nutrients, and cations to lakes and streams (e.g., refs *22* and *23*). LRL is surrounded by a mixed conifer/hardwood forest (primarily oak and birch), and an estimated 14.6 g m^{-2} yr^{-1} of leaves is deposited to the littoral zone of the lake (*23*). The elemental composition of leaves collected from the LRL shore was analyzed (*21*, *24*) (Table 2), and rates of leaf decomposition under different pH conditions were measured (*23*, *24*). Acidification to pH 5.1 and 4.7 reduced rates of leaf decomposition (*11*) and rates of C and N release (*23*) but had little effect on release of Ca, Mg, and K (*24*).

Organic C is the largest contribution of leaf litter to lake chemistry. The nature of the organic C released from leaves (e.g., concentration of carboxylate groups) is poorly understood, however, and the contributions of leaf-derived organic C to ANC budgets thus are difficult to quantify. TOC levels in LRL were low (ice-free surface averages < 3 mg/L). Consequently, leaf contributions of organic acids probably were small and not included in the ANC budgets.

The effects of leaf inputs on other ANC-related elements in LRL are only partly known, and the overall contribution of leaf inputs to the ANC budgets is not clear. For example, although the concentrations of nitrogen and sulfur in LRL leaf litter are known, the forms in which they are released, which determines whether they add or consume ANC, are not known. Nitrogen inputs from leaf litter likely occur as organic N and NH_4^{+}, which probably is assimilated rapidly by periphyton. Although leaf-derived N may be significant in the littoral zone, it probably has little effect on the lake's overall ANC budget. Similarly, sulfur likely is released from leaf litter as organic S, but whether the released S was assimilated by algae or oxidized to sulfate is unknown. The concentration of sulfur in LRL leaf litter was low and not important compared with other sources.

In contrast to C, N, and S, the release of Ca, Mg, and K from leaf litter occurred rapidly and as unbound inorganic ions (*24*); Na likely behaved similarly. The fate of these ions, which determines whether they contribute to the ANC budget, is not known, however. If they are transported to the open water, they contribute to ANC, but if they are sequestered in the littoral zone by periphyton uptake or adsorption to sediments below the leaves, they would not be important in basin ANC budgets. A final consideration is the lack of information on the concentration and fate of chloride in leaf litter. This anion would tend to offset the contributions of base cations to ANC.

We used a mass deposition rate of leaves of 3.4 g m^{-2} yr^{-1} to the lake (calculated from (*23*) and the average concentrations of Ca, Mg, K, and Na in Table 2. Inputs of $NO_3^{-} + NH_4^{+}$ (assuming N was converted to one of these ions) and sulfate inputs (assuming all S was converted to SO_4^{2-}) were calculated similarly.

Groundwater. Inflow of groundwater occurred intermittently to the reference basin during 1984–1986 and 1991–1993. During the former period, the chemistry of groundwater was analyzed monthly, and these results were applied to monthly inflows in the same way as for precipitation chemistry. Few groundwater samples were analyzed during the recovery period. To estimate ion inputs from groundwater during this time, average ion concentrations measured in groundwater during periods of groundwater inflow in 1984–1986 were applied to flows calculated for 1991–1993.

Groundwater outflow occurs mainly in the littoral zone of LRL, which has highly permeable sand and gravel; fine-grained organic sediments with much lower hydraulic conductivity underlie the deeper areas of the lake. The chemistry of groundwater recharge was estimated from the near-surface chemistry of each basin. A running average of the data from 2 to 3 dates was used to estimate monthly recharge chemistry. Monthly chemistry values were applied to monthly outflow volumes in the same way described for wet precipitation to account for changes in lake area.

Transfer. The chemistry of transfer outflow from the reference basin was estimated as the running average of near-surface concentrations, as described above. The chemical composition of transfer inflow depends on the length of the flow path through the sandy lake sediment and sand/gravel that forms the subsoil and shallow unconfined aquifer. Transfer inflow with a short flow path (around the edges of the curtain) should have an ionic content similar to the reference basin, but inflow with a longer path in the subsoil should have an ionic content similar to shallow groundwater. Most constituents that contribute to ANC have higher concentrations in groundwater than in the reference basin.

TABLE 3. Annual Additions of Concentrated Sulfuric Acid[a] to North (Treatment) Basin of Little Rock Lake

period	acid added (L)	acid added Kequiv	target pH
4/84–3/85	0	0	(~6.1; background)
4/85–3/86	376	13.54	5.6
4/86–3/87	150	5.40	5.6
4/87–3/88	408	14.69	5.1
4/88–3/89	227	8.17	5.1
4/89–3/90	454	16.34	4.7
4/90–3/91	322	11.59	4.7
4/91–3/94	0	0	(recovery)

[a] Technical grade; 36 N (equiv/L).

Groundwater flow patterns and the observation that water levels in the basins were virtually the same suggest that transfer occurred rapidly near the curtain. We concluded that TI would have an ionic content more similar to the reference basin than to groundwater, and monthly values of reference basin chemistry were applied to monthly amounts of TI, taking lake area into account. Mean values of shallow groundwater chemistry from 7 years of data for a well near the curtain were used to provide an upper limit of transfer inputs.

Change in Storage. We determined annual change in storage, ΔS, from lake level and chemical data for the first sampling date after ice-out, typically in mid-to-late April. This represented the same point in the annual hydrogeochemical cycle—i.e., post-snow and ice melt (so that lake chemistry reflected winter precipitation inputs), but before thermal stratification, spring plankton blooms, and start of acid additions. In most years the first open-water sampling was within two weeks of ice-out. In 1992 and 1994, 3–4 weeks elapsed before the first open-water sampling. For these years, inventories also were calculated for the last under-ice sampling date, and an interpolated value between the two dates was used for ΔS. Because of the variability in dates, each treatment year varied slightly in length. The inventory of each ion was calculated by summing the mass in each depth interval. The volume of each interval was adjusted to account for lake level. Sampling depths were 0, 4, 6 m for both basins plus 8 and 9 m in the treatment basin.

Acid Additions. Technical grade sulfuric acid was added to the treatment basin during the ice-free period (Table 3); additions began shortly after ice-out and continued through fall mixing. The acid was assumed to be 18 M and contained

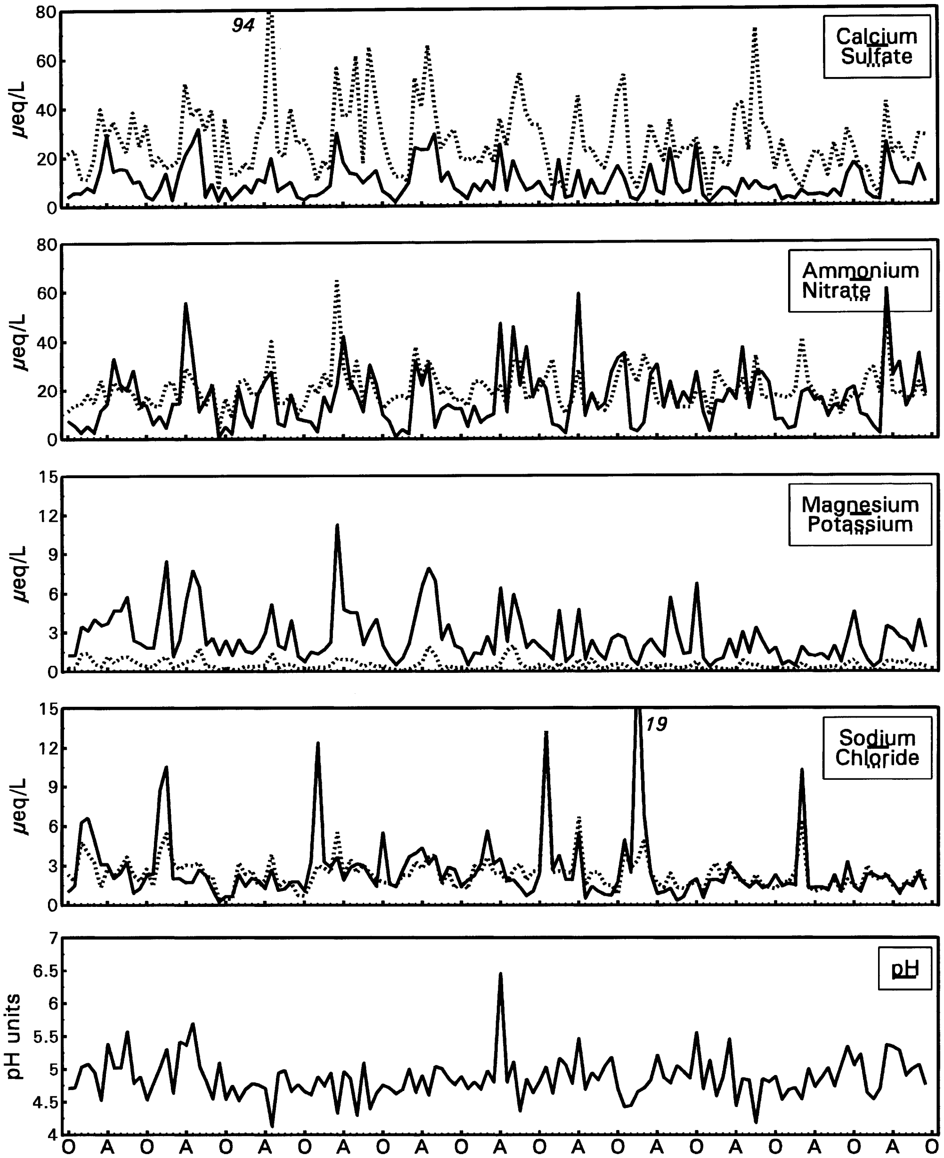

FIGURE 3. Temporal variations in chemistry of wet-only atmospheric deposition, 1984–1994; data from NADP Trout Lake site.

negligible amounts of contamination (*15*).

Results

Budget Components. Annual budgets for major ions affecting ANC were assembled for the LRL basins from measured or estimated components as described above. Annual in-lake reaction, *R*, was computed for each ion from the equation: $R = \Delta S + \Sigma(\text{Outputs}) - \Sigma(\text{Inputs})$.

Inputs, Outputs, and Change in Storage (ΔS). As expected for a lake with a precipitation-dominated hydrology, inputs of inorganic ions were dominated by atmospheric sources, except for sulfate in the treatment basin, which was dominated by acid additions (*13*). Atmospheric inputs were distributed among wet and dry inputs according to the ratios used to calculate dry deposition fluxes. Total inputs of most ions were dominated by wet precipitation; K^+ was the only ion with an input mostly from dry deposition.

Precipitation chemistry (Figure 3) showed some long-term trends. Sulfate decreased from 1984 to 1994, probably as a result of efforts to reduce SO_x emissions (*25*), and Ca^{2+} and Mg^{2+} also decreased for unknown reasons (*26*), but NO_3^- and NH_4^+ increased slightly. These trends offset each other with respect to ANC, where ANC was calculated as Σbase cations $-$ Σacid anions). Precipitation ANC showed no trend during the period (average for 1984−1994 = -17.4 μeq/L), and the average pH was 4.78. Seasonal patterns suggest possible origins of the ions. In most years Ca^{2+}, Mg^{2+}, K^+, and NH_4^+ increased during March−June, reflecting agricultural or land-based sources. Nitrate peaked in early spring, also probably because of agricultural sources, but NO_3^- minima were not as low as those of NH_4^+, possibly reflecting important contributions of NO_x emissions to NO_3^- deposition. In contrast, Na^+ and Cl^- were highest in winter, reflecting use of salt as a deicer on roads. Sulfate usually was lowest in winter, possibly a result of seasonal shifts in weather patterns (prevailing winds) and power usage.

For the reference basin, the total input of ions (Table S2; Supporting Information) was the sum of inputs from wet precipitation, dry deposition, and groundwater inflow. During most years, atmospheric inputs accounted for >90% of ion inputs to the reference basin, and ANC input was negative. Groundwater inputs were important during 1984−1985, 1986−1987, and 1992−1993, when 10−15% of the Ca and 3−10% of the sulfate was from groundwater. Groundwater inflow, when it occurred, always contributed ANC. For the treatment basin, the total ion input (Table S2) was the sum of contributions from wet precipitation, dry deposition, transfer inflow (TI), and acid additions. Atmospheric inputs were less important for the treatment basin because it receives 5−13% of its water from the reference basin. TI provided ~50% of the K^+ input and 20−35% of the Ca^{2+}, Mg^{2+}, Na^+, and Cl^- inputs to the treatment basin. During years when no acid was added to the treatment basin, TI provided ~15% of the sulfate input. During years in which acid was added, acid additions provided 63−87% of the sulfate to the treatment basin. TI provided only ~1% of NH_4^+ and NO_3^- inputs, most of which came from atmospheric deposition.

Ions were lost from the reference basin by groundwater recharge (GO) and transfer outflow. GO was the only loss term for the treatment basin. On average, ion outputs were higher from the treatment basin than the reference basin (Table S3) because of higher outflow of water from the former basin and higher concentrations of some ions in the treatment basin. The greatest differences were observed for Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-}, the ions that responded most to acidification.

ΔS varied from year to year for all ions, but the net change from 1984 to 1994 (Table S4) confirms observations about the chemistry of the basins (*13*, *15*). For the reference basin, ΔS was near zero for all ions, and average near-surface concentrations for the open-water periods of 1984 and 1994 were the same. For the treatment basin, Ca^{2+}, Mg^{2+}, K^+, and SO_4^{2-} increased, and ANC decreased. No differences were observed between 1984 and 1994 for near-surface, open-water averages of Na^+, Cl^-, NH_4^+, and NO_3^- in the treatment basin.

TABLE 4. 10-Year Average Values for Input, Output, Change in Storage and Reaction Terms in Little Rock Lake Ion Budgets[a]

reference basin	input	output	Δstorage	reaction
Ca^{2+}	12.25	14.69	0.67	3.11
Mg^{2+}	3.76	7.78	−1.21	2.81
K^+	1.02	4.40	−0.73	2.65
Na^+	2.16	2.28	0.51	0.64
NH_4^+	16.47	0.76	0.46	−15.25
SO_4^{2-}	30.65	17.92	1.08	−11.65
Cl^-	2.03	2.73	−0.71	−0.01
NO_3^-	18.98	0.70	0.38	−17.90
Gran ANC[b]	−12.04	6.94	−3.52	15.47
calc ANC[b]	−16.01	8.56	−1.05	23.52

treatment basin	input[c]	output	Δstorage	reaction
Ca^{2+}	15.16	24.07	5.94	14.91
Mg^{2+}	5.16	10.88	2.39	8.11
K^+	2.05	6.27	1.98	6.24
Na^+	2.59	2.48	0.31	0.32
NH_4^+	16.15	1.03	0.58	−15.02
SO_4^{2-}	160.76	39.96	19.59	−50.29
Cl^-	2.64	2.92	−0.72	−0.39
NO_3^-	19.33	0.67	0.60	−17.87
Gran ANC[b]	−140.98	0.53	−7.66	83.21
calc ANC[b]	−141.62	1.18	−8.27	83.09

[a] Positive reaction term: in-lake production; negative value: in-lake consumption. All values in meq m^{-2} yr^{-1}. [b] Gran ANC = sum of measured values (dry fall not included in the inputs); calc ANC = sum of base cations minus sum of acid anions for each budget term. [c] Input includes acid inputs.

Reaction. For each basin, the internal reaction of each ion, *R*, was calculated by mass balance (Table S5). Positive *R* indicates production in the lake (including the sediments), and negative *R* indicates in-lake consumption. To evaluate the importance of budget uncertainties on *R* and select budget components that yield the best estimate of *R*, we calculated *R* for the reference basin using four sets of conditions: (1) I and O for April 1−March 30, dry deposition from regional D:W ratios (*18*), no leaf litter inputs; (2) I and O for May 1−April 30, dry deposition from regional D:W ratios (*18*), no leaf litter inputs; (3) I and O for April 1−March 31, dry deposition from average of measured values ((*20*, *21*) Table 1), no leaf inputs; (4) I and O for April 1−March 31, dry deposition from regional D:W ratios (*18*), leaf litter inputs of base cations included (Table 2).

The following analysis of results from the four sets of input conditions indicates that input set 1 provided the best budget estimates. Table 4 lists 10-year averages of I, O, and *R* for this set. No difference was observed in *R* between input sets 1 and 2, suggesting that small variations in dates for calculation of ΔS did not affect *R*. Calculated *R* values for input set 3 were slightly lower (by ~1 meq m^{-2} yr^{-1}) than those for input set 1, a result of slightly higher *I* values for set 3. Use of regional D:W ratios (set 1) may underestimate dry deposition during drought years because the ratios were developed from data for years with (mostly) normal precipitation. Nevertheless, absent more information for the variable climatic conditions of 1984−1994, we conclude that the regional D:W ratios give a better estimate of dry deposition than the average measured values (input set 2). With input set 4, *R* for Ca^{2+}, Mg^{2+}, and K^+ was shifted from reactive to nonreactive. Although it is possible that these cations behave conserva-

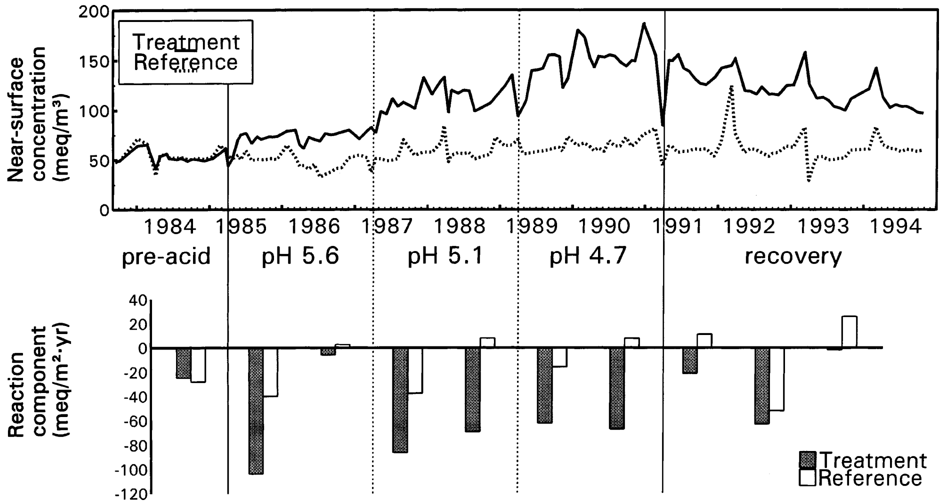

FIGURE 4. Temporal plot of sulfate concentrations in LRL treatment and reference basins with annual reaction terms shown as bars (negative values denote in-lake consumption).

tively, leaf litter inputs are imprecisely known, and evidence from sediment characteristics and porewater profiles suggests they did not behave conservatively (*9*). Moreover, input set 4 does not provide the anions that must have been associated with cations from leaf litter input (because the nature of those anions is unknown). Thus, it provides a lower limit of Ca^{2+}, Mg^{2+}, and K^{+} production and a lower limit of IAG. Based on these considerations, we conclude that input set 1 provides the best estimate of *R*.

R values for the reference basin indicate that small amounts of Ca^{2+}, Mg^{2+}, and K^{+} were produced, and NH_4^{+}, NO_3^{-}, and SO_4^{2-} were removed, for a net production of ANC. Moreover, ANC_{calc}, that is, Σ(base cations) − Σ(acid anions), approximated ANC_{Gran} reasonably well. This suggests that the constituents important in IAG were accounted for by the budgets and that Fe^{2+}, Mn^{2+}, and organic acids were not important. During 1984−1994, SO_4^{2-} removal in the reference basin contributed ~50% of the generated ANC_{calc}. Production of Ca^{2+}, Mg^{2+}, and K^{+} contributed ~14, 13, and 12%, respectively. Although reaction terms for the N ions were more negative than that for SO_4^{2-}, NH_4^{+} loss (ANC consumption) roughly balanced NO_3^{-} loss (ANC production). Consequently, net N transformations provided only ~12% of the generated ANC_{calc}. The small *R* values for Na^{+} and Cl^{-} support the hypothesis that these ions generally behave conservatively in lakes.

R values for the treatment basin were calculated for three sets of input conditions to select the best estimate and likely ranges of *R*: (1) TI based on surface water chemistry of reference basin, dry deposition from regional D:W ratios (*18*), and no leaf litter inputs; (2) TI based on groundwater chemistry, dry deposition from regional D:W ratios, and no leaf litter inputs; (3) same as set 1 except that leaf litter inputs of base cations were included. I and O were calculated for April 1−March 30 based on results for the reference basin; O and ΔS were the same in all three sets.

For most ions, *R* values for input set 2 are similar to those for input set 1. The largest effect of set 2 is to decrease *R* for Ca^{2+} and Mg^{2+} by 4−5 meq m^{-2} yr^{-1}. However, Na^{+} and Cl^{-} behaved less conservatively under these conditions, suggesting that groundwater chemistry is not an accurate reflection of TI chemistry. Also, *R* values for 1984−1985 from input set 1 more closely approximated observed values in the reference basin than do *R* values for input set 2. Regarding input set 3, an evaluation similar to that for reference basin input set 4 is appropriate: it is likely that low pH mobilized Ca^{2+}, Mg^{2+}, and K^{+} from exchange sites resulting in production of these cations. Input set 3 provides a lower limit of production of Ca^{2+}, Mg^{2+}, K^{+}, and IAG. Based on these factors, we conclude that input set 1 provides the best estimates of *R* for the treatment basin.

The 1984−1994 average *R* for ANC_{calc} (Σbase cations − Σacid anions) is close to ANC_{Gran}, supporting the conclusion that the budgets accounted for all important IAG constituents. *R* values indicate that Ca, Mg, and K were produced in the treatment basin and NH_4^{+}, NO_3^{-}, and SO_4^{2-} were removed, with a net result of ANC production (similar to the reference basin). However, because acid additions stimulated sulfate reduction, sulfate removal was more important in the treatment basin. During 1984−1994, SO_4^{2-} removal contributed ~61% of the generated ANC_{calc}, and Ca^{2+}, Mg^{2+}, and K^{+} production contributed ~18, 10, and 8% of the generated ANC_{calc}, respectively. Similar to the reference basin, NH_4^{+} consumption roughly balanced NO_3^{-} consumption, and net N transformations provided only ~3% of the generated ANC. *R* values for Na^{+} and Cl^{-} are small and support the hypothesis that these ions behave conservatively in LRL.

Budgets of Individual Ions and Near-Surface Concentration Trends

Sulfate. Near-surface concentrations of SO_4^{2-} in both LRL basins had a weak seasonal pattern with slightly higher concentrations under ice-cover, possibly from decreased sulfate reduction and increased S oxidation in winter, and lower levels after ice-out, possibly from algal assimilation. Sulfate in the reference basin was ~10 μeq/L higher during 1989−1991 than 1984−1988 and ~5 μeq/L lower in 1992−1994 than in 1989−1991 (Figure 4). The increase during 1989−1991 likely resulted from the drought that lowered the lake level and exposed sediments with reduced S to the atmosphere. High precipitation in 1990−1991 raised the lake level and mobilized reoxidized S into the basin. Others (*27, 28*) have found similar responses in lakes experiencing drought.

Internal reaction (*R*) in the reference basin was slightly positive (indicating internal production) in half the years. Three years with $R_{SO4} > 0$ (1988−1989, 1990−1991 and 1991−1992) might be explained by effects of the dry-wet cycle on SO_4^{2-} inputs from littoral sediments. Lake level declined in 1986−1987 but increased starting in 1988. Omission of reoxidation of sediment S from the mass balance would cause *R* to be underestimated. This might explain why SO_4^{2-} appeared to be produced in the basin during these years. Despite the variability in R_{SO4}, net consumption of SO_4^{2-} occurred in the reference basin during 1984−1994 and maintained concentrations at a near constant level.

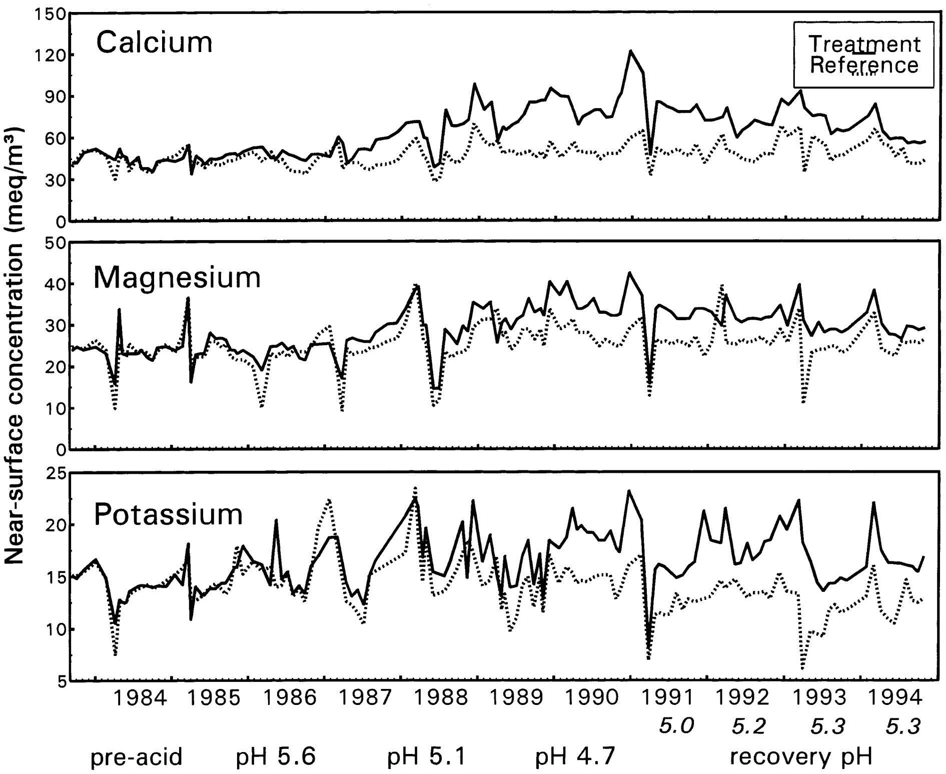

FIGURE 5. Temporal variations in major cations, Ca^{2+}, Mg^{2+}, and K^{+}, in LRL treatment and reference basins, 1984–1994.

Response to sulfuric acid additions in the treatment basin was immediate (Figure 4). Sulfate increased in 1985 (first year of additions) and remained higher than reference basin values through 1994. In 1985, the treatment basin R_{SO4} was $2.5 \times R_{SO4}$ in the reference basin, and SO_4^{2-} was consumed in the treatment basin in all years of the study. Increased SO_4^{2-} consumption in the treatment basin helped neutralize about half the acid inputs. If treatment basin R had not become more negative (but had remained the same as in the reference basin during a given year), $[SO_4^{2-}]$ in the treatment basin in 1991 would have been ~220 meq/m³ rather than the observed 145 meq/m³.

Other Major Ions. Near-surface concentrations of Ca^{2+}, Mg^{2+}, and K^{+} exhibited weak seasonal patterns in both basins. All three cations increased slightly under ice-cover, possibly from decomposition of suspended or sedimented organic matter, and decreased following ice-out, possibly because of algal assimilation (Figure 5). All three cations increased in response to acid additions. Ca^{2+} increased during all three steps of acidification; Mg^{2+} and K^{+} increased at pH 5.1 and 4.7. During recovery, Ca^{2+} and Mg^{2+} steadily decreased but did not return to preacidification levels. K^{+} did not decrease during recovery but remained ~1.3 × reference levels. All three cations were fairly constant with no detectable long-term trends in the reference basin during 1984–1994. For all three cations, the patterns of budget component values were similar except that R was higher in the treatment basin. The greatest increases in treatment basin R corresponded to years with the greatest increases in concentration. For example, Ca^{2+} budgets in the two basins were similar during 1984–1986, when the increase in Ca^{2+} was small, but treatment basin R_{Ca} was larger than that for the reference basin during 1987–1990 when increases in Ca^{2+} were large. During 1991, treatment basin R_{Ca} was large and negative, indicating that Ca^{2+} did not remain in the water column as the pH rose.

Overall, Na^{+} and Cl^{-} behaved conservatively during 1984–1994, and no significant difference was observed between basins. Both ions tended to be slightly higher in the reference basin, possibly because of road salt inputs from a nearby highway. Values for both ions were noisy, reflecting analytical variability at the low concentrations, and R cycled between negative and positive values, probably a result of random uncertainties.

Ammonium and Nitrate. No differences were observed in NO_3^{-} and NH_4^{+} between the basins during the study period (Figure 6). Both ions varied seasonally, a result of plankton assimilation, decomposition, and nitrification, and both increased slightly during 1988–1991 as a result of the drought. Although the budget components varied from year to year, several generalizations can be made. For example, outputs were small compared with other budget components, reflecting low concentrations of the ions. R usually was large and negative, reflecting ion removal from the water column. Although productivity in LRL is limited by phosphorus, the large negative R values suggest that LRL is not saturated with N, a fate predicted for lakes receiving higher N inputs (*29*).

Acid Neutralizing Capacity. As a result of seasonal cycles in the ions affecting IAG, ANC had a slight seasonal pattern in both basins (Figure 7). All ions involved in IAG increased slightly under ice-cover, but the sum of the increase in Ca^{2+}, Mg^{2+}, K^{+}, and NH_4^{+} exceeded the sum of the increase in SO_4^{2-} and NO_3^{-}. Consequently, ANC increased slightly before ice-out in both basins. For similar reasons ANC declined slightly following ice-out. Reference basin ANC was ~10 μeq/L lower during 1989–1991 than during 1984–1988, possibly because of an increase in SO_4^{2-} during the drought. ANC increased by ~5 μeq/L in 1992–1994 but did not reach 1984–1988 levels. ANC in the treatment basin decreased as acid was added and approached zero at pH 5.1. It increased steadily during recovery but remained negative through 1993 and below reference basin values through 1994.

ANC inputs to both basins were negative in all years, reflecting the acidity of regional precipitation. In most years, R_{ANC} in the reference basin was mostly composed of R_{SO4} and R_{Ca}, but in 1990–1991 R_{SO4} was minor (possibly reflecting unmeasured sulfate inputs), and ~50% of the ANC produced was from NO_3^{-} consumption. R_{ANC} in the treatment basin was always positive; from 1985 forward, it was larger than

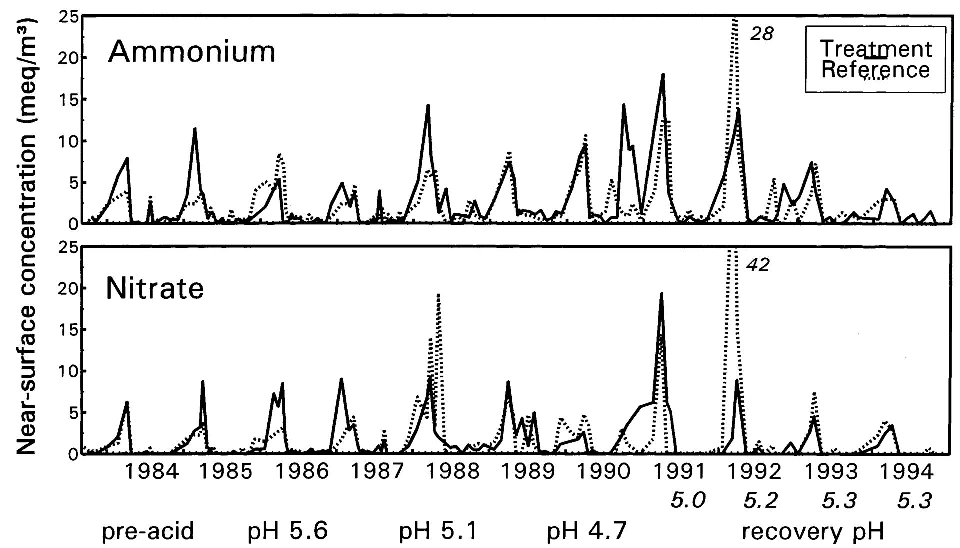

FIGURE 6. Temporal trends in nitrate and ammonium concentrations in LRL treatment and reference basins, 1984−1994.

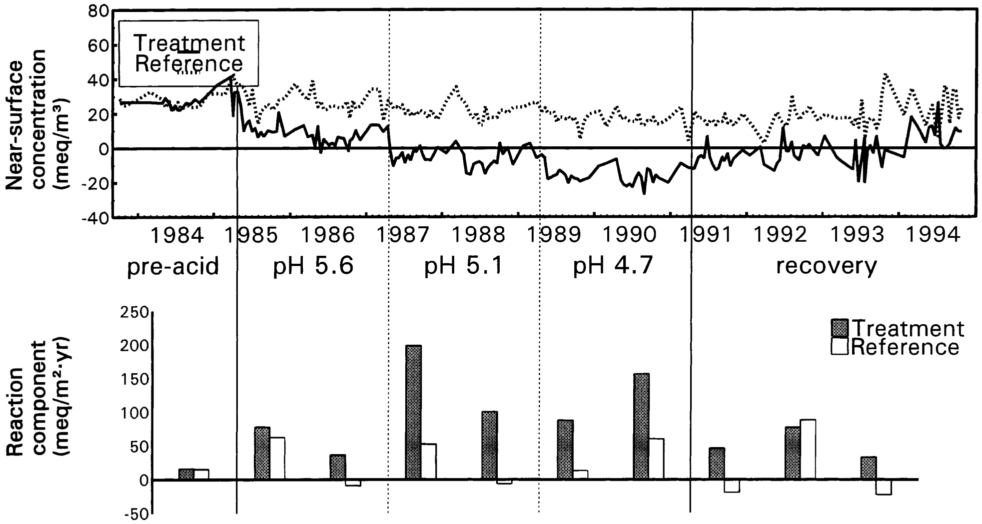

FIGURE 7. Measured acid neutralizing capacity (ANC) in treatment and reference basins with annual reaction terms shown as bars (positive values denote in-lake production).

that of the reference basin, because added H_2SO_4 stimulated sulfate reduction. Treatment basin R_{ANC} was highest at pH 5.1 and 4.7 (3.7−8.5 × the reference basin 10-year average). Treatment basin R terms decreased during recovery but remained ~2× reference basin values. Treatment basin R_{ANC} was driven by R_{Ca} and R_{SO4} (as in the reference basin), but NO_3^- removal was the primary source in 1991−1992, contributing > 50% of the generated ANC.

Discussion

Mass balances help assess the sources and fates of major ions, nutrients, and metals, all of which may influence the ability of aquatic systems to neutralize acid inputs. Most ion budget components for LRL, including calculated internal reaction terms, showed fairly large interannual variations; e.g., inputs (dominated by atmospheric deposition) varied by a factor of about two, and ΔS varied from positive to negative depending on climatic conditions. The length of the study period for the LRL budgets helps greatly in smoothing out year-to-year variability (noise) from climatic variations and analytical uncertainties. Over the 10-year period, ANC terms calculated from the budgets as the difference between base cation and acid anion terms agreed well with measured ANC terms for the budget components, indicating that the budgets accounted for all important IAG constituents.

The concept of IAG was developed largely based on lake and watershed mass balance studies (e.g., refs *2−4, 7, 30−32*). Because SO_x deposition was the most important agent of acidification, most mass balance studies have focused on SO_4^{2-}. Internal reaction for sulfate (R_{SO4}) from other mass balances (Table 5) range from +30 to −246 meq m^{-2} yr^{-1}. Positive values indicate release of SO_4^{2-} into the lake water (e.g., via sulfide oxidation); negative values indicate SO_4^{2-} consumption (removal from lake water). This process contributed as much as 300% of IAG, sometimes more than compensating for cation losses. The average R_{SO4} for non-experimentally acidified North American lakes is −35 meq m^{-2} yr^{-1}, representing ~50−60% of IAG. Cation production usually contributed most of the rest, but in some lakes NO_3^- removal contributed up to 33%. R_{SO4} for experimentally acidified lakes is much more negative, ca. −240 meq m^{-2} yr^{-1}.

Detailed annual budgets of the ions involved in IAG are rare. Most published budgets report averages for several years or values only for SO_4^{2-}, Ca^{2+}, and ANC. Budgets for three lakes are relevant to this study: Vandercook Lake (*7, 30*), a seepage lake near LRL, provides a comparison for the

TABLE 5. Summary of In-Lake Sulfate Reduction Rates and Contributions to IAG

lake	location	time	rate^a	% of IAG	notes	reference
Vandercook	NC Wisconsin	1981–1983	−18	54	groundwater inflow	(*7*)
		1984–1987	−15	32	intermittent inflow	(*30*)
		1987–1989	−40	156	no groundwater inflow	(*30*)
Lake 223	ELA, Ontario	1976–1983	−246	85	acidified with H_2SO_4	(*3*)
Lake 302S	ELA, Ontario	1980–1981	−117	300	preacidification, pH 6.6	(*31*)
		1982–1988	−242	61	acidified with H_2SO_4	
		1989–1991	+30		pH held at 4.5–4.6	
Lake 302N	ELA, Ontario	1982–1986	−50	16	acidified with HNO_3	(*32*)
Lake 239	ELA, Ontario	1981–1983	−39	53		(*4*)
McCloud	NC Florida	1981–1982	−28	57		(*33*)
Langtjern	S Norway	1974–1980	−57			(*34*)
Piburger	Austria	1975–1985	−234	20		(*35*)
8 lakes	Dorset, Ontario	1980–1992	0 to −54	0–33		(*36*)

[a] Values in meq m^{-2} yr^{-1}; loss (reduction) indicated by negative sign.

TABLE 6. Summary of Internal Reaction Terms Determined by Ion Budgets for Two Lakes[a]

	Vandercook Lake			ELA Lake 223		
	1981–1983	1984–1987	1987–1989	1977–1978	1979–1980	1981–1983
Ca^{2+}	27.1	−24.9	−2.5	63.3	−18.0	75.9
Mg^{2+}	20.0	−1.8	−9.1	−0.6	−38.7	−37.4
K^+	3.5	−3.2	−3.6	2.4	−8.6	−12.5
Na^+	1.2	−9.6	−2.1	25.3	−18.2	−9.7
NH_4^+	−20.6	−33.0	−19.7	−7.9	−19.8	−19.9
SO_4^{2-}	−18.0	−15.1	−40.0	−197.8	−154.9	−368.8
Cl^-	2.7	−1.0	−4.0	−18.7	−1.8	−11.5
NO_3^-	−25.8	−24.2	−18.7	−11.7	−19.8	−19.1
measd ANC	33.2	−11.1	17.1	144–385	307	364
calc ANC	72.3	−32.2	25.7	311	73	396
reference	(*7*)	(*30*)	(*30*)	(*3*)	(*3*)	(*3*)

[a] Values in meq m^{-2} yr^{-1}; measured ANC is by Gran titration; calculated ANC is by ion balance (3 base cations − 3 acid anions).

reference basin; ELA Lakes 223 and 302S, drainage lakes experimentally acidified with H_2SO_4, provide comparisons for the treatment basin.

Vandercook Lake and LRL are similar in hydrology and depth, but the former is larger in area. Sulfate levels were higher in Vandercook than in the LRL reference basin (82 versus ~55 μeq/L), but internal sulfate losses were similar in the lakes (Tables 4 and 6) for the same time periods. Data from postdrought years are not available for Vandercook that might support the idea that sulfur from exposed lake sediments was reintroduced to LRL during this period. R for Ca^{2+}, Mg^{2+}, and K^+ varied widely between the two Vandercook studies. Ca^{2+} production occurred in 1981–1983 (*7*), but an equal amount of Ca^{2+} consumption was found in 1984–1986 (*30*). The LRL reference basin had less Ca^{2+} consumption in 1984–1986. Values of R_{NO3} and R_{NH4} were similar for Vandercook and LRL, and losses of the ions roughly balanced each other. Na^+ and Cl^- were slightly more reactive in Vandercook than in LRL, but both lakes had similar year-to-year variability.

LRL differs in size and hydrology from Lake 223, which receives ~40% of its water from streamflow and ~20% from runoff and is larger and deeper than LRL (*8*). The initial pH and ANC of L223 (6.6 and 101–154 μeq/L) also were higher than corresponding LRL values. Lake 302S (*31*, *32*) is deeper and slightly larger than the LRL treatment basin. L302S received ~24% of its water from runoff and inflow from ephemeral streams and 76% from precipitation to its surface. Both L223 and L302S are dominated geologically by Precambrian Shield granodiorite overlain by shallow soils (sand and gravel < 1 m deep or peat < 20 cm deep). Background ANC in L302S was ~2.5× that of LRL and its background pH was 6.6–6.7.

Sulfuric acid additions to L223 started in 1976. ANC (but not pH) decreased during year 1, but thereafter (until 1983) acid additions decreased the pH gradually to 5.13. After 1984, acid additions were decreased, and pH increased to 6.6 by 1995. Although LRL and L223 have many differences, the manipulations were similar in sulfate loadings (3–4 × the input from atmospheric deposition and other hydrologic inflows). Although L223 has a 135 ha watershed, it contributes little ANC to the lake (~5% of IAG), reflecting the regional geology. Sulfate reduction accounted for ~85% of the IAG, and cation production contributed ~10%. IAG neutralized ~66–81% of the added acid (*3*).

Ion budgets for L223 are summarized (Table 6) for periods with pH values similar to the background period and first two target pH values for LRL. Although similar pH values were achieved by acid additions, sulfate concentrations were higher in L223, and R_{SO4} thus was more negative in L223. Rates of sulfate reduction generally are first order in $[SO_4^{2-}]$ (*8*). The average $[SO_4^{2-}]$ in L223 at pH 5.1 was 250 μeq/L, and R_{SO4} was −370 meq m^{-2} yr^{-1}. In LRL at pH 5.1, the average $[SO_4^{2-}]$ was ~105 μeq/L and R_{SO4} was −78 meq m^{-2} yr^{-1}. Nonetheless, trends were similar in both lakes (R_{SO4} became more negative as pH decreased and $[SO_4^{2-}]$ increased). Reaction terms for Ca^{2+} varied widely among the three periods, but at pH 5.1 R_{Ca} in L223 (76 meq m^{-2} yr^{-1}) was similar to that in LRL (50 meq m^{-2} yr^{-1}). In contrast to LRL, where Mg^{2+} and K^+ together provided ~17% of IAG, Mg was consumed in L223, and K had a net loss during 1977–1983. Na was more reactive in L223 than in LRL but overall was conservative during 1977–1983. Chloride consumption provided ~4% of the IAG in L223, but this value is probably within the limits of experimental error. No evidence exists for nonconservative behavior of Cl^- in lakes. R_{NO3} and R_{NH4} for L223 were similar to values for LRL, and losses of the N ions roughly balanced each other.

Beginning in 1982, acid additions to L302S decreased the pH by ~0.3 per year (to pH 4.8 in 1987). The lake was held at pH 4.5–4.6 during 1988–1991. During 1982–1991, sulfate from acid additions was 4.2 × the inputs from atmospheric deposition and runoff. Beginning in 1992, acid additions were decreased, and pH increased to 5.1 in 1992–1993 and 5.8 in 1994–1997. Contributions of all ions to IAG have not been published for L302S, but values for SO_4^{2-} and Ca^{2+} in 1982–1986 (*32*) are similar to those for LRL. SO_4^{2-} reduction provided 56% of IAG and Ca^{2+} production yielded 28%.

Ion budgets indicate that the S and N cycles were altered at low pH in L302S. The S cycle may have been altered by an extended period at pH 4.5–4.6 (*31*). During 1980–1987 (pH ≥4.8), R_{SO4} became more negative (from −90 to −265 meq m^{-2} yr^{-1} as acid additions increased $[SO_4^{2-}]$ from 60 to

224 μeq/L, but during 1988−1991 (pH 4.5−4.6) and 1992 (first year of recovery, pH < 5.1) when [SO_4^{2-}] was 260−410 μeq/L, R_{SO4} varied from −407 to +174 meq m^{-2} yr^{-1} (net oxidation). The years with net S oxidation were attributed to under-ice accumulation of SO_4^{2-} from increased oxidation of reduced S (*31*). In turn, this was attributed to changes near the sediment−water interface from autumnal decomposition of filamentous algal mats, which shifted the zone of SO_4^{2-} reduction from below the interface to above the interface (within the decomposing mat). Sulfate also accumulated under the ice in LRL, but there was no increase in accumulation at pH 4.7. Some differences were observed in sediment pore-water profiles of sulfate between sites with an algal mat and those not covered (*37*), but net S oxidation was not observed in the treatment basin during 1984−1994.

Although increased under-ice accumulation of SO_4^{2-} is apparent in L302S during 1989−1991, the manner in which ΔS was calculated may have affected the values of R_{SO4}. Kelly et al. (*31*, *32*) calculated ΔS_{SO4} for 1990 by subtracting the 1989 mean annual mass of SO_4^{2-} from the 1990 mean annual mass. This may diminish errors from analytical measurements but introduces uncertainty by essentially offsetting ΔS from the other budget components by 6 months. For example, from a figure in Kelly et al. (*31*) we estimated $\Delta S_{SO4} = -15$ keq for calendar year 1990, which results in $R_{SO4} = -260$ meq m^{-2} yr^{-1}. In contrast, Kelly et al. (*31*) reported $\Delta S_{SO4} = +14$ keq, resulting in $R_{SO4} = 0.9$ meq m^{-2} yr^{-1} for 1990. Large differences thus may arise between the methods of calculation.

A pH of ∼5.3 seems to mark changes in the N cycle of L302S. Above this pH, R_{NH4} was negative, but at pH < 5.3 NH_4^+ production increased steadily, probably because inhibition of nitrification was observed at pH < 5.7 (*38*). If R_{NO3} remained the 1982−1986 average (−18 meq m^2 yr^{-1} (*32*)), the higher NH_4^+ production increased the importance of N transformations in IAG. Ca^{2+} and Mg^{2+} were consumed in L302S prior to acidification, but large rates of production began during the first year of acid addition (as in LRL). In contrast, inhibition of nitrification was not observed in LRL (*39*), and there were no apparent effects of acidification on NO_3^- and NH_4^+ budgets down to pH 4.7.

Supporting Information Available

Water budgets for treatment and reference basins of Little Rock Lake (Table S1), total ion inputs to (Table S2) and total ion outputs from (Table S3) reference and treatment basins of Little Rock Lake, annual change in storage in reference and treatment basins of Little Rock Lake (Table S4), and reaction terms for reference and treatments basins of Little Rock Lake (Table S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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