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Acidification and alkalinization of lakes by experimental addition of nitrogen compounds

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Abstract. Fertilization of a small lake with ammonium chloride for four years as part of a eutrophication experiment caused it to acidify to pH values as low as 4.6. Implications for acidification of lakes via precipitation polluted with ammonium compounds are discussed.

When phosphate was supplied with the ammonium, biological nitrogen uptake, apparently by phytoplankton, was the main mechanism causing acidification. When ammonium was applied without phosphate, it accumulated to high concentrations in solution, after which nitrification caused rapid acidification. In both cases, the whole-lake efficiency of acidification was low, averaging about 13% of the potential acidification of supplied ammonium chloride (Table 2).

Subsequent application of phosphate plus sodium nitrate for two years caused the pH of the lake to increase. The efficiency of alkalinization was higher than for acidification, averaging 69% of the potential alkalinization of the supplied sodium nitrate.

Introduction

Acidification of lakes is usually regarded as the result of inputs of the strong acids, HNO_3 and H_2SO_4. Yet some ecologists believe that acidification is more strongly correlated with total sulfate deposition than with strong acid inputs (Almer et al., 1978; NRCC, 1981; MOI, 1983), despite the fact that in the atmosphere much of the sulfate is bound to ammonium, which atmospheric scientists regard as a neutral species (EPA, 1983).

Evidence from fertilization in agriculture and forestry suggests that compounds of ammonium in combination with a more biologically-conservative anion are not neutral in the biosphere. Indeed, the acidification of soils fertilized with ammonium compounds has been known for some time (Russell, 1961). Similar reactions occur in algal chemostats (Goldman and Brewer, 1980), and increased alkalinity has been shown to accompany fertilization of lakes with nitrate plus phosphate (Kelly et al., 1982). From studies of streams and their watersheds, we know that inorganic nitrogen is strongly retained by forests. In the Precambrian Shield, retention of ammonium and nitrate are usually almost equal (Schindler et al., 1976, 1980a and unpublished data) while in areas subjected to anthropogenic acidification ammonium is usually more strongly retained than nitrate (Likens et al., 1977;

Galloway et al., 1983). This biological nutrient uptake would be expected to alter the acid-base balance of soils or waters, i.e. alkalinity would be generated or consumed. The amount and the direction of change depend on the charge of nutrients, their transformation in the environment, rates of uptake, and whether any resulting organic matter is decomposed or permanently deposited in soils and sediments. In general, oxidation reactions are net consumers of alkalinity, while reduction is an alkalinity producer. Examples of pertinent biogeochemical reactions for aquatic systems are given by NRCC (1981), Kelly et al. (1982) and Schindler (1984).

To date, no study has examined the potential role of ammonium compounds in lake acidification, even though ammonium is typically the second most important cation in precipitation, constituting between 12 and 25% of all protolytic cations according to U.S. National Atmospheric Deposition Project (NADP) and Canadian Atmospheric Network for Sampling Acid Deposition (CANSAP) reports. It therefore seemed worthwhile re-examining an earlier experiment performed at the Experimental Lakes Area (ELA), where acidity increased when ammonium chloride was added to a small lake.

Lake 304 was fertilized in the early and mid 1970's as part of an experimental study of eutrophication (Schindler and Fee, 1974; Schindler, 1975). Three fertilization regimes were used for periods of two years each (Table 1). During the first two periods, ammonium chloride was used as a nitrogen source. In the final period, sodium nitrate was used instead. Prior to fertilization, the pH of the epilimnion in Lake 304 was maximum in summer, as expected for lakes in the area, due to photosynthetic activity (Schindler, unpublished data). In contrast, the annual pH pattern was reversed during fertilization with ammonium chloride (1971–1974), with pH minima occurring in late summer (Figure 1). During 1975–1976, when sodium nitrate was used as a nitrogen source, pH maxima were again recorded in summer, but of much greater magnitude than observed in natural lakes. As a result, we decided to examine the effects of nitrogen inputs on the acid-base balance of Lake 304. This was most easily expressed as an alkalinity budget for the lake.

To understand what follows, several definitions must be kept in mind. Firstly, alkalinity consumption may be regarded as synonymous with acidification (H^+ generation).

The significant ionic contributors to alkalinity in freshwater at ELA may be described simply as the difference between nonprotolytic cations and anions, assuming that conditions of electroneutrality are maintained:

$$\mathrm{Alk} = \mathrm{Ca}^{+2} + \mathrm{Mg}^{+2} + \mathrm{Na}^{+} + \mathrm{K}^{+} + \mathrm{NH}_4^{+} - \mathrm{SO}_4^{-2} - \mathrm{Cl}^{-} - \mathrm{NO}_3^{-} - \mathrm{A}^{-} \tag{1}$$

where A^- represents organic anions.

An alternative, equivalent expression for alkalinity is:

$$\mathrm{Alk} = \mathrm{HCO}_3^{-} + \mathrm{CO}_3^{=} + \mathrm{CO}_3^{-} + \mathrm{OH}^{-} + \mathrm{A}^{-} - \mathrm{H}^{+} \tag{2}$$

If biological uptake (Equation (3)) or oxidation to nitrate (Equation (4))

Table 1. Fertilization schedule for Lake 304. All additions were made as 20 to 21 weekly additions between mid May and mid October

Year	Treatment	Nitrogen, kg yr^{-1}	Sucrose, kg C yr^{-1}	Phosphoric acid, 85%, kg P yr^{-1}
1971	H_3PO_4 + NH_4Cl + sucrose	187 as NH_4	200	16.9
1972		178 as NH_4	191	16.1
1973	NH_4Cl + sucrose	187 as NH_4	200	0
1974		188 as NH_4	200	0
1975	H_3PO_4 + $NaNO_3$	524 as NO_3	–	43.0
1976		524 as NO_3	–	43.0

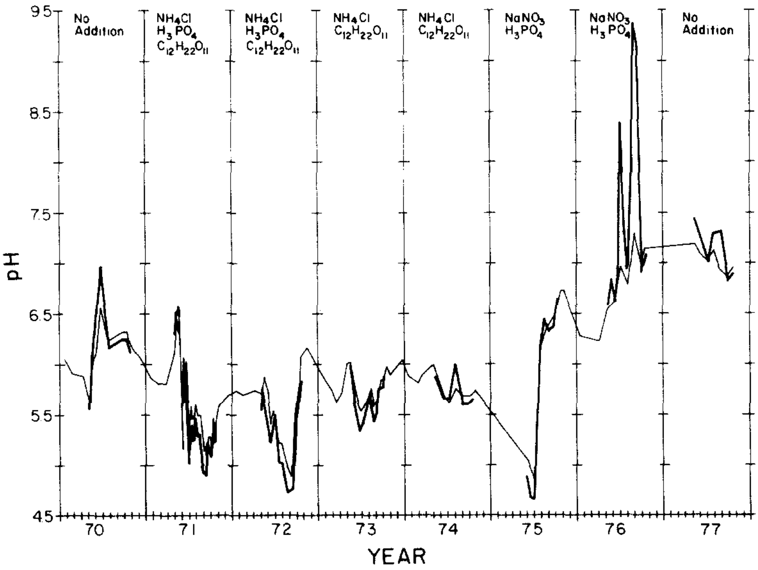

Figure 1. Changes in hydrogen ion concentration of Lake 304. Values given are whole lake averages (thin line) and epilimnion averages (thick line). Compounds added to the lake in each year are indicated at the top of each panel.

of the ammonium compounds in 1971–1974 was complete and permanent, considerable alkalinity would be consumed by alteration of the balance between nonprotolytic cations and anions or generation of hydrogen ion:

$$106CO_2 + 106H_2O + 16NH_4^+ \rightarrow (CH_2O)_{106}(NH_3)_{16} + 16H^+ + 106O_2 \qquad (3)$$

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad (4)$$

On the other hand, permanent uptake (5a) or denitrification of nitrate (5b) in 1975–76 would be expected to generate alkalinity or consume H^+.

$$106CO_2 + 138H_2O + 16NO_3^- \rightarrow (CH_2O)_{106}(NH_3)_{16} + 16OH^- + 138O_2 \qquad (5a)$$

$$24NO_3^- + 5C_6H_{12}O_6 + 24H^+ \rightarrow 30CO_2 + 12N_2 + 42H_2O \qquad (5b)$$

While complete ionic balances for Lake 304 were not done in all years, enough information was available to examine the changes in alkalinity of the lake due to the above additions.

Description of the lake

The surface area of Lake 304 is 3.62 ha. The mean depth is 3.2 m, the maximum depth 6.7 m. The lake is usually dimictic, with a thermocline at 2–8 m from May through early September, and an anoxic hypolimnion during much of that period. The lake was surrounded by virgin forests of Pinus banksiana and Picea mariana throughout the experimental period. The geology of the basin is Precambrian gneisses, covered by a thin (0–30 cm) mat of mosses, lichens and decaying organic matter. There are shallow, isolated pockets of non-calcareous till. Small acidic bogs occur at the western and northwestern corners of the lake. Brunskill and Schindler (1971) give a complete morphometric map of the lake and more detailed geological information.

Materials and methods

Some background chemical data were collected in the summers of 1968 and 1969, and a complete year of background data was collected in 1970. In 1971–74, fertilizer additions described in Table 1 were made weekly from mid May until early October, by flooding an outboard-powered boat with lake water, dissolving the weekly aliquot of fertilizer, then criss-crossing the lake while allowing the solution to discharge through the drain-cock at the back of the craft. In 1975–76, the weekly fertilizer addition was dissolved in two 200 L polyethylene barrels on a rock-ledge at the lake shore, then allowed to drip into the surface water of the lake over a period of 3–5 days. On each sampling date, the lake was sampled at 7 or 8 depths in 1970–74, and at five depths in 1975–76.

The methods of Stainton et al. (1977) were used for chemical analysis. Dissolved nitrogen, phosphorus and carbon species were analyzed within a few hours after collection.

Lake level was monitored continuously during the period. Outflow was estimated from change in lake level, which was continuously recorded from 1969 onward, plus evaporation rates measured on nearby lakes. From calibrations done on other lakes in the area, such estimated water budgets are known to be within 5% of values measured with a v-notch weir (R. W. Newbury and K. G. Beaty, unpublished data). Amounts of various chemical elements leaving via the outflow were estimated from weekly chemical analyses of the epilimnion and weekly outflow volumes estimated as above. Water renewal times for the lake were 1.1 to 2.3 yr during the period of study.

Because the experiment was not designed for the purpose that we use it here, the alkalinity data have some shortcomings. Alkalinity was not measured by direct titration. It was therefore estimated by calculating bicarbonate concentration from measured hydrogen ion concentrations (Moles/L), temperature (°C) and dissolved inorganic carbon (Moles/L):

$$[\mathrm{HCO_3^-}] = \frac{[\mathrm{H^+}]\mathrm{K_1}[\mathrm{DIC}]}{[\mathrm{H^+}]^2 + [\mathrm{H^+}]\mathrm{K_1} + \mathrm{K_1}, \mathrm{K_2}}, \tag{6}$$

where $\mathrm{K_1} = 10^{-(6.57-(0.00926\,T))}$ and $\mathrm{K_2} = 10^{-(10.614-(0.0117\,T))}$ (Stainton et al., 1977), and

$$\mathrm{AlK} = [\mathrm{HCO_3^-}] - [\mathrm{H^+}] + [\mathrm{OH^-}] + [\mathrm{CO_3^{2-}}] \tag{6a}$$

This technique ignores protolytic organic ions, and is now known to underestimate alkalinity slightly (Herczeg and Hesslein, 1984). However, the degree to which organic contributors to alkalinity change as the result of acidification is not known at present, and in what follows, alkalinity is calculated from Equation (6a).

Sucrose was added to the lake weekly as part of the fertilization regime in 1971–74. This was decomposed within hours (Thompson and Hamilton, 1972), adding approximately $12\,\mu\mathrm{M\,L^{-1}}$ of CO_2 to the epilimnion every week. Lakes the size of Lake 304 in the area have mass transfer coefficients averaging 0.5 m per day (Emerson, 1975). Once steady-state with this CO_2 generation had been reached (about 3 weeks), the lake should have been about 20% oversaturated with CO_2 with respect to the atmosphere when sampled, because chemical sampling was done weekly 7 days after fertilization (just before the next fertilization). This supersaturation would depress pH slightly. In 1971 and 1972, when phosphate was added, algal blooms might also have caused undersaturation. While these problems could cause slight distortions of seasonal values shown in the figures, their effect on annual calculations should be negligible because of the choice of May dates, when problems would be minimal, for budget calculations.

Total budgets for all significant cations and anions would be necessary to tell whether exchange of H^+ for base cations in sediments or permanent sedimentation of anions other than nitrate was responsible for the generation or consumption of alkalinity as expressed in Equation (1). Not all major ions were measured during all of the years of study, so that a detailed analysis of ions responsible for the changes in alkalinity is not possible. Efficiencies reported here therefore assume that all alkalinity changes are due directly or indirectly to our fertilization. The effects of changes in other ions on alkalinity are discussed by Schindler and Turner, 1982 and Cook et al., 1985.

Annual alkalinity budgets for the entire lake were calculated from early May of one year to early May of the next, beginning just before fertilization began each year. This period of calculation thus includes an entire annual cycle of loss via outflow and permanent sedimentation, as well as the annual cycle of production and decomposition both above and below the compensation depth. It also minimizes the effect of seasonal P_{CO_2} changes on our calculated budgets. The chemistry of direct runoff and precipitation during the year were assumed to be similar to those observed for the Northwest Subbasin at Rawson Lake (Schindler et al., 1976, 1980a and unpublished data). In that case, alkalinity as measured by Gran titration was almost exactly zero. As a result, only nitrogen species were assumed to affect alkalinity, so that potential alkalinity production (A_p) is assumed to equal the difference between inputs and outputs of four ions which were added, measured or calculated regularly:

$$(A_p) = HCO_{3r}^- + NO_{3r}^- - NH_{4r}^+ - H_r^+ \tag{7}$$

where each of the terms on the right hand side of the equation represents net retention of the ion, i.e. input-output. This calculation could then be compared to the actual alkalinity change in the lake during the year.

Similar calculations were done for the 0 to 3 m stratum of the lake during the period May through August. This calculation provides a maximum efficiency of alkalinity generation or consumption, because it does not include the return of NH_4^+ from decomposition, which occurs below this stratum.

The input of ammonium from the watershed and precipitation is almost exactly balanced by inputs of nitrate from the same sources (Schindler et al., 1976 and Table 2, 1970–71). Both are almost completely utilized, so that under natural conditions the net effect of nitrogen input on alkalinity is negligible. As mentioned earlier, the input of alkalinity from precipitation and runoff was insignificant. As a result, the only input affecting alkalinity should have been our fertilizer. Therefore, if nitrate in the lake increased during the period of fertilization with ammonium, it was assumed to be from nitrification of ammonium (Equation (4)), yielding two hydrogen ions for each missing ion of ammonium. The remainder of the missing ammonium was assumed to have been removed by biological uptake (Equation (3)). Biological consumption of any added phosphate would not normally be expected to generate alkalinity, because fertilizer was added as H_3PO_4, and was completely utilized. Phosphate input from natural sources is too low to significantly affect budgets (D. W. Schindler, unpublished data). The overall efficiency of ammonium additions (in consuming alkalinity, E_a) was thus assumed to be:

$$E_a = \frac{\Delta HCO_3^- - \Delta H^+}{\Delta Cl^-} \tag{8}$$

when all factors on the right hand side are based on actual measurements in equivalents, except for HCO_3^-, which was calculated from Equation (6) where ΔCl^- is assumed to be an estimate of the input of NH_4^+, which is possible because Cl^- is unreactive.

Conversely, in 1975–6, when $NaNO_3$ was added to the lake, the efficiency of nitrate additions in generating alkalinity, E_n was:

$$E_n = \frac{\Delta HCO_3^- - \Delta H^+ + \Delta OH^- + \Delta CO_3^{2-}}{\Delta Na^+}, \tag{9}$$

where Na^+ is again assumed to be biologically inert. The terms ΔOH^- and ΔCO_3^{2-} are negligible below pH 8.

Occasional measurements of nitrite (NO_2) indicated that it was insignificant ($< 3\,\mu g\,N\,L^{-1}$). Other nitrogen 'intermediates' are even less common in ELA Lakes (Chan and Campbell, 1980).

In order to check the relative importance of other factors which could potentially affect the alkalinity budget, a simple box model was developed to calculate changes in the lake's alkalinity at the frequency of actual measurement, based solely on observed data for input of nitrogen species. While such a model would not be expected to reproduce exact alkalinities because of the absence of data for such potential alkalinity producers and consumers as cation exchange and sulfate reduction, the model should reproduce the major features of observed alkalinity changes, if the oxidation and reduction of nitrogen were the major reactions controlling alkalinity. Model inputs were:

$$Alk_{t+\Delta t} = Alk_t + Alk_{net} - NH_{4\,net}^+ + NO_{3\,net}^- + \Delta NH_4^+ - \Delta NO_3^-, \tag{10}$$

where Alk_t was $HCO_3^- - H^+$ at time t, the subscript 'net' represents inflow-outflow, and ΔNH_4^+ and ΔNO_3^- are the changes in mass during the period Δt. This calculation is analogous to that outlined for annual budgets above.

The model was initialized by using the January, 1971 measured alkalinity in the lake as an initial Alk_t value. Inputs were set equal to zero, based on data from the Northwest Subbasin. Linear interpolation and integration were used where necessary to match times scales for the various data. In general, inflow concentrations were measured weekly, outflow concentrations monthly, lake masses weekly to monthly during the ice-free season and monthly to bimonthly under ice.

Results

Changes in pH

In 1970, prior to fertilization, maximum epilimnion pH values were 6.95 in June (Figure 1). Minimum pH values occurred late under winter ice, when pCO_2 was supersaturated with respect to the atmosphere. The lowest pH values observed in 1970 and 1971 were 5.55 and 5.75, respectively.

In contrast, when ammonium chloride and phosphate were added, in the summers of 1971 and 1972, pH decreased from June through late summer (Figure 1). Lowest epilimnion values in 1971 were 4.9 in late August. In late August of 1972, the epilimnion pH decreased to 4.75. In both years, pH returned to near-normal values during late fall and winter.

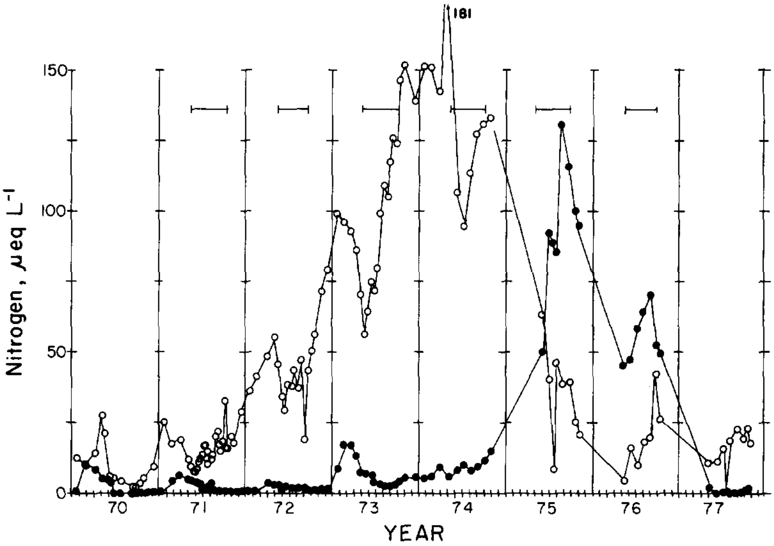

Figure 2. The concentrations of nitrate and ammonium in Lake 304. Data are whole lake averages. Bars at the top of 1971 to 1976 panels indicate periods of the year when fertilizer was added. ● = NO_3^- – N; ○ = NH_4^+ – N.

In 1973 and 1974, when ammonium chloride was added without phosphorus, there was little variation in pH. Neither midsummer maxima, as observed under natural conditions, nor minima as observed under $NH_4^+ + PO_4$ fertilization occurred. In 1973, the range of pH was only from 5.35 to 6.0; in 1974 from 5.5 to 6.0.

The largest overwinter pH decline occurred in 1974–75, with a springtime pH of 4.60. Reasons for this will be discussed later.

The change from ammonium to nitrate fertilizer was made in May, 1975. By early July, the pH began to increase rapidly. A mid-autumn pH maximum of 6.7 was observed in 1975. In 1976, pH values continued to increase, exceeding 9.0 in the epilimnion during August. In 1977, when no fertilizers were added, relatively stable pH values of 6.8–7.4 were measured. These pH values and alkalinities were slightly higher than those recorded prior to fertilization, presumably because of delays in reaching equilibrium due to water renewal and sediment water exchange.

Changes in nitrogen species

The increase in ammonium in the lake in 1971–72 occurred primarily in the hypolimnion (Figure 2), undoubtedly as the result of increased sedimentation and decomposition of plankton. NH_4^+ accumulated in 1973 and 1974, including considerable increases in the epilimnion. The drastic decline in ammonium during the late winter of 1974–75, prior to the onset of nitrate addition, was accompanied by an almost equal increase in nitrate. Additions of nitrate during the period could only account for 10% of the observed increase, indicating that nitrification had taken place. A similar, but smaller

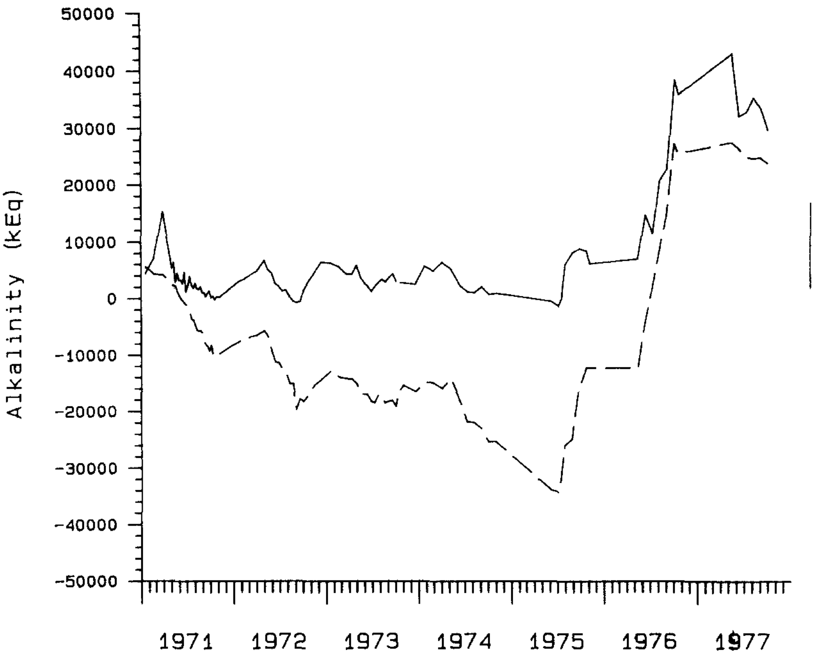

Figure 3. Alkalinity calculated from the net inputs of ammonium and nitrate (Equation (10) and alkalinity measured in Lake 304. — — — model alkalinity; ——— observed $HCO_3^- - H^+$.

nitrate peak accompanied the decline in ammonium during the winter of 1972–73. From May, 1975 onward ammonium decreased, with near-normal annual cycles occurring in 1976 and 1977. Nitrate increases were noted in the summers of both 1975 and 1976, due to high rates of nitrate fertilization. In 1977, after fertilization had ceased, near-background values of both nitrogen species were observed.

Changes in alkalinity

Bicarbonate data for Lake 304 for 1970–71, the year prior to fertilization, indicated an internal alkalinity generation rate of 0.15 eq m^{-2} yr^{-1} by transfer of protons to the sediments. This value is similar to the results of a detailed three-year study of alkalinity done by Gran titration in Lake 239, where an average alkalinity generation of 0.16 eq m^{-2} yr^{-1} from sediments was observed (Schindler, Turner and Linsey, unpublished data). *In situ* anion reduction and cation exchange appear to be the dominant sources of alkalinity production in unperturbed ELA lakes.

As expected, alkalinity decreased markedly after ammonium addition, during the periods when pH declined (Figure 3). During 1975–76 and 1976–77, when phosphate plus nitrate were added, there was clearly net alkalinity production in the lake (Figure 3 and Table 2). In 1975, much of the generated alkalinity was used in neutralizing the acidity generated by uptake of remaining ammonium in the lake. In 1976, the observed alkalinity increase was nearly equal to the total alkalinization potential of nitrate inputs for that year. The alkalinity of the lake remained high in 1977, even though no nutrients were added (Figure 3).

The simple mass balance model predicting the response of the lake to NH_4Cl and $NaNO_3$ additions matched the observed variations in alkalinity remarkably well, indicating that the changes in alkalinity were caused by our fertilization. (Figure 3). The absolute value of the predicted alkalinity value was consistently lower than the observed, simply indicating the continued alkalinity input of unmeasured *in situ* processes not incorporated in the model, such as sulfate reduction and cation exchange. It is obvious that the alkalinity changes during the period of experimentation were dictated by the nitrate and ammonium budgets alone.

Discussion

Year to year changes in the alkalinity of the whole lake

In 1970–71 the actual increase in alkalinity ($HCO_3^- - H^+$; col 8–col 7 in Table 2) was 2947 eq. This indicates that under normal conditions the lake was a substantial net generator of alkalinity. This agrees with more detailed ionic budgets for other ELA lakes, where reduction of sulfate to sulfide followed by sedimentation of FeS (Schindler et al., 1980b; Cook and Schindler, 1983; Cook et al., 1985), algal uptake and sedimentation of anions (D. W. Schindler, unpublished data) and mineral diagenesis (Lerman and Brunskill, 1971; Cook et al., 1985) are all significant alkalinity sources. During the first year of fertilization with NH_4^+ and phosphorus, the generation of alkalinity was reduced, with an observed increase of only 1422 eq. The following year, a net alkalinity decrease of 2931 eq. took place. In 1973, when NH_4Cl was added without phosphorus, and ammonium accumulated in the water column, the net increase in alkalinity was 5619 eq., i.e. the lake became less acid. The ammonium values observed in the lake were higher than would be expected from ammonium inputs alone, and must indicate a delayed anoxic decomposition of the organic matter which had been produced in the course of biological ammonium uptake and sedimentation of organic matter in 1971–73. This would explain the high alkalinity production in the lake, as predicted by Equation (7).

The greatest net alkalinity consumption of any year occurred in 1974–75, with 9941 eq. consumed. Most consumption occurred during the late winter, when nitrification of ammonium occurred. As mentioned earlier, two equivalents of alkalinity would be consumed for every equivalent of ammonium nitrified (Equation (4)).

In 1975, after additions of phosphate and sodium nitrate, the lake produced 7615 eq. of alkalinity. As for ammonium addition, fertilization with nitrate had a greater effect on alkalinity during the second year of fertilization

Table 2. Year to year changes in the alkalinity of Lake 304 as a function of net nitrogen inputs. Calculations are begun on the earliest sampling date after ice-out of each year. Data are in equivalents.

Budget year	Input-output[a]			ΔM					
	(1) NH_4^+	(2) NO_3^-	(3) NCO_3^-	(4) NH_4^+	(5) NO_3^-	(6) $A_p = (2-1) - (5-4)^c$	(7) ΔH^+	(8) $\Delta HCO_3^{-\,b}$	(9) = Eff% $= \frac{(8)-(7)}{(6)}$
1970–71	412	467	−2753	100	−107	−2 698	−314	2 633	−109
1971–72	12 880	1 195	−2784	4900	−206	14 469	155	1 577	−10
1972–73	11 379	455	−874	164	474	−11 798	−129	−3 060	25
1973–74	7 718	−59	−1663	8493	100	−9 440	37	5 656	−60
1974–75	6 069	−429	−4127	−7714	4764	−10 625	1078	−8 863	94
Overall, 71–75	38 046	1 162	−9448	5843	5132	−46 332	1141	−4 690	13
1975–76	−2 597	35 255	−629	−6711	−514	37 223[c]	−1210	6 405	20
1976–77	107	34 054	−8003	653	−4845	25 944	−31	35 844	138
Overall, 76–77	−2 490	69 309	−8632	−6058	−5359	63 167	−1241	42 249	69

[a] Includes runoff extrapolated from the northwest Subbasin of Rawson Lake, precipitation and fertilizer.

[b] Bicarbonate is calculated from DIC, pH and temperature (Equation (6))

[c] A_p is potential alkalinity generation as defined in Equation (7).

Table 3. Changes in mass of nitrate, ammonium, hydrogen ion and calculated alkalinity in the upper 3 m of Lake 304 from early May to late August or early September of each year. All data are in equivalents except column 6.

Budget Year	(1) Net NH_4^+ Input (= ΔCl^-)	(2) ΔNH_4^+ in lake	(3) ΔH^+ in lake	(4) ΔHCO_3^- in lake[a]	(5) = (3) − (4) Net Acidification (alkalinity consumption)	(6) = 100[(5)/(1)] = Acidification efficiency, %
1971	7396	−460	888	−3475	4363	59
1972	6149	−1692	1170	−2396	3566	58
1973	8857	4772	223	−903	1126	13
1974	4739	−71	−3	−3380	3377	71
Year	(1) Net NO_3^- Input (= ΔNa^+)	(2) ΔNO_3^- in lake	(3) ΔH^+ in lake	(4) ΔHCO_3 in lake[a]	(5) = (4) − (3) Net alkalinization	(6) = 100[(5)/(1)] = Alkalinization efficiency, %
1975	30 152	10 432	−199	1881	2080	18
1976	30 057	1 990	−18	9494	9512	18

[a] Calculated from DIC, pH and temperature (Equation (6))

(Table 2). The lower efficiency of alkalinity generation in the first year was probably due partly to the biological uptake of the large quantities of ammonium which persisted after addition in 1974. Diffusion of ammonium from, and alkalinity to the sediments would also lower the efficiency. Higher efficiencies of alkalinity generation would undoubtedly have been obtained if the lake had been in a "background" condition prior to nitrate addition in the spring of 1975.

Changes in the epilimnion during the ice-free season

As mentioned earlier, this calculation represents the maximum efficiency of alkalinity consumption or generation. This would be expected in the euphotic zone, where the ratio of biological uptake to decomposition and excretion is maximum. As expected, these yielded somewhat higher efficiencies than for the whole lake, annual calculations shown in Table 2. The efficiency of ammonium addition at consuming alkalinity (Equation (8)) was 59, 58, 13 and 71% in the summers of 1971–74, respectively (Table 3).

A comparison of ΔNO_3^- and ΔNH_4^+ indicates that residual ammonium left over from the 1974 fertilization lowered the efficiency of alkalinity generation of the epilimnion in 1975. A total of 6422 eq. of ammonium disappeared from the upper 3 m, compared to 9280 eq. of nitrate. The overall efficiency of alkalinity generation was 18% of nitrate added in that year.

In 1976, the second year of nitrate addition, nitrate retention by the lake, as judged by ΔNa, was higher than in 1975. Seventy-three percent of the nitrate retained by the lake was utilized (Table 3). The alkalinity increase was almost 5 times that of 1975, and the conversion efficiency was much higher, presumably due to the fact that the lake had recovered from the earlier ammonium addition.

Changes in acidity due to nitrogen addition

It is obvious that the rate and pathway by which alkalinity is generated or consumed following fertilization with nitrogen depends on four factors:

(1) Whether the nitrogen is added in cationic or anionic form.
(2) Whether or not phosphorus is added.
(3) The microbial processes involved in uptake and utilization.
(4) The long-term balance of anabolic, catabolic and sedimentation processes involved in the nitrogen cycle.

The first point, while well discussed in the scientific literature (Brewer and Goldman, 1976; Goldman and Brewer, 1980; NRCC, 1981; Kelly et al., 1982), seems to be overlooked by many who propose to 'fertilize' lakes or streams in order to ameliorate acidification. Further studies must be done in order to quantify the relative roles of denitrification and conversion to organic matter in alkalinity generation. While either biological uptake or denitrification would generate one equivalent of alkalinity per equivalent of nitrate used, denitrification is a certain generator of permanent alkalinity, because any excess N_2 would be rapidly degassed to the atmosphere, with probable residence times in the water column of less than a week (Emerson, 1975; Hesslein et al., 1980). On the other hand, organic matter sedimenting to the bottom of the lake might be less permanent, with decomposition occurring for a period of several years after initial biological uptake and sedimentation. Permanent sedimentation of nitrogen added as nitrate in Lake 227, which is quite similar in size to Lake 304, has averaged 54% over a 13 year period, (Schindler et al., 1973 and in prep.), generating an equivalent amount of alkalinity (Schindler, 1984). If decomposition of the organic matter produced from this nitrate occurred in an anoxic hypolimnion, where nitrogen was released as ammonium upon decomposition, an even higher efficiency of alkalinity generation would result than if all nitrate were simply converted to organic matter and sedimented, provided that the ammonium is reoxidized or consumed by photosynthesizing plants at overturn.

It is obvious from 1973–4 results from Lake 304 and our studies in Lake 226 (Schindler, 1975, 1977 and unpublished data) that nitrogen added without phosphorus is inefficiently transformed to organic matter. On the other hand, small additions of phosphorus alone neither generate nor consume appreciable alkalinity, but depend upon an ample supply of nitrogen of the appropriate ionic form. Our studies (Schindler et al., 1973, and unpublished data; Schindler, 1977) suggest that an N:P ratio of less than 15:1 by weight is necessary to ensure complete biological uptake by ionic nitrogen. In natural lakes of the area, all incoming nitrate and ammonium is consumed rapidly, so that the concentrations of both ions in the euphotic zone are below the limits of detection ($1\,\mu g\,N\,L^{-1}$) through much of the ice-free season.

The microbiota which govern nitrification, denitrification, decomposition and ammonification are obviously an important key to the effect of fertilization on the hydrogen ion balance. The appearance of nitrifying organisms in the winter of 1974–5 made the lake a net generator of acidity, whereas in the previous winter, when nitrification was insignificant, other *in situ* processers had been net consumers of hydrogen ion, even though the ammonium input to the lake was the same in both years. High rates of nitrification also occurred in enriched 'mesocosms' in nearby Lake 302, with similar results (J. Rudd, Freshwater Institute, Winnipeg, pers. comm.).

Clearly, inputs and throughputs of all biologically-reactive ions can play a major role in altering the alkalinity budgets of lakes. They are of potential importance in managing the anthropogenic acidification of lakes. For example, Galloway et al. (1983) showed that three lakes in the Adirondacks retained ammonium much more efficiently (87–98%) than nitrate (35–54%). If inputs of both forms of nitrogen were equal, a considerable *in situ* consumption of alkalinity would be expected. Fortunately, inputs of nitrate to the Adirondacks are nearly twice as high as ammonium (Johannes and

Altwicker, 1980), so that proton generation and consumption due to biological nitrogen cycling are nearly equal. This situation could be fortuitous, because ammonium and nitrate in precipitation have somewhat different origins (NRC, 1981; Gorham et al., 1984), so that their relative proportions and retentions by ecosystems may be different in different areas. Elsewhere, we have shown that biological sulfur cycling can also have a major influence on the alkalinity balance of poorly buffered lakes (Schindler et al., 1980b; Cook, 1981; Kelly et al., 1982; Cook et al., 1984). It is clear that deposition and ecosystem utilization of nonprotolytic ionic nutrients must be incorporated in comprehensive models of lake acidification.

The efficiency of ammonium chloride at consuming alkalinity in lakes is expected to be lower than the efficiency resulting from the addition of hydrochloric acid, because some of the ammonium taken up biologically is recycled during decomposition. A relative index of this efficiency can be obtained by comparing the alkalinity consumption in Lake 223, which is acidified weekly with H_2SO_4 (Schindler et al., 1980; Schindler and Turner, 1982; Cook et al., 1984), with that in Lake 304. An E_a value for Lake 223 which is comparable to that of Equation (8) is simply:

$$E_a = \frac{\Delta \text{ alkalinity}}{\text{acid added} - \text{outflow}}.$$

For the five years, 1978 through 1982 when Lake 223 was between pH 5.0 and 6.0, i.e. roughly the pH range in Lake 304 prior to fertilization, the average efficiency of alkalinity consumption due to H_2SO_4 addition was 19 to 34%, slightly higher than the average observed in Lake 304. As in lakes 304 and 239, almost all of the alkalinity was generated by biological processes in the lake, not supplied by terrestrial runoff (Cook, 1981; Cook et al., 1985). However, in Lake 223, sulfate reduction was the predominant biological mechanism, with transformations of the small natural inputs of nitrate and ammonium having little effect.

In summary, our data suggest that ammonium compounds may be important in causing lake acidification, and that stimulation of denitrification or biological uptake by fertilization with nitrate or nitrate plus phosphate may be a useful ameliorative technique. More detailed whole ecosystem experiments specifically designed to test the effects of nitrogen inputs on the acidification of lakes are desirable. In particular, effects of cation exchange, consumption of inorganic anions, and changes in organic anions, topics which it was not possible to address here.

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References

Almer, B., W. Dickson, C. Ekstrom, and E. Hornstrom. 1978. Sulfur pollution and the aquatic ecosystem, p. 271–311. IN: Nriagu, J. (ed.), Sulfur in the environment. Part II. Ecological impacts. John Wiley and Sons, New York.

Bangay, G. E. and C. Riordon (ed.). 1983. Work Group I. Impact Assessment. Final Report submitted to the Coordinating Committee in fulfillment of the requirements of the Memorandum of Intent on Transboundary Air Pollution signed by Canada and the United States.

Brewer, P. G. and J. C. Goldman. 1976. Alkalinity changes generated by phytoplankton growth. Limnology and Oceanography 21: 108–117.

Brunskill, G. J. and D. W. Schindler. 1971. Geography and bathymetry of selected lake basins, Experimental Lakes Area, northwestern Ontario. Journal of the Fisheries Research Board of Canada 28: 139–155.

Chan, Y. K. and N. E. Campbell. 1980. Denitrification in Lake 227 during summer stratification. Canadian Journal of Fisheries and Aquatic Science 37(3): 506–612.

Cook, R. B. 1981. The biogeochemistry of sulfur in two small lakes. Ph.D. Thesis, Columbia University, New York, NY. 248 p.

Cook, R. B., C. A. Kelly, D. W. Schindler and M. A. Turner. 1985. Mechanisms of hydrogen ion neutralization in an experimentally-acidified lake. (Under review).

Cook, R. B. and D. W. Schindler. 1983. The biogeochemistry of sulfur in an experimentally acidified lake. In: Hallberg, R. O. (ed.), Environmental Biogeochemistry, Ecological Bulletin (Stockholm) 35: 115–127.

Dillon, P. J., N. D. Yan, W. A. Scheider and N. Conroy. 1979. Acidic lakes in Ontario, Canada: characterization, extent and responses to base and nutrient additions. Archiv für Hydrobiologie, Beiheft 13, Ergebnisse der Limnologie 13: 317–336.

Emerson, S. 1975. Chemically enhanced CO_2 gas exchange in a eutrophic lake: A general model. Limnology and Oceanography 30: 743–753.

EPA. (U.S. Environmental Protection Agency). 1983. Critical Assessment Document. (In draft).

Galloway, J. N., C. L. Schofield, N. E. Peters, G. R. Hendrey and E. R. Altwicker. 1983. Effect of atmospheric sulfur on the composition of three Adirondack lakes. Canadian Journal of Fisheries and Aquatic Science 40: 799–806.

Goldman, J. C. and P. G. Brewer. 1980. Effect of nitrogen source and growth rate on phytoplankton – mediated changes in alkalinity. Limnology and Oceanography 25: 352–357.

Gorham, E., F. B. Martin and J. T. Litzau. 1984. Acid rain: Ionic correlations in the eastern United States, 1980–81. Science 225: 407–409.

Herczeg, A. L. and R. H. Hesslein. 1984. Determination of hydrogen ion concentration in softwater lakes using carbon dioxide equilibria. Geochimica et Cosmochimica Acta 48: 837–845.

Hesslein, R. H., W. S. Broecker, P. D. Quay and D. W. Schindler. 1980. Whole-lake radiocarbon experiment in an oligotrophic lake at the Experimental Lakes Area, northwestern Ontario. Canadian Journal of Fisheries and Aquatic Science 37(3): 454–463.

Johannes, A. H. and E. R. Altwicker. 1980. Atmospheric inputs to three Adirondack lake watersheds, pp. 256–257. In: Drablos, D. and A. Tollan (eds.), Ecological Impact of Acid Precipitation. SNSF Project, Oslo, Norway.

Kelly, C. A., J. W. M. Rudd, R. B. Cook and D. W. Schindler. 1982. The potential importance of bacterial processes in regulating rate of lake acidification. Limnology and Oceanography 27: 868–882.

Lerman, A. and G. J. Brunskill. 1971. Migration of major constituents from lake sediments into lake water and its bearing on lake water composition. Limnology and Oceanography 16: 888–890.

Likens, G. E., F. H. Bormann, R. S. Pierce, J. S. Eaton and N. M. Johnson. 1977. Biogeochemistry of a Forested Ecosystem. Springer-Verlag, New York. 146 p.

MOI (Memorandum of Intent on Transboundary Air Pollution) US-Canada. 1983. Volume 1. Impact Assessment.

NRC (National Research Council). 1981. Atmosphere-biosphere interactions: toward a better understanding of the ecological consequences of fossil fuel combusion. National Academy Press, Washington, DC., National Academy of Science. 163 p.

NRC (National Research Council). 1981. Acidification in the Canadian aquatic environment. No. 18475. Ottawa.

Russell, W. E. 1961. Soil conditions and plant growth. Longmans, Green and Co. Ltd., London. 688 p.

Schindler, D. W. 1974. Eutrophication and recovery in experimental lakes: Implications for lake management. Science 184: 897–899.

Schindler, D. W. 1975. Whole lake eutrophication experiments with phosphorus, nitrogen and carbon. Internationale Vereinigung fuer Theoretische und Angewandte Limnologie Verhandlungen 195: 3221–3231.

Schindler, D. W. 1977. Evolution of phosphorus limitation in lakes. Science 195: 260–262.

Schindler, D. W. 1984. The coupling of elemental cycles by organisms: Evidence from whole lake chemical perturbations. In: Stumm, W. (ed.), Chemical Processes in Lakes. John Wiley and Sons, New York.

Schindler, D. W. and E. J. Fee. 1974. Experimental lakes area: Whole-lake experiments in eutrophication. Journal of the Fisheries Research Board of Canada 31: 927–953.

Schindler, D. W. and M. A. Turner. 1982. Biological, chemical and physical responses of lakes to experimental acidification. Water, Air, and Soil Pollution 18: 259–271.

Schindler, D. W., H. J. Kling, R. V. Schmidt, J. Prokopowich, V. E. Frost, R. A. Reid and M. Capel. 1973. Eutrophication of Lake 227, Experimental Lakes Area, northwestern Ontario by addition of phosphate and nitrate, part 2: the second, third and fourth years of enrichment, 1970, 1971 and 1972. Journal of the Fisheries Research Board of Canada 30(10): 1415–1440.

Schindler, D. W., R. W. Newbury, K. G. Beaty and P. Campbell. 1976. Natural water and chemical budgets for a small Precambrian lake basin in central Canada. Journal of the Fisheries Research Board of Canada 33(11): 2526–2543.

Schindler, D. W., R. W. Newbury, K. G. Beaty, J. Prokopowich, T. Ruszczynski and J. A. Dalton. 1980a. The effects of a windstorm and a forest fire on chemical losses from forested watersheds on the quality of receiving streams. Journal of the Fisheries Research Board of Canada 37(3): 328–334.

Schindler, D. W., R. Wagemann, R. Cook, T. Ruszyczynski and J. Prokopowich. 1980b. Experimental acidification of Lake 223, Experimental Lakes Area: I. Background data and the first three years of acidification. Canadian Journal of Fisheries and Aquatic Science 37(3): 342–354.

Stainton, M. P., M. J. Capel and F. A. J. Armstrong. 1977. The chemical analysis of fresh water. 2nd edition. Canadian Fisheries and Marine Service Miscellaneous Special Publication 25: 166 p.

Thompson, B. M. and R. D. Hamilton. 1972. Heterotrophic utilization of sucrose in an artificially enriched lake. Journal of the Fisheries Research Board of Canada 30(10): 1547–1552.