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Mechanisms of hydrogen ion neutralization in an experimentally acidified lake

R. B. Cook
Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

C. A. Kelly
Department of Biology, University of Winnipeg, Winnipeg, Manitoba R3B 2E9

D. W. Schindler and M. A. Turner
Department of Fisheries and Oceans, Freshwater Institute, Winnipeg, Manitoba R3T 2N6

Abstract

The experimental acidification of Lake 223 (Experimental Lakes Area, northwestern Ontario) with sulfuric acid in 1976–1983 allowed a detailed examination of the capacity of the lake to neutralize hydrogen ion. A whole-lake alkalinity and ion budget for Lake 223 showed that 66–81% of the added sulfuric acid was neutralized by alkalinity production in the lake. Nearly 85% of in situ alkalinity production was accounted for by net loss of sulfate through bacterial sulfate reduction, coupled with iron reduction and iron sulfide formation, in littoral sediments (60%) and in the hypolimnion (25%). Exchange of hydrogen ion for calcium and manganese in the sediments accounted for 19% of the alkalinity generated, while other cations were net sinks for alkalinity. Alkalinity input from the watershed of Lake 223 was very small, averaging about 5% of that produced in the lake.

The seasonal production of 1,000 μeq liter^{-1} alkalinity in the anoxic hypolimnion of this soft-water lake could be attributed to bacterial sulfate reduction coupled with iron sulfide formation, ammonium production, and iron (II) production. Only the alkalinity produced from bacterial sulfate reduction coupled with iron sulfide formation remained throughout the annual cycle.

Although the acidification of lakes in Europe and North America has been well documented (e.g. Drablos and Tollan 1980; Natl. Res. Counc. Can. 1981; Natl. Res. Counc. 1981; U.S. EPA 1983), the biogeochemical mechanisms involved are still incompletely understood. To understand how lakes become acidic and to predict the rate of future acidification or recovery of lakes under known atmospheric inputs of acids, we need to improve our knowledge of the capacity of watersheds and lakes to neutralize hydrogen ion.

Recent work has shown the significance of various mechanisms in neutralizing acidity in terrestrial and aquatic ecosystems (e.g. Sollins et al. 1980; Hemond and Eshleman 1984; Schindler 1985) and wetlands (Hemond 1980). Schindler et al. (1986) have shown that in situ biogeochemical processes, rather than processes in the terrestrial drainage, are the predominant sources of alkalinity for lakes in poorly buffered geological strata.

Most studies of lake acidification have been carried out after the fact. In very few studies have the preacidification conditions of the lakes been well enough known to describe the progress of lake acidification so that a detailed understanding of the acidification process could be gained. The whole-lake, experimental acidification of Lake 223, Experimental Lakes Area (ELA), northwestern Ontario, provides an ideal opportunity for examining how biogeochemical processes respond to lake acidification. The background conditions for this soft-water, low alkalinity (100 μeq liter^{-1}; pH 6.6) lake were determined in 1974 and 1975. Additions of electrolyte-grade sulfuric acid were made for the next 7 years at a hydrogen ion loading rate about four times that of the northeastern U.S., causing the pH to drop to between 5.2 and 5.0. In contrast to the situation in lakes acidified by atmospheric deposition, the input of acid to Lake 223 is known precisely. Sulfur budgets and various chemical and biological changes resulting from the acidification of Lake 223 have been reported elsewhere (e.g. Schindler 1980; Nero and Schindler 1983; Mills 1984).

Schindler et al. (1980) reported that during the first 2 years, the sulfuric acid additions were only 31–38% efficient in decreasing pH and alkalinity in Lake 223. The lake has continued to exhibit this resistance to acidification, even though it is now 1.5 pH units more acidic than before acidification. Our objective here is to examine the capacity of the lake system to neutralize hydrogen ion and to quantify the mechanisms involved.

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Theoretical background

The chemistry of alkalinity production is well understood (Stumm and Morgan 1981). Many models for marine and estuarine systems successfully predict alkalinity production from sulfate depletion due to bacterial sulfate reduction, from calcium and magnesium increases due to carbonate mineral dissolution, and from ammonia production resulting from the decomposition of organic matter (e.g. Knull and Richards 1969; Berner et al. 1970; Einarsson and Stefansson 1983). Goldman and Brewer (1980) have examined the alkalinity produced in cultures of marine algae when nitrate is consumed during photosynthesis. In lake fertilization experiments at ELA, additions of neutral ammonium chloride and of sodium nitrate, followed by biological reactions, caused the alkalinity to decrease and to increase (Schindler et al. 1985).

Hydrogen ion added to a lake, either naturally or experimentally, will meet one of four chemical fates: (1) remain in the water, causing the pH to decrease; (2) react with alkaline species present in the water; (3) exchange with nonprotolytic ions in the sediments; or (4) be taken up by the biota in the water or sediments in conjunction with the uptake of anions such as SO_4^{2-} or NO_3^-. Because the last three fates will not necessarily cause a pH change within the lake, we will examine hydrogen ion neutralization using alkalinity (or acid-neutralizing capacity), which is the chemical term that embodies all of the fates of hydrogen ion. Alkalinity (Alk) is defined as:

$$\mathrm{Alk} = [HCO_3^-] + [CO_3^{2-}] + [OH^-] + [A^-] - [H^+] \qquad (1)$$

where A^- represents organic anions that are protolytic in the pH 4–7 range and all terms are eq liter^{-1}.

Acid additions to a lake may cause the alkalinity of the water to decrease (fates 1 and 2, and Eq. 1). The capacity of a lake to neutralize acid in this way can be determined simply by an alkalinity titration.

The reaction of hydrogen ion with the sediments or the uptake of hydrogen ion by the biota can be determined from an alternative definition of alkalinity. Combining Eq. 1 with the condition of electroneutrality for typical surface freshwaters having a pH <7,

$$\begin{aligned}&[Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}] + [NH_4^+] \\ &\quad + [Mn^{2+}] + [Fe^{3+}] + [H^+] \\ &= [Cl^-] + [SO_4^{2-}] + [NO_3^-] \\ &\quad + [HCO_3^-] + [A^-], \end{aligned} \qquad (2a)$$

or anoxic hypolimnion waters having a pH <7,

$$\begin{aligned}&[Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}] + [NH_4^+] \\ &\quad + [Fe^{2+}] + [Mn^{2+}] + [H^+] \\ &= [Cl^-] + [SO_4^{2-}] + [NO_3^-] \\ &\quad + [HCO_3^-] + [A^-] + [HS^-], \end{aligned} \qquad (2b)$$

yields

$$\begin{aligned}\mathrm{Alk} = &[Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}] \\ &+ [Mn^{2+}] + [Fe^{3+}] + [NH_4^+] \\ &- [Cl^-] - [SO_4^{2-}] - [NO_3^-] \end{aligned} \qquad (3a)$$

or

$$\begin{aligned}\mathrm{Alk} = &[Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}] \\ &+ [Fe^{2+}] + [Mn^{2+}] + [NH_4^+] \\ &- [Cl^-] - [SO_4^{2-}] - [NO_3^-] \end{aligned} \qquad (3b)$$

where all units are μeq liter^{-1}. The concentrations of other ions (e.g. Al) are negligible in Lake 223.

Production of bases or exchange of H^+ for basic cations in the sediments changes the alkalinity (Eq. 1) and must be accompanied by increases in nonprotolytic cations, decreases in nonprotolytic anions, or both (Eq. 3a and b). The processes that produce alkalinity in natural waters (fates 3 and 4) include, for example, denitrification, nitrate uptake during photosynthesis, dissimilatory sulfate reduction coupled with iron reduction and precipitation of iron sulfides, assimilatory sulfate reduction coupled with net sedimentation of organic material, calcite dissolution, weathering of aluminosilicate minerals, and cation exchange. Processes consuming alkalinity are strong acid additions (acidic deposition), ammonium uptake during photosynthesis, nitrification, and oxidation of reduced sulfur compounds. Examination of the alkalinity of Lake 223 using an empirical model based on Eq. 3b and chemical measurements over time enabled us to determine the mechanisms of hydrogen ion neutralization.

Materials and methods

Paralimnology—Lake 223 has a surface area of 27.3 ha, a maximum depth of 14.4 m, and an average depth of 7.2 m (Schindler et al. 1980). The direct watershed of Lake 223 is 135.2 ha in area and is dominated by Precambrian Shield granodiorite, which outcrops frequently on ridge rests and valley slopes. As is typical for lakes in the ELA area (Brunskill and Schindler 1971), overburden consists of Pleistocene deposits of quartz, plagioclase, and K-feldspar sand and gravel and is usually <1 m deep. Much of the Lake 223 watershed has no overburden at all, with bedrock either exposed or covered only by a shallow (5–20 cm) layer of organic matter in which a mature forest of jack pine (*Pinus banksiana*) and black spruce (*Picea mariana*) is rooted. The lake is oligotrophic, with primary production falling within the range for natural ELA lakes (Fee 1979; Fee et al. 1982; J. A. Shearer unpubl. data) before and during the acidification experiment (Schindler 1980; Schindler and Turner 1982). ELA lakes have chemical compositions typical of lakes most vulnerable to acidification (Armstrong and Schindler 1971; Schindler and Ruszczynski 1983); before the experiment the ionic strength in Lake 223 was 300 μmol liter^{-1}, alkalinity was 101–154 μeq liter^{-1}, and pH 6.6.

Lake 223 receives water from precipitation falling directly on the surface (40% of total input), direct runoff from the portion of the watershed not drained by a stream (40% of total input), and from a small stream draining nearby Lake 224 (20% of total input: Beaty 1981). Water from the last and loss through the Lake 223 outlet are monitored by continuously recording V-notch weirs. Groundwater flow is insignificant for Lake 223 (Beaty 1981). Water renewal times averaged 8.7±5.4 (1 SD) yr for 1976–1983 (range: 3.7–20.5 yr: Beaty 1981 and unpubl. data).

Electrolyte-grade concentrated sulfuric acid was added to the lake surface, from one to several times a week during the ice-free seasons of 1976–1983, by slowly pouring acid into the propeller backwash of a moving motorboat; the vertical and horizontal distribution of sulfate and hydrogen ion in the epilimnion became uniform within a few hours (Schindler et al. 1980). In 1976, acid was added to lower the buffering capacity but not the pH; in the following 7 years enough acid was added to maintain an average epilimnetic pH of 6.13, 5.93, 5.64, 5.59, 5.02, 5.09, and 5.13 throughout the ice-free season (Cruikshank 1984). The weekly addition data are given by Schindler et al. (1980) and Cruikshank (1984). The total amount of acid added in 8 years was 991.9 keq, which converts to an average loading to the lake surface of 454 meq H^+ m^{-2} yr^{-1}. Hydrogen ion loading in wet and dry deposition to the northeastern U.S. averages 132 meq m^{-2} yr^{-1} (Driscoll and Likens 1982).

Sampling and analytical methods—Water samples collected at a station over the deepest point in the lake were analyzed for major ions, ammonium, nitrate, pH, dissolved inorganic carbon (DIC), dissolved organic carbon, and ΣH_2S (Stainton et al. 1977). Dissolved manganese, iron, and aluminum were determined with graphite furnace/atomic absorption spectroscopy on samples filtered through 0.2-μm membrane filters. Until July 1978, carbonate alkalinity was calculated from pH and DIC (Herczeg and Hesslein 1984) and alkalinity from Eq. 3a and b. After that, alkalinity was measured by potentiometric titration in a closed vessel; the end point was determined from a Gran plot (Stumm and Morgan 1981). After August 1978, samples were taken from a manifold anchored at constant depth to minimize sampling variability.

Bulk precipitation was collected at a site 4 km from Lake 223 and sampled after every storm. We used bulk precipitation rather than the sum of wet plus dryfall because the latter was not measured at the site until 1979. Comparisons from 1979 to 1982 reveal that bulk precipitation is quite similar to the sum of wet plus dryfall for most ions at ELA (Linsey in prep.), which is not unusual for a relatively unpolluted site. Samples for chemical analyses were taken from the inflow and outflow streams once a week when the streams were flowing. Precipitation and streams were analyzed for the same constituents as the water of the lake. Direct runoff of water and ions to the lake was assumed to be the same per unit area as that of the northwest subbasin of Lake 239, which is similar in size, slope, and geology.

Porewater samples were collected with a close-interval membrane equilibrator (Hesslein 1976).

Whole-lake budgets—The individual ion budgets comprise measured inputs (precipitation, stream inflow, direct runoff), measured outputs (stream outflow), and the observed change in water column mass from one year to the next (change in storage). Production or consumption of ions within the lake (by the sediments or by biota in the water column) was calculated from:

$$\pm \text{ production/consumption} = \text{inputs} - \Delta\text{storage} - \text{outputs}.$$

Before August 1978 alkalinity was not titrated but calculated in two ways: from carbonate alkalinity

$$\text{Alk} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}] - [\text{H}^+] \quad (4)$$

which does not include protolytic organic anions (A^-); and from the charge balance (Eq. 3a and b). Comparisons of alkalinity so calculated with alkalinity measured after 1978 revealed that Eq. 4 underestimated alkalinity (due to the A^- contribution: Herczeg and Hesslein 1984) and Eq. 3a and b overestimated it (due to major-ion complexes that contributed to nonprotolytic cations as measured by atomic absorption). Therefore we present a range of alkalinity for 1976–1978 which should include the true value.

Results

Alkalinity budget—Only 19–34% of the acid added since the beginning of the experiment caused a decrease in alkalinity in the water of Lake 223 (Table 1, column 4). The rest (66–81%) was neutralized by alkalinity generated by in situ processes (Table 1, column 5). Hydrologic inputs of alkalinity were very small during the 8 years and were about equal to outflow. In fact, of streamflow, runoff, and precipitation, only streamflow from Lake 224 was a significant alkalinity source. To determine the exact nature of the in-lake neutralization processes, we examined input-output budgets for the individual ions in Eq. 3a and b.

Individual ion budgets—Inputs and outputs of all ions are affected by the amount of precipitation on the watershed in any given year. Redox-sensitive species are also affected by the completeness of spring and fall overturn, which are highly variable in the continental climate at ELA. There is, therefore, a considerable year-to-year variation in inputs and outputs of all elements (Table 2), and hence in the alkalinity budget (Table 1).

Cations—Calcium was by far the largest cationic contributor to alkalinity production, yielding 120 keq during the 8 years (Table 2). Manganese was the next most important (14.3 keq during the period), which is not surprising in view of the increases in concentrations of this element observed during acidification (Schindler and Turner 1982). The contribution of sodium, 2.7 keq, is not significant, being well within the limits of error for sampling and analysis.

Concentrations increased in the water for Mn^{2+} (from 5 to 160 μg liter^{-1}), Fe^{3+} (from 16 to 60 μg liter^{-1}), and for total dissolved Al (from 11 to 38 μg liter^{-1}) during 1976–1983. The oxidation states for these ions were not determined, but estimated based on stability at lake pH and redox potential (Stumm and Morgan 1981).

Table 1. Alkalinity input-output budget for Lake 223. Units are keq. Values in parentheses are ranges based on alkalinity calculated from Eq. 4 and 3a, with lower numbers calculated from DIC, pH, and temperature and higher ones from charge balance. Values not in parentheses are Gran titration results, except for acid added.

	(1) Alk inputs*	(2) Acid added	(3) Alk outflow	(4) Change in Alk storage	(5) Alk prod. = 4 + 3 − 1 − 2
1976	(0.4–1.3)	−203.4	(14.5–26.1)	(−90.7 to −116.5)	(111.7–126.8)
1977	(0.2–0.4)	−106.8	(2.9–9.3)	(−6.5 to −82.6)	(26.7–109.5)
1978	15.6	−125.8	10.1	(−20.1 to −68.3)	(52.0–100.2)
1979	6.5	−103.4	3.1	−38.4	61.6
1980	0	−113.8	0.4	−8.4	105.8
1981	−2.6	−130.1	−0.9	−10.0	121.8
1982	8.9	−126.8	−3.5	−5.0	109.4
1983	3.6	−81.8	−0.4	−11.0	66.8
1976–1983	32.6–33.7	−991.9	26.2–44.2	−190.0 to −340.2	655.8–801.9

* The sum of inputs from precipitation, runoff, and stream inputs.

Unexpectedly, all other cation budgets showed net consumption in the lake (Table 2), resulting in consumption of alkalinity. Values for potassium and iron were quite small and probably not significant, but losses of magnesium and ammonium from the lake were large enough to balance the alkalinity generated by calcium increases, particularly from 1979 to 1983. Thus, the overall effect of cations on the alkalinity budget was small.

Anions—Under natural conditions sulfate would be the largest anionic input to the lake (Table 3) and the sulfuric acid additions made this input even larger. Although nitrate reduction was a significant generator of alkalinity, its magnitude was very similar to that of ammonium oxidation (Table 2), so that the net effect of input-output budgets of inorganic nitrogen was almost zero. Chloride values fluctuated from year to year, and overall the ion did not contribute significantly to alkalinity changes (Table 2).

At the beginning of acidification there were apparently some titratable organic anions in the lake. These were not measured but their existence is inferred from the fact that in January 1976 there were 53 μeq liter^{-1} of positive charges that were unbalanced by any measured anion or by bicarbonate. In later years, this decreased to 30 μeq liter^{-1} (January 1977), 3 (January 1978), and 0 (1979–1982). Such titratable organic anions have recently been shown to exist in nonacidified ELA lakes, with pK values between 3.5 and 6.5 (Herczeg and Hesslein 1984). As the pH of Lake 223 decreased to pH 5.6 in 1979, these organic anions were protonated along with the bicarbonate.

Alkalinity production—Within limits of error, ion budgets accounted for nearly all of the alkalinity production; sulfate reduction coupled with iron reduction and iron sulfide formation furnished 85% of the alkalinity generated in situ and neutralized 54% of the added acid (Table 4).

Hypolimnetic processes—We used data from 1978–1979 to compare in detail the alkalinity changes measured with those predicted by the sum of the individual reactions involved. In the anoxic hypolimnion of Lake 223, we found that bacterial degradation of organic matter caused a depletion of SO_4^{2-} and a production of Fe^{2+} and NH_4^+ (Fig. 1). Chemical changes accompanying bacterial activity in the hypolimnion caused pH to increase by one unit over the value at shallower depths and alkalinity to increase from 30 to 2,000 μeq liter^{-1} (Fig. 1).

Although bacterial sulfate reduction decreased SO_4^{2-} from 90 to 10 μmol liter^{-1}, hydrogen sulfide was rarely present in the water in 1978–1979 because the high Fe^{2+} concentration precipitated all sulfides as either amorphous FeS or pyrite (FeS_2) (Schindler et al. 1980; Cook 1981). Another possible sink for hypolimnetic SO_4^{2-} is assimilatory sulfate reduction; earlier work demonstrated that this is a minor process compared to dissimilatory sulfate reduction in Lake 223 (Cook 1981; Cook and Schindler 1983).

Table 2. Nonprotolytic ion budgets for Lake 223, except for sulfate. Total inputs are the sum of stream inflow, precipitation, and direct runoff. Units are keq.

	(1) Total inputs	(2) Stream outflow	(3) Change in ion storage	(4) Total ion prod. (+) or consumption (−) = 2 + 3 − 1
Na^+				
1976	6.4	8.9	4.2	6.7
1977	12.9	11.8	0.0	−1.1
1978	18.8	23.5	10.2	14.9
1979	19.0	16.0	1.7	−1.3
1980	15.4	5.1	1.7	−8.6
1981	18.4	7.5	11.0	0.1
1982	22.7	21.1	−0.8	−2.4
1983	11.8	8.6	−2.4	−5.6
1976–1983	125.4	102.5	25.6	2.7
K^+				
1976	1.9	2.0	1.5	1.6
1977	1.9	2.2	0.5	0.8
1978	3.9	4.9	−0.5	0.5
1979	3.7	3.1	0.0	−0.6
1980	2.8	0.7	−2.0	−4.1
1981	6.4	1.3	4.2	−0.9
1982	8.7	4.2	−4.7	−9.2
1983	5.4	1.8	3.5	−0.1
1976–1983	34.7	20.2	2.5	−12.0
Ca^{2+}				
1976	16.8	28.3	21.4	32.9
1977	30.5	33.3	10.7	13.5
1978	39.7	65.6	−4.9	21.0
1979	42.9	47.2	1.9	6.2
1980	29.4	12.4	1.0	−16.0
1981	42.0	22.9	14.6	−4.5
1982	49.6	64.6	15.6	30.6
1983	26.6	25.6	37.0	36.0
1976–1983	277.5	299.9	97.3	119.7
Mg^{2+}				
1976	9.4	10.6	1.6	2.8
1977	15.8	12.7	−3.2	−6.3
1978	19.7	25.7	0.0	6.0
1979	24.0	17.9	0.0	−6.1
1980	16.0	4.2	−3.2	−15.0
1981	28.2	8.4	15.2	−4.6
1982	27.2	24.0	−5.6	−8.8
1983	14.5	9.3	−12.0	−17.2
1976–1983	154.8	112.8	−7.2	−49.2
Fe^{3+}				
1976	1.3	0.4	3.1	2.2
1977	4.2	0.8	10.5	7.1
1978	4.6	1.5	−7.3	−10.4
1979	4.6	1.6	−2.1	−5.1
1980	2.9	0.2	3.1	0.4
1981	5.1	0.5	−8.5	−13.1
1982	5.0	2.4	11.7	9.1
1983	2.9	0.6	−1.8	−4.1
1976–1983	30.6	8.0	8.7	−13.9
Mn^{2+}				
1976	0.4	0.1	−0.2	−0.5
1977	0.7	0.2	0.8	0.3
1978	0.8	0.8	1.7	1.7
1979	0.7	0.8	3.4	3.5
1980	0.4	0.4	3.4	3.4
1981	0.3	1.2	−3.3	−2.4
1982	0.8	8.6	4.8	12.6
1983	0.5	2.1	−5.9	−4.3
1976–1983	4.6	14.2	4.7	14.3
NH_4^+				
1976	3.0	0.3	4.5	1.8
1977	3.5	0.2	0.9	−2.4
1978	3.3	1.0	0.3	−1.9
1979	7.2	1.1	−3.3	−9.4
1980	3.1	0.3	1.4	−1.4
1981	3.4	0.2	−2.2	−5.4
1982	8.1	0.7	−3.3	−10.8
1983	4.2	0.5	3.6	−0.1
1976–1983	35.8	4.3	1.9	−29.6
NO_3^-				
1976	2.4	0.4	0.4	−1.6
1977	4.2	0.0	−0.3	−4.5
1978	2.8	0.7	0.2	−1.9
1979	5.1	0.1	0.5	−4.5
1980	4.8	0.1	−1.6	−6.3
1981	7.3	0.0	−1.1	−8.4
1982	6.9	0.1	1.1	−5.7
1983	1.5	0.0	0.0	−1.5
1976–1983	35.0	1.4	−0.8	−34.4
Cl^-				
1976	5.0	4.3	−5.2	−5.9
1977	11.4	5.8	11.9	6.3
1978	9.6	10.1	−17.0	−16.5
1979	10.9	7.4	22.3	18.8
1980	17.6	0.7	−31.1	−19.8
1981	11.7	2.2	9.9	0.4
1982	11.0	5.4	−3.5	−9.1
1983	5.9	5.6	−0.3	−0.7
1976–1983	83.1	41.5	−13.0	−26.5

Reactions occurring in the profundal sediments that would affect hypolimnetic chemistry are presented in Table 5. Algae, the primary source of organic matter to the sediments of Lake 223, have a composition similar to that of marine algae (Redfield 1958; D. W. Schindler unpubl. data). The stoichiometries in Table 5 are based on a simplified Redfield molecule. The exact

Table 3. Sulfate budget for Lake 223 for 1976–1982. Units are keq.

	Natural inputs	Acid add.	Total inputs	Stream outflow	Change in storage	Sulfate reduction: Whole-lake*	Sulfate reduction: Hypolimnion† (10–14 m)	Sulfate reduction: Epilimnion‡ (0–10 m)
1976	28.4	203.4	231.8	16.8	173.5	41.5	7.4	34.1
1977	34.4	106.8	141.2	46.8	26.0	68.4	23.6	44.8
1978	47.6	125.8	173.4	87.2	46.7	39.5	17.6	21.9
1979	38.6	103.4	142.0	75.8	61.0	5.2	21.2	−16.0
1980	29.2	113.8	143.0	19.0	44.7	79.3	21.0	58.3
1981	38.0	130.1	168.1	40.7	−4.1	131.5	25.1	106.4
1982	75.4	126.8	202.2	112.8	24.3	65.1	29.8	35.3
1983	41.8	81.9	123.7	43.0	−24.4	105.1	14.8	90.3
1976–1983	333.4	992.0	1,325.4	442.1	347.7	535.6	160.5	375.1

* Total inputs − storage − stream outflow; uncertainty on these values is ±15%.

† From Cook and Schindler (1983). Area of 10–14-m sediment is 8.25 ha.

‡ Whole-lake sulfate reduction minus that in the hypolimnion. Area of 0–10-m sediment is 18.8 ha.

stoichiometry is not essential for the treatment that follows; as will be shown below, alkalinity production is determined by production or consumption of nonprotolytic ions.

The production of alkalinity in the hypolimnion of Lake 223 was analyzed from the reactions occurring in the hypolimnion (Table 5) and Eq. 1 and 3b. Oxic respiration (reaction a) and methanogenesis (d) do not affect alkalinity, but alkalinity is produced by Fe^{2+} production (b), ammonium production (e), manganese production (g), and by iron sulfide formation (h). Negligible amounts of nitrate are reduced in the hypolimnion (Kelly et al. 1982). The other ions in Eq. 3b all remain constant in the hypolimnion during any one stratification period.

The alkalinity resulting from reaction h (Table 5) is dependent on organic matter oxidation by iron reduction and sulfate reduction and the formation of an iron sulfide phase. The overall effect of reaction h on alkalinity can only be inferred from either the loss of sulfate or the production of iron sulfide.

The change in alkalinity, ΔAlk, between overturn and some later time is therefore:

$$\Delta \mathrm{Alk} = \Delta[\mathrm{Fe}^{2+}] + \Delta[\mathrm{NH_4}^+] + \Delta[\mathrm{Mn}^{2+}] - \Delta[\mathrm{SO_4}^{2-}] \quad (5)$$

where all units are μeq liter^{-1} and $\Delta[SO_4^{2-}]$ represents the net production of iron sulfide from sulfate reduction and iron reduction. Equation 5 is based on the relationship used by marine chemists to examine alkalinity

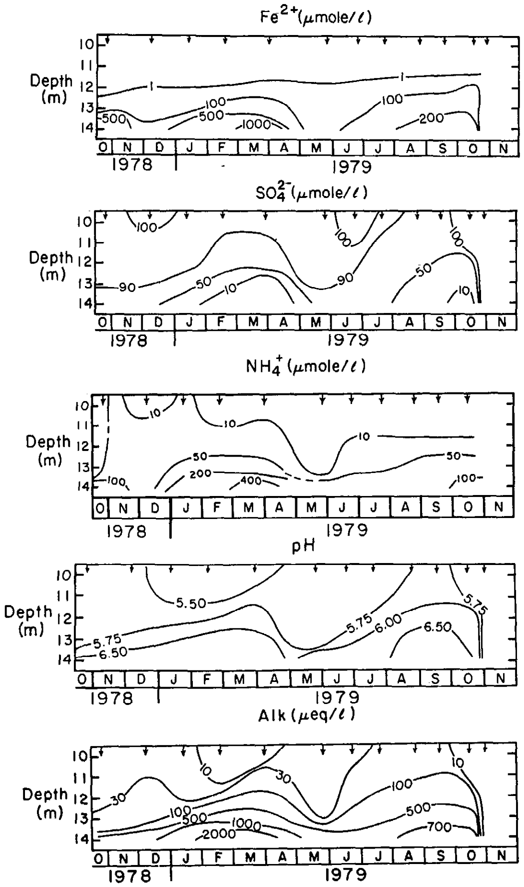

Fig. 1. The distribution of Fe^{2+} and SO_4^{2-} (μmol liter^{-1}; =½ μeq liter^{-1}), NH_4^+ (μmol liter^{-1}; =1 μeq liter^{-1}), pH, and Alk (μeq liter^{-1}) between 10 and 14 m from October 1978 to October 1979. Arrows indicate sampling dates.

production in anoxic saline waters (Knull and Richards 1969; Gaines and Pilson 1972) and in anoxic porewaters (Berner et al. 1970; Murray et al. 1978).

To calculate the alkalinity produced by various reactions occurring in the hypolimnion, we used Eq. 5 in the following way. The amount of an ion present in the 10–14-m zone was expressed as a volume-weighted average concentration. The production of alkalinity from Fe^{2+}, SO_4^{2-}, Mn^{2+}, and NH_4^+ was determined by the increase or decrease in these species with time. During the period concerned there would be some diffusive loss of alkalinity, NH_4^+, and Fe^{2+} and gain of SO_4^{2-} at the top of the 10–14-m zone. Diffusive loss or gain was calculated from the gradient for a given sampling day and the time between sampling days. The value for the eddy diffusion coefficient at 10 m was determined with the heat flux method (Quay 1977). The calculated diffusive loss or gain was $<30\%$ of the total change in any ion (Cook 1981).

The agreement between the alkalinity predicted by Eq. 5 and that observed was nearly perfect in summer; in winter the predicted value was 10–20% greater than observed (Fig. 2). Sulfate reduction produced more alkalinity in summer than in winter. This was expected because fall overturn was generally more complete than spring overturn in Lake 223 and more oxygen was entrained in the hypolimnion (Schindler et al. 1980). Because oxygen was more abundant in the hypolimnion in winter, oxic decomposition was more important; in summer, anoxic decomposition processes were more important. The amount of sulfate reduced and sulfate reduction rates were higher in summer than in winter (Cook and Schindler 1983).

When oxygen was mixed into the hypolimnion at overturn, aqueous iron (II) was oxidized (Fig. 1) to iron (III) hydroxide (Stumm and Morgan 1981). From Eq. 5, alkalinity gained from Fe^{2+} production during stagnation was lost when aqueous iron (II) concentrations decreased at overturn. Similarly, NH_4^+ and Mn^{2+} were oxidized at overturn and alkalinity gained from these ions was lost.

For the alkalinity produced by iron sul-

Table 4. Alkalinity generated from reactions of different ions in Lake 223, as deduced from mass-balance budgets. Data are in keq.

	Ca^{2+}	Mg^{2+}	Na^+	K^+	Fe^{3+}	Mn^{2+}	NH_4^+	SO_4^{2-}	NO_3^-	Cl^-	Σ cation (C)	Σ anion (A)	C + A	Measured Alk prod.
1976	32.9	2.8	6.7	1.6	2.2	−0.5	1.8	41.5	1.6	5.9	47.5	49.0	96.5	111.7–126.8
1977	13.5	−6.3	−1.1	0.8	7.1	0.3	−2.4	68.4	4.5	−6.3	11.9	66.6	78.5	26.7–109.5
1978	21.0	6.0	14.9	0.5	−10.4	1.7	−1.9	39.5	1.9	16.5	31.8	57.9	89.7	52.0–100.2
1979	6.2	−6.1	−1.3	−0.6	−5.1	3.5	−9.4	5.2	4.5	−18.8	−12.8	−9.1	−21.9	61.6
1980	−16.0	−15.0	−8.6	−4.1	0.4	3.4	−1.4	79.3	6.3	19.8	−41.3	105.4	64.8	105.8
1981	−4.5	−4.6	0.1	−0.9	−13.1	−2.4	−5.4	131.5	8.4	−0.4	−30.8	139.5	108.7	121.8
1982	30.6	−8.8	−2.4	−9.2	9.1	12.6	−10.8	65.1	5.7	9.1	21.1	79.9	101.0	109.4
1983	36.0	−17.2	−5.6	−0.1	−4.1	−4.3	−0.1	105.1	1.5	0.7	4.6	107.3	111.9	66.8
Total	119.7	−49.2	2.7	−12.0	−13.9	14.3	−29.6	535.6	34.4	26.5	32.0	596.5	628.5	655.8–801.9
Total Alk prod. (%)	19	−8	0	−2	−2	2	−5	85	5	4	5	95		

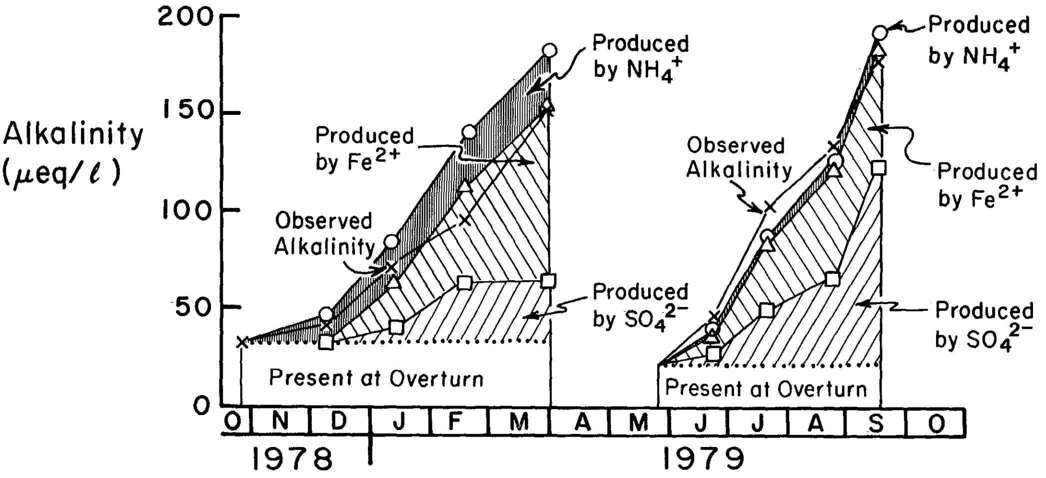

Fig. 2. Observed volume-weighted average alkalinity in the hypolimnion and that predicted from Fe^{2+} production, SO_4^{2-} reduction, and NH_4^+ production. Mn^{2+} also accounts for alkalinity production (9 μeq $liter^{-1}$ in winter and 7.5 μeq $liter^{-1}$ in summer), which were not plotted for the sake of clarity. A description of the calculation technique is given in text. The volume of the 10–14-m zone is 2.22×10^3 m^3 and the area of sediment in this zone is 8.25 ha.

fide formation to remain after overturn, the iron sulfide must not be oxidized back to sulfate. Therefore, the amount of alkalinity permanently gained from sulfate reduction and iron sulfide formation will be equal to the amount of sulfide permanently stored in profundal sediments.

Analysis of the Lake 223 sediments (12–14 m) in 1979 for reduced sulfur species (Cook 1981; Cook and Schindler 1983) revealed an inventory of 25±13 kmol S as FeS and FeS_2. On the basis of the observed sulfate loss from the hypolimnion, 31±5 kmol S as FeS and FeS_2 should have formed between 1976 and 1979 (Cook and Schindler 1983). The preacidification accumulation of FeS was small (Cook and Schindler 1983). Thus, within the uncertainty of the measurements, the sediments in 1979 could have contained the three previous years' accumulation of iron sulfide, and the alkalinity produced by sulfate reduction in the hypolimnion could have remained in the water column. It is possible, however, that some of the reduced S was oxidized and returned to the water at overturn. This is difficult to substantiate because an increase in the whole-lake SO_4^{2-} concentration from hypolimnetic oxidation of reduced S at overturn would be within analytical uncertainty.

Epilimnetic sulfate reduction—We have estimated total sulfate reduction in the epilimnion by subtracting hypolimnetic sulfate reduction from whole-lake sulfur retention (Table 3). All terms in the budget, except epilimnetic sulfate reduction, were independently estimated. The equivalents of sulfate reduced in the hypolimnion were calculated by Cook and Schindler (1983) from depletion of sulfate during stagnation.

In 7 of the 8 years, the amount of sulfate

Table 5. Reactions taking place in the hypolimnion of Lake 223 during stagnation. The form of reactions (a), (b), and (d) is taken from Froelich et al. (1979) with CH_2O representing a simplified Redfield molecule (Redfield 1958). The full Redfield molecule is $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$. The NH_3 in reaction (e) is derived from the NH_3 in the Redfield molecule.

(a) $CH_2O + O_2 \rightarrow CO_2 + H_2O$
(b) $\frac{1}{4} CH_2O + Fe(OH)_3 + 2 H^+ \rightarrow Fe^{2+} + \frac{1}{4} CO_2 + \frac{1}{4} H_2O$
(c) $2 CH_2O + SO_4^{2-} \rightarrow S^{2-} + 2 CO_2 + 2 H_2O$
(d) $CH_2O \rightarrow \frac{1}{2} CH_4 + \frac{1}{2} CO_2$
(e) $CO_2 + NH_3 + H_2O \rightarrow NH_4^+ + HCO_3^-$
(f) $Fe^{2+} + S^{2-} \rightleftharpoons FeS$
(g) $CH_2O + 2 MnO_2 + 4H^+ \rightarrow 2 Mn^{2+} + CO_2 + 3H_2O$

The sum of (b), (c), and (f) is

(h) $\frac{9}{4} CH_2O + SO_4^{2-} + Fe(OH)_3 + 2H^+ \rightarrow FeS + \frac{9}{4} CO_2 + \frac{19}{4} H_2O$

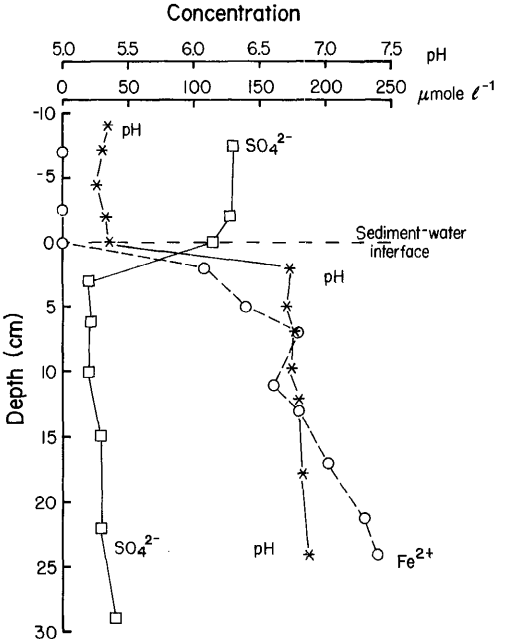

Fig. 3. Porewater pH, sulfate, and Fe^{2+} at 4 m in Lake 223. Sulfate was measured on 25 August 1981 and pH and Fe^{2+} on 12 October 1981.

reduced in the epilimnion was greater than that reduced in the hypolimnion. In 1979, the apparent oxidation of sulfur in the epilimnion nearly balanced hypolimnetic sulfate reduction, with little net storage of sulfur within the lake. One would expect this year-to-year variability in a residual determined as the difference in three terms (inputs, outputs, and changes in storage) each having some uncertainty (5%, 5%, and 10%) (LaBaugh and Winter 1984). Over the 8 years of the experiment, the net mass of sulfate reduced in the epilimnion was greater than twice that reduced in the hypolimnion (Table 3).

Table 6. Epilimnetic (4 m) porewater (SO_4^{2-} gradients and estimated fluxes.

	Concn gradient (μmol liter^{-1} cm^{-1})	Sample interval (cm)	Est. flux* (μmol m^{-2} d^{-1})	Est. flux† (keq/yr^{-1})
25 Aug 81	34.3	0 to −2.8	−97.7	−13
21 Oct 81	53.9	0 to −2.8	−154	−21
5 Aug 82	77.6	−0.5–1.5	−221	−30
26 Jul 83	75.0	−0.5–1.5	−213	−29

* Using a bulk diffusion coefficient of 3.3×10^{-6} cm^2 s^{-1}, based on modeling of tritiated water diffusion (C. A. Kelly and R. H. Hesslein unpubl. data) and data of Li and Gregory (1974).

† Assuming flux at this site is the same as that for entire epilimnetic area (0–10 m, 18.8 ha). Eight-year average loss calculated from whole-lake budget was 47 keq yr^{-1} for the epilimnion (Table 3).

Epilimnetic sulfate reduction examined by analysis of porewater in littoral sediments (4-m water depth) revealed marked sulfate depletion along with an increase in pH and Fe^{2+} (Fig. 3). ΣH_2S concentrations in the porewater were extremely low (<1 μmol liter^{-1}) in July, August, or October of several recent years (Kelly unpubl. data). Because these sediments are anoxic about 1 cm below the surface (Kelly and Rudd 1984), the reactions occurring there are similar to those taking place in the anoxic hypolimnion of Lake 223 (Fig. 1), resulting in loss of SO_4^{2-}, formation of iron sulfide, production of alkalinity, and an increase in pH.

To calculate the rate of sulfate reduction from these porewater data we assumed that all sulfate transported into the sediments by diffusion was reduced. The bulk diffusion coefficient for SO_4^{2-} was calculated from measurements of ^3H_2O diffusion into these sediments (C. A. Kelly and R. H. Hesslein unpubl. data) and the size of the sulfate ion (Li and Gregory 1974). From the sulfate gradient, the bulk diffusion coefficient for sulfate, and Fick's first law, we determined that the amount of sulfate that diffused into the littoral sediments ranged from 98 to 221 μmol m^{-2} d^{-1} (Table 6). The flux rates estimated from porewater profiles (Table 6) were somewhat lower than those estimated by the sulfate budget (8-year average was 340 μmol m^{-2} d^{-1}; Table 3). However, the porewater profiles were only taken from one site. Also this gradient tends to underestimate the true gradient because of the 1-cm resolution of the porewater sampler. The gradient is probably nonlinear and the finer the sampling resolution, the more accurate the calculation. These results show that the epilimnetic sediments can remove sulfate at rates that could account for the magnitude of the losses observed in the whole-lake budget.

Discussion

An estimate of the average natural alkalinity production in Lake 223 before acidification can be obtained by combining alkalinities measured in 1974–1975 with average alkalinity inputs and water renewal rates during the 8 years of our study. During this period, an average of 4.1 keq yr^{-1} entered the lake from precipitation, terrestrial runoff, and the stream from Lake 224. Average annual outflow was 2.26×10^5 m^3 yr^{-1}; at preacidification alkalinity concentrations (101–154 μeq $liter^{-1}$) this means that annual alkalinity losses were 28.2 keq yr^{-1}. If we assume steady state ($\Delta Alk = 0$), 24.1 keq yr^{-1} of alkalinity must have been generated in the lake. On an areal basis this yields a rate of 88.3 meq m^{-2} yr^{-1}, which is comparable to rates in nearby Lake 239 (56.9 meq m^{-2} yr^{-1}: Schindler et al. 1986). Thus, under natural conditions, 85% of the alkalinity of Lake 223 was generated in situ, while only 15% originated outside the lake.

Clearly, while acid additions have caused the lake to become acidic, they have also caused an increase in alkalinity production (from 24 keq yr^{-1}, above, to 82–100 keq yr^{-1} average: Table 1). This increase was the most important factor in determining the amount of acid required to acidify the lake. The next most important factor was the lake's "natural" (preacid) rate of in situ alkalinity production, and least important was the contribution of alkalinity from the watershed. The most important single mechanism was sulfate reduction, which increased in proportion to sulfate concentration (Cook and Schindler 1983; Schindler 1985).

Other scientists have expressed the belief that the high sulfate reduction in Lake 223 is a feature of the anoxic hypolimnion and would not occur in lakes that have totally oxic mud–water interfaces throughout the year. As did Kelly and Rudd (1984), we have shown here that sulfate reduction occurred in littoral sediments, even though the littoral sediments were overlain by oxygen-rich waters. Oxygen is depleted in the upper 1 cm of littoral sediment in Lake 223 (Kelly and Rudd 1984), thereby allowing bacterial sulfate reduction to occur below this depth. On a per unit area basis, reduction rates in the epilimnion (8-yr average of 340 μmol m^{-2} d^{-1}) were similar to profundal rates (8-yr average of 330 μmol m^{-2} d^{-1}: Tables 3 and 6); because of their greater area, littoral sediments contributed twice as much as the hypolimnetic sediments to whole-lake sulfate reduction in Lake 223. Schindler and Turner (1982) showed that sulfate reduction is a high proportion of the mass balance in Lake 114, where the hypolimnion is <1% of the volume. An anoxic hypolimnion is certainly not necessary for the occurrence of bacterial sulfate reduction.

Sulfate reduction occurred in the littoral sediments of Lake 223, although the overlying water was acidic. Sulfate gradients in epilimnetic sediments in 1980–1983 were as steep as those in unacidified ELA lakes (Kelly and Rudd 1984). In addition, a large water-column enclosure experiment showed that an increase in sulfate concentration resulted in steeper sulfate gradients, with the gradients being independent of the pH of the overlying water. The sulfate reduction rates estimated here for the littoral sediments (340 μmol m^{-2} d^{-1}) are much lower than the total decomposition rates in the same sediments (5,000–8,000 μmol m^{-2} d^{-1} in winter, probably larger in summer: Kelly et al. 1984). The overall microbial activity has not decreased as a result of the acidification (Kelly et al. 1984). If it had, this might have decreased the degree of biologically mediated neutralization observed. However, the sulfate reduction rates have increased with the increase in sulfate concentration (Cook and Schindler 1983).

Porewater profiles in the littoral sediments of lakes in northern Wisconsin (R. B. Cook unpubl. data), the Adirondack Mountains, N.Y., southeastern Ontario, and southern Norway (Kelly and Rudd 1984, unpubl. data) also show bacterial sulfate reduction and iron reduction. In all of these cases sulfate and iron reduction were associated with elevated pH within the sediments, with the notable exception of the Norwegian lakes. There sulfate reduction appeared to be offset by sulfur oxidation, resulting in a decrease in pH.

Stuiver (1967) observed that sulfate was reduced in the metalimnion of Linsley Pond at rates approaching those in the anoxic hypolimnion. Hemond (1980) examined input-output budgets for an acidic bog and calculated that 64% of atmospheric H^+ deposition was neutralized by bacterial sulfate reduction and 23% by algal nitrate uptake;

the sink for reduced sulfur in this bog was apparently H_2S lost to the atmosphere. At the ELA, sulfate reduction and deposition of iron sulfides accounted for almost all of the sulfate input to a bog experimentally acidified with H_2SO_4 (S. E. Bayley unpubl. data). Brown (1980) has shown similar results for British peatlands acidified by atmospheric deposition and groundwater. Wright and Johannessen (1980) attributed 30% of the hydrogen ion neutralization in a small Norwegian lake to sulfate reduction. Clearly, sulfate reduction is an important component of the sulfur cycle and alkalinity balance of both acidic and circumneutral lakes and wetlands.

Galloway et al. (1983*b*) calculated that in three Adirondack lakes the inputs of sulfate equaled or were less than outputs and concluded that sulfate reduction was not important. Such conclusions must be questioned, however, due to the difficulty of measuring sulfate inputs from dry deposition and terrestrial runoff with sufficient accuracy in polluted areas. For example, Jeffries et al. (1984) calculated that in lakes of the Sudbury area unmeasurable SO_2 deposition was 1.2–2.6 times the sum of all other acidifying substances. In a recent visit to Woods Lake, one of three lakes studied by Galloway et al., one of us (C.A.K.) found high rates of sulfate reduction and large quantities of reduced sulfur in the sediments, indicating that processes similar to those at the ELA were occurring. In another of the lakes (Sagamore), however, both SO_4^{2-} profiles in porewater and radiosulfate reduction measurements indicated very little SO_4^{2-} reduction.

Increased sulfate reduction does not necessarily lead to increased alkalinity production. In 1982 and 1983, the production of H_2S from enhanced sulfate reduction activity in Lake 223 exceeded the capacity of the Fe^{2+} to form additional iron sulfide and H_2S appeared in the hypolimnion (18–36 μmol liter^{-1}). The mass of sulfates precipitated as iron sulfide may have reached a maximum limited by the supply of reduced aqueous iron, despite high total Fe concentrations in sediments of 650–1,225 μmol g^{-1} (3.6–6.7% Fe, dry wt) (Cook 1981). The neutralization of H^+ by sulfate reduction in the hypolimnion may have also reached a maximum rate. Porewater data from the littoral sediments in 1982 (Kelly unpubl. data) show that Fe^{2+} concentrations were as high as in 1981 (Fig. 3), which suggests that the supply of Fe^{2+} is not limiting iron sulfide formation in the epilimnion. When examining the capacity of sulfate reduction to neutralize H^+, one must consider both sulfate and iron reduction.

The ultimate fate of the SO_4^{2-} removed from the water column of Lake 223 is not entirely certain. The steep SO_4^{2-} and Fe^{2+} gradients in the epilimnetic sediments, plus the ΣH_2S and Fe^{2+} concentrations in the hypolimnion, suggest that formation of FeS and FeS_2 is the major initial mechanism of removal. Detailed whole-lake sulfur budgets showed that insoluble sulfide formation was 10 times the organic-S sedimentation (Cook and Schindler 1983). This is supported by radiosulfate incubations in sediments similar to those in Lake 223. Organic sulfur may be derived from a process other than sedimentation; in the sediments of lakes in northern Ontario it has the same isotopic composition as H_2S formed by dissimilatory sulfate reduction in the sediments, suggesting a common origin (Nriagu and Soon 1985). In 24-h core incubations with radiosulfate, part of the ^{35}S was converted to organic-S (Landers et al. 1983; C. A. Kelly and J. W. M. Rudd unpubl. data). Further, long term (8 month) in situ incubations showed that the ^{35}S in the organic phase was more resistant to conversion to other forms than that in inorganic sulfide phases. Organic sulfur is important in sediments (Nriagu and Coker 1983; Landers et al. 1983; Nriagu and Soon 1985) and is the most abundant form in Lake 223 profundal sediments below 7 cm (Cook 1981; Cook and Schindler 1983). Some sulfur may also be lost through formation of volatile compounds. In all of these mechanisms the effect on H^+ concentration is the same, as long as the SO_4^{2-} is reduced and permanently removed from the water column. The identities and relative persistence of these reduced sulfur compounds are important in understanding freshwater sulfur cycling and may vary among lakes, with different long term consequences for acidification.

As the hydrogen ion activity increases in lakes due to acidic atmospheric deposition, the production of major cations should also increase. At a pH below 5, the reaction of H^+ with alumino-silicate sediments and with $Fe(OH)_3$ will become a more important sink for H^+ within lakes (Last et al. 1980; Henriksen 1980; Schnoor and Stumm 1985).

The release of nonprotolytic cations from soils and sediments has been recognized as controlling natural water acidity (e.g. Dillon *et al. 1980; Dickson 1980; Galloway et al.* 1983*a*; Kahl and Norton 1983). In each case the major source of the cations was thought to be the terrestrial watershed. Evidence from the Elbe River watershed suggests that anthropogenic acidification caused in part by acidic deposition resulted in an increase in cation weathering (Paces 1983). Henriksen (1982) found that the ratio of the increase in cation equivalents in lakes in Norway to the sulfate due to acid precipitation was 0.4 and surmised that the cation increase was caused by terrestrial processes. This ratio was the same in Lake 223, where the watershed was not acidified (the change in storage terms in Tables 2 and 3, 131.6/347.7 = 0.4), showing that processes in Lake 223 were primarily responsible for the increase in cation storage. It is necessary to distinguish between cation production and cation storage in a lake. In practice, when one is dealing with synoptic prediction of lake acidity for small, slowly flushing lakes, cation storage may be a reasonable surrogate for cation production. When water renewal times are shorter, cation production will be considerably greater than cation storage.

Hydrogen ion loading due to acidic deposition will occur to both the terrestrial and aquatic portions of a watershed; much of the acidity will be neutralized by reactions with soils and bedrocks. Because acid was added directly to the water column of Lake 223 the alkalinity-generating mechanism responded to this loading. The alkalinity budget for Lake 223 probably makes within-lake processes seem relatively more important than if the terrestrial watershed were also being acidified. Nevertheless, the lake system clearly neutralized a large portion of the input acid, while the terrestrial watershed did not contribute significantly to the alkalinity budget.

Models of lake acidification (e.g. Henriksen 1979; Thompson 1982; Booty and Kramer 1984; Chen et al. 1984; Christophersen et al. 1982) are primarily concerned with terrestrial mechanisms of H^+ neutralization. Yet here we show, as did Schindler et al. (1986), that in situ biogeochemical processes are far more important sources of alkalinity to extremely acid-vulnerable lakes than are terrestrial inputs. Within-lake biogeochemical processes are important components of the watershed/lake system that should be included in acidification models.

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