

ACID PULSES FROM SNOWMELT AT ACIDIC CONE POND, NEW HAMPSHIRE

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Abstract. A study was undertaken to examine whether 'acid pulses' from snowmelt created permanent changes in a pond's chemistry. Water samples were collected from clearwater acidic Cone Pond in the White Mountain National Forest, New Hampshire. The pond, inlet, and outlet were intensively sampled throughout winter and early spring 1983–84. Thaws brought more H^+ into upper waters of the pond, but most was gone within a week. In contrast, SO_4^{2-} and Al showed dilution with increased streamflow into the pond, and NO_3^- was only detected in ice, slush, and surface waters. Bottom waters were anoxic throughout the winter and had pH 6.0 compared to 4.7 for most of the water column. Alkalinity at the bottom rose from 0 in November 1983 to $190 \mu eq L^{-1}$ in April 1984. Between November and April the pond gained Al but lost SO_4^{2-} and H^+ . Most of the Al gain came after ice-out when loading through the inlet increased, but during the final snowmelt a temporary increase in Al concentration was also seen throughout the water column.

1. Introduction

In the Northeastern United States, HNO_3 and H_2SO_4 derived from the atmosphere can accumulate in the winter snowpack until warmer temperatures cause melting. However, as snow melts it releases dissolved substances unevenly, so that most of the solutes are found in the earliest meltwater fractions (Leivestad and Muniz, 1976; Hornbeck *et al.*, 1977; Johannessen and Henricksen, 1978; Colbeck, 1981). Acid meltwater can mobilize Al as it percolates through soils (Cronan and Schofield, 1979). When meltwater finally reaches streams, lakes, and ponds, it can be high in atmospherically derived pollutants and Al, and can cause abrupt changes in chemistry which may have negative effects on fish and other aquatic organisms (Schofield, 1977). Meltwater with elevated acidity and Al is of special concern in regions receiving acid deposition, and the phenomenon of 'acid pulses' has been documented in Scandanavia (Henricksen and Wright, 1977), Ontario (Jeffries *et al.*, 1979), the Adirondack Mountains of New York (Schofield, 1977) and New Hampshire (Buso *et al.*, 1984). Depression of pH accompanying snowmelt has also been reported in the Rocky Mountains in a watershed not currently receiving acid deposition (Baron *et al.*, 1984). This suggests that severe pH depressions seen in regions affected by acid deposition may be superimposed on an already stressed environment for pH-sensitive biota.

While acid pulses have been extensively documented in streams, their effects on chemistry and biota in lakes and ponds have received little attention. There is potential for significant and long-term changes in water chemistry brought on by acid pulses, given the high volume of water involved in a spring snowmelt event. For example, in New England, the spring snowmelt contributes the largest single input of water to lakes and ponds (Likens *et al.*, 1977). Thus, loading of acidity, Al, SO_4^{2-} and NO_3^- , which are reportedly concentrated in early meltwater runoff, could be at a yearly maximum during snowmelt. However, permanent effects on pond chemistry and biota may be considerably reduced since ice-covered ponds are strongly stratified and resistant to mixing. The acid pulses that enter a water body in a midwinter thaw or during the final snowmelt may have effects that are limited to a narrow stratum just beneath the ice (Schindler *et al.*, 1974; Bergmann and Welch, 1985). The extent to which acidic meltwater mixes with pondwater before exiting via the outlet should depend on the strength of the density gradient resulting from temperature variation in the pond, and on the volume and velocity of the incoming stream.

We designed an intensive sampling program to evaluate physical and chemical changes that were brought on by snowmelt in a pond in the White Mountains of New Hampshire. Objectives were (1) to quantify loading of H^+ , Al, SO_4^{2-} , and NO_3^- to the pond by inlet streams, and removal of these elements by outlet flow, and (2) to follow spatial and temporal patterns in chemistry that resulted from influxes of meltwater.

2. Study Area and Methods

The study area was Cone Pond (N 43°54', W 71°36'), in West Thornton, New Hampshire. Background information on this pond was developed in an earlier study (Buso *et al.*, 1984), including water chemistry data from 3 yr of sampling. Cone Pond is a clearwater acidic pond (volume weighted pH 4.5 to 4.8) with a surface area of 3 ha and mean depth 3.2 m, surrounded by a predominantly coniferous watershed of 60 ha. About 20% of the watershed area is exposed bedrock composed of quartz and mica schists (Bailey, 1984). The pond's maximum depth is 9 m (Figure 1), and its morphometry is such that the top meter occupies more than 25% of the total volume. This suggested that acid pulses were likely to change whole-pond chemistry since they could affect a large percentage of the total volume while remaining in the 0 to 1 m stratum.

Sampling was done at the major inlet stream and the outlet at weekly intervals between February and May, 1984. Water samples from the pond were collected at biweekly intervals from the deepest station and on an occasional basis from other stations. We used access pipes frozen into the ice to reduce mixing of surface water that sometimes results when cutting holes to sample through (Baird *et al.*, 1985). The access pipes also made it possible to record temperature profiles, using a YSI-57 thermistor, from as many as 35 stations around the pond within a few hours (Figure 1). During one thaw, 30-mL samples were collected from all 35 stations at three depths using a hand pump and analyzed for pH and conductivity. For normal biweekly sampling from the pond a peristaltic pump was used to collect samples beginning in early February.

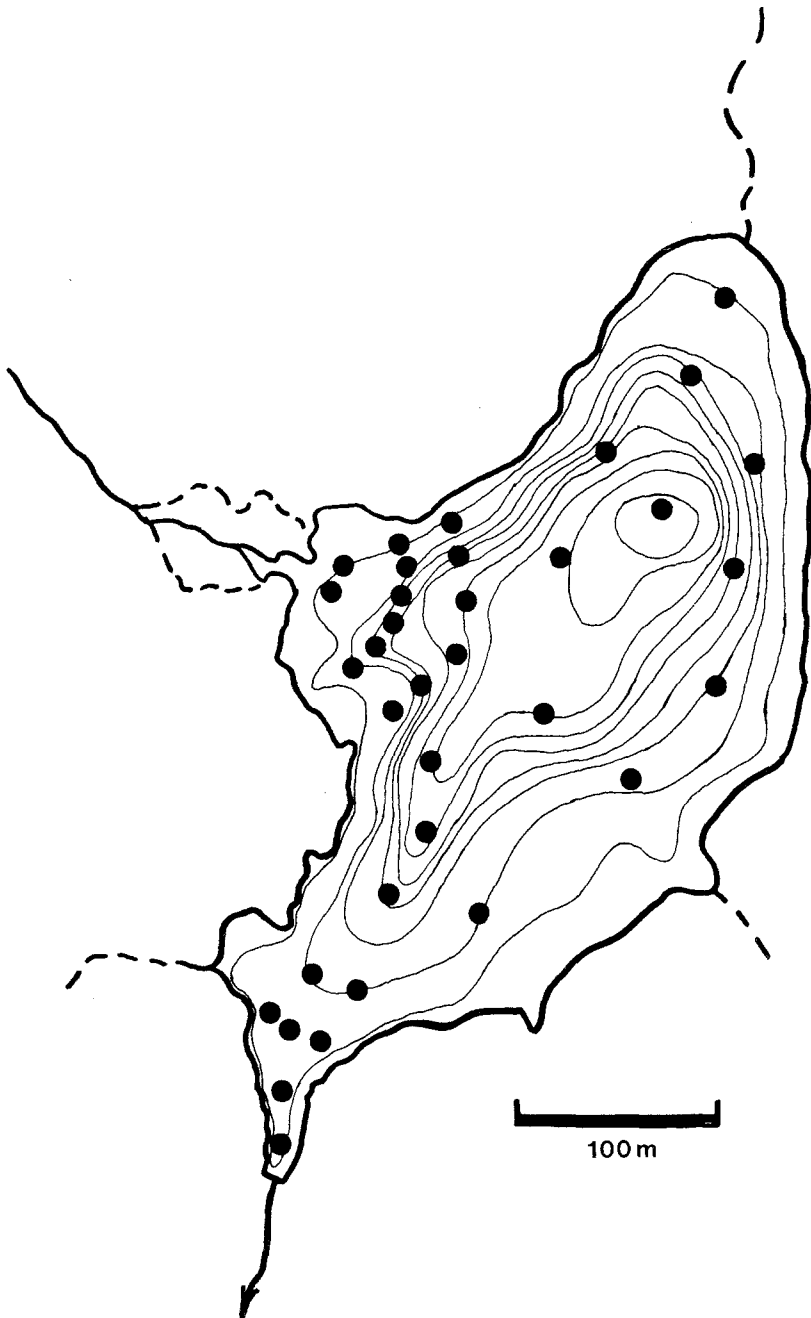


Fig. 1. Morphometry of Cone Pond, with locations of sampling stations. Contour interval is 1 m.

Water samples were analyzed for pH, alkalinity, SO_4^{2-} , NO_3^- , Al, dissolved oxygen (DO) and dissolved inorganic carbon (DIC). pH was measured with an Orion model 407 glass electrode, calibrated with commercial buffers (Fisher) of pH 4.0 and 7.0. Alkalinity was determined by a modified Gran plot analysis after potentiometric titration with 0.01 N HCl (Barnes, 1964). Analyses for SO_4^{2-} and NO_3^- were performed colorimetrically with a Technicon auto-analyzer, using complexation with BaCl_2 and color reduction with methyl thymol blue for SO_4^{2-} (McSwain *et al.*, 1974), and Cu–Cd reduction for NO_3^- (Technicon Inst., 1973). Monomeric Al was measured on a Perkin–Elmer 603 atomic absorption spectrophotometer, after complexation with hydroxyquinoline and extraction with methyl-isobutyl ketone (Barnes, 1975). Extractions for Al were performed within 6 hr of sample collection. Water samples for dissolved gases were collected in ground glass-stoppered bottles, and analyses were done within hours of collection. DO was measured using the Winkler procedure (APHA, 1976) with azide modification. DIC was measured with a gas chromatograph after stripping with acid and helium (Stainton, 1973). All analyses were performed at the Hubbard Brook Experimental Forest Laboratory 10 km distant in West Thornton, N.H. except for Al, NO_3^- and SO_4^{2-} , which were done at the U.S. Forest Service Forestry Sciences Laboratory in Durham, N.H. Samples for NO_3^- and SO_4^{2-} were frozen prior to analysis.

In the absence of measured streamflow entering and leaving Cone Pond, we used a computerized hydrologic model, BROOK (Federer and Lash, 1978) to simulate daily streamflows throughout the season. BROOK is a sophisticated model which uses daily measurements of temperature and precipitation, along with watershed parameters such as soil characteristics, slope, aspect, exposed bedrock area, and leaf area index, to simulate daily streamflow as a unit depth. This was combined with watershed size to obtain flow in $\text{m}^3 \text{ day}^{-1}$ throughout the season (Baird, 1984). Temperature and precipitation were taken from a Hubbard Brook weather station with similar aspect and elevation to Cone Pond. Soil characteristics such as thickness of the rooting zone and unsaturated zone, conductivity, and water storage properties were assumed to be similar to those at Hubbard Brook. Modeling studies performed to compare BROOK's simulated hydrographs with measured streamflow in the Hubbard Brook Experimental Forest show accuracy of $\pm 3\%$ (Hornbeck *et al.*, 1986), compared to an error range of 3 to 5% associated with stream gage measurements.

Water and ion input-output budgets were prepared by modeling pond outflow with BROOK, using carefully measured changes in pond water level along with morphometry to evaluate water storage at each sampling visit, and then solving the water balance equation for stream input. Chemistry measured at the major inlet stream was assumed to be representative of all surface inflows over the season. We have no information about the relative importance of groundwater in the water budget of Cone Pond, but the watershed's extremely shallow depths to bedrock and abundant outcroppings make it reasonable to assume negligible input from groundwater.

3. Results

Profiles of temperature and chemistry measured on March 8, 1984, are typical of those seen before ice-out (Figure 2). A strong temperature stratification is seen with the thermocline between 0.5 and 1.5 m. Above the thermocline, chemistry was variable

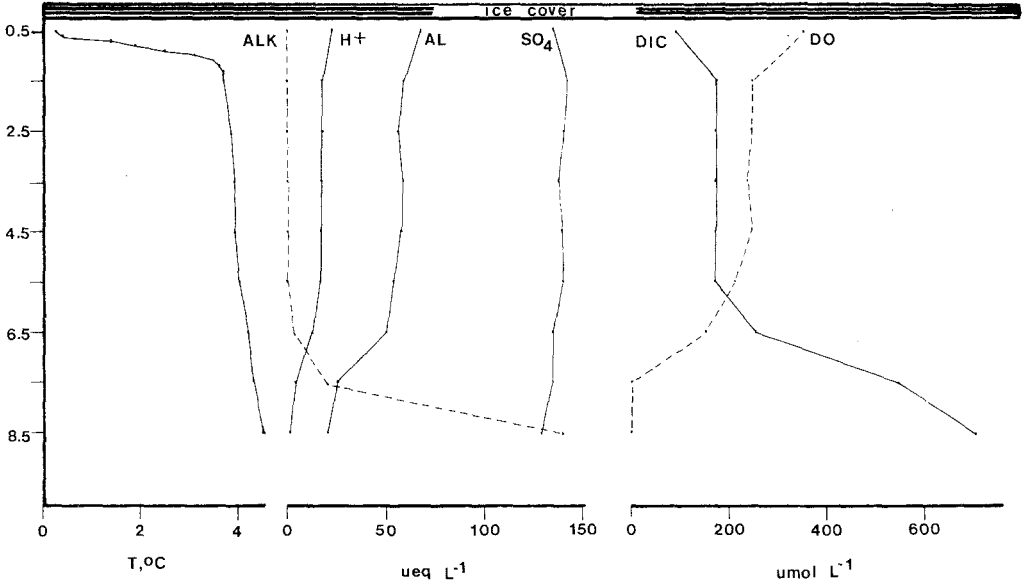


Fig. 2. Depth profiles of chemistry, Cone Pond, March 8, 1984.

throughout the season because of floating streamwater and dilution from melting ice. Below the thermocline, oxygen saturation remained consistent to a depth of 5.5 m, where depletion became apparent. DIC was high in these anoxic bottom waters, and pH at the bottom was 6.0 on March 8, compared to 4.7 at the surface and 4.8 for most of the water column. Alkalinity, which was never detected at the inlet and is typically zero in Cone Pond samples (Buso *et al.*, 1984), was 140 $\mu\text{eq L}^{-1}$ at 8.5 m on March 8, and was as high as 190 $\mu\text{eq L}^{-1}$ on April 6. NO_3^- was never detected in inlet samples, and was only found in water derived from melting ice in the pond.

The effect of acid streamwater on surface waters was most pronounced in the midwinter thaw which occurred in late February (Figure 3). H^+ concentration rose at the inlet, outlet, and 0.5 m stratum, suggesting that a layer of relatively acid water covered the pond. Analysis of surface water temperature gain and loss associated with the midwinter thaw, based on temperature profiles at 30 stations, shows that the colder more acid streamwater affected the inlet stations most strongly and lowered temperatures slightly at most stations (Figure 4). In contrast, the major snowmelt in April did not decrease surface water temperatures over the entire pond (Figure 5), and there were temperature gains or no change at 9 out of 30 stations. pH and conductivity measured

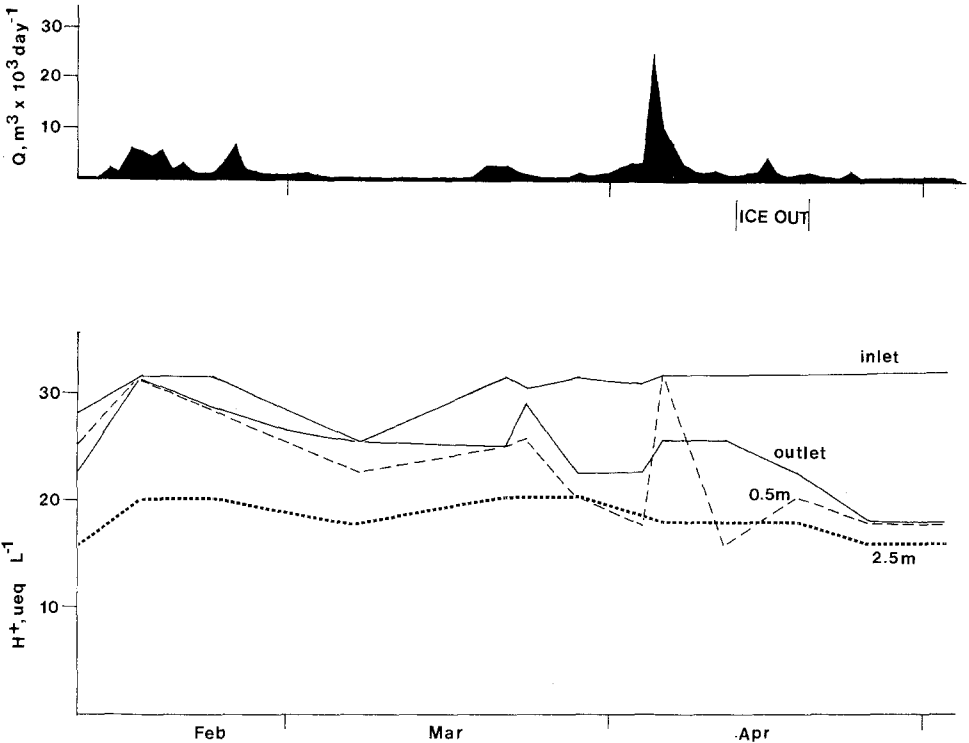


Fig. 3. Hydrogen ion concentration, $\mu\text{eq L}^{-1}$, at inlet, outlet, 0.5 and 2.5 m, February 10–May 3, 1984. Upper graph shows modelled streamflow at the major inlet.

at three depths for 35 stations in late March also support the idea that acid meltwater was confined to surface waters near inlet streams (Baird *et al.*, 1985).

Al concentrations at the inlet, outlet and 0.5 m did not increase during melt periods (Figure 6). This was in contrast to what was expected, based on the idea of acid mobilization of Al in forest soils during snowmelt. Hooper and Shoemaker (1985) conducted intensive stream sampling concurrently with our study in a study of Al mobilization during high-flow periods at Watershed 3 in the Hubbard Brook Experimental Forest. They found higher streamwater concentrations of Al in the midwinter thaw compared to later melts, and suggest that in early and mid-winter labile Al accumulates in soils where it is flushed out by the first thaw. Yet in the final snowmelt at Cone Pond, a dilution effect from melting ice was evident, especially in surface waters (0.5 m). Deeper waters showed an Al gain during the final snowmelt, although this was not permanent (Figure 6). Acid meltwater in the littoral zone could have mobilized Al from sediments there, and density currents resulting from temperature instabilities could move this Al-rich water deeper into the pond.

Input-output budgets for H^+ , Al, and SO_4^{2-} (Table I) show unexplained gains for H^+ and Al between February and May, along with a loss of SO_4^{2-} . An evaluation of storage changes between fall turnover in November 1983 and spring turnover in May

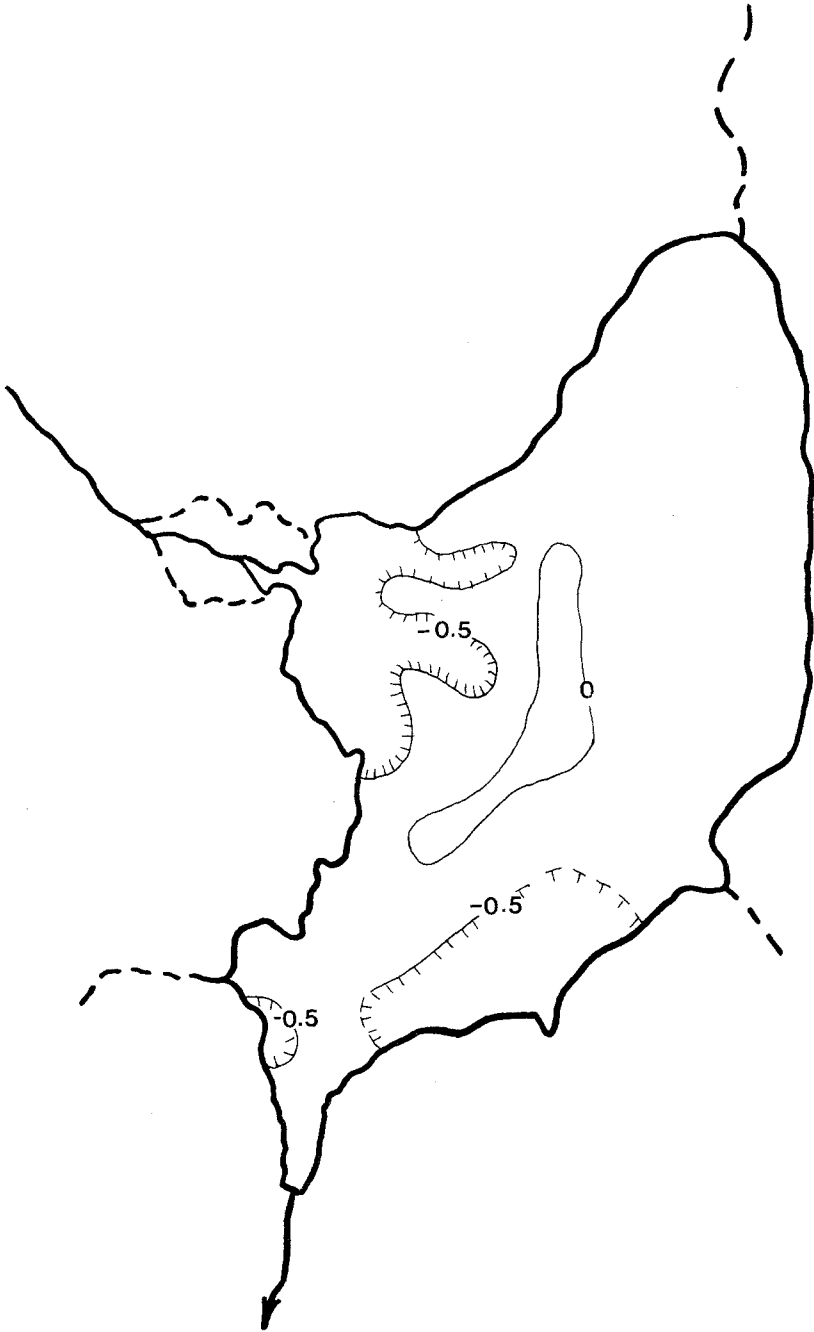


Fig. 4. Measured change in temperature ($^{\circ}\text{C}$) at 0.9 m depth at 30 stations between February 10 and February 16, 1984, Cone Pond.

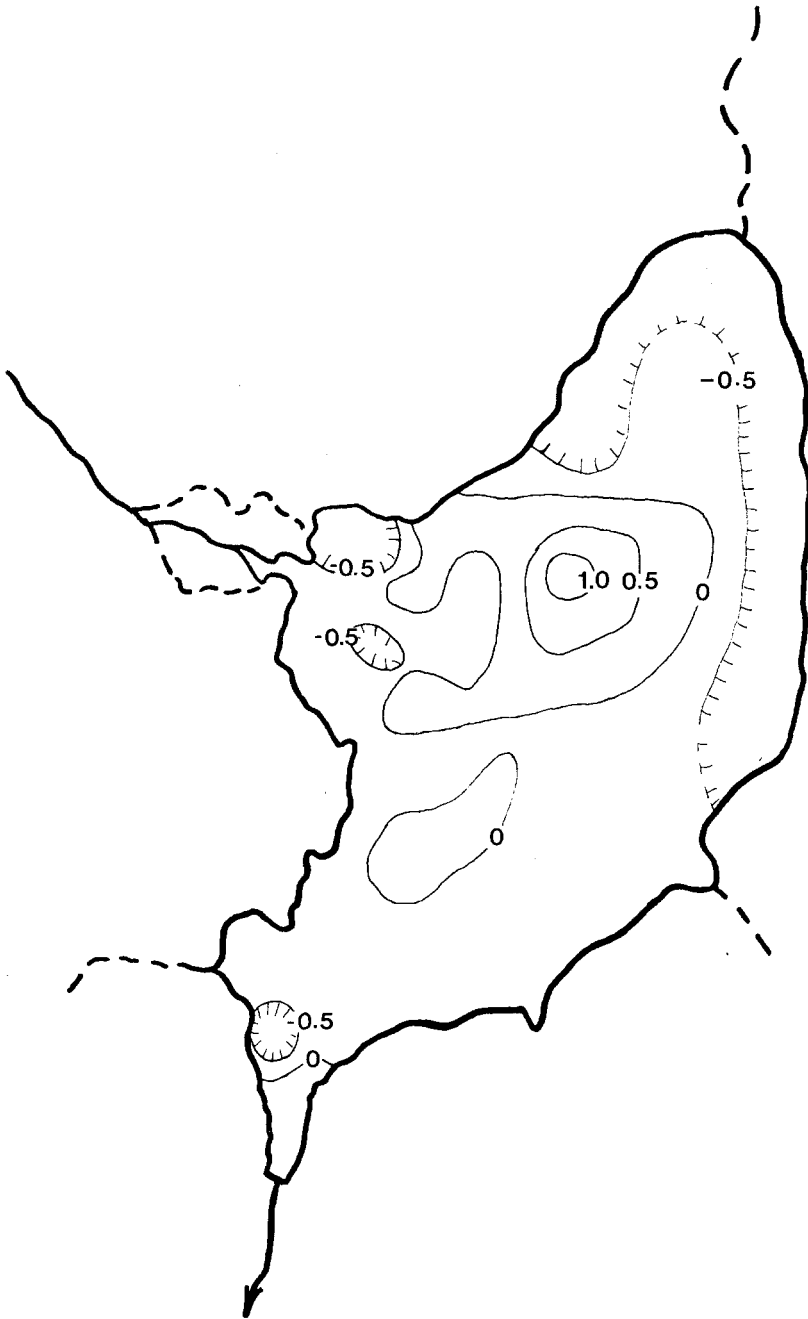


Fig. 5. Measured change in temperature ($^{\circ}\text{C}$) at 0.9 m depth at 30 stations between February 10 and April 6, 1984, Cone Pond.

TABLE I
Budgets for H^+ , Al, and SO_4^{2-} , Cone Pond, winter 1983-1984. Values in equivalents (kg)

	In, Feb.-May (1)	Out, Feb.-May (2)	Measured storage change, Feb.-May ^a (3)	Unaccounted for, Feb.-May ^b (4)	Measured storage change, Nov.-Feb. ^c (5)	Net change Nov.-May ^d (6)
H^+	7.16 (7.16)	5.52 (5.52)	0.33 (0.33)	1.31 (1.31)	-0.96 (-0.96)	-0.63 (-0.63)
Al	16.6 (149)	14.0 (126)	1.29 (11.6)	1.27 (11.4)	-0.767 (-6.9)	0.523 (4.7)
SO_4^{2-}	34.4 (1650)	30.0 (1420)	-0.27 (-13)	-5.04 (-242)	-2.94 (-141)	-3.21 (-154)

^a Measured change of load in water column between 10 February and 3 May, 1984.

^b (1)-(2)-(3).

^c Measured change of load in water column between 8 November, 1983 and 10 February, 1984.

^d (3) + (5).

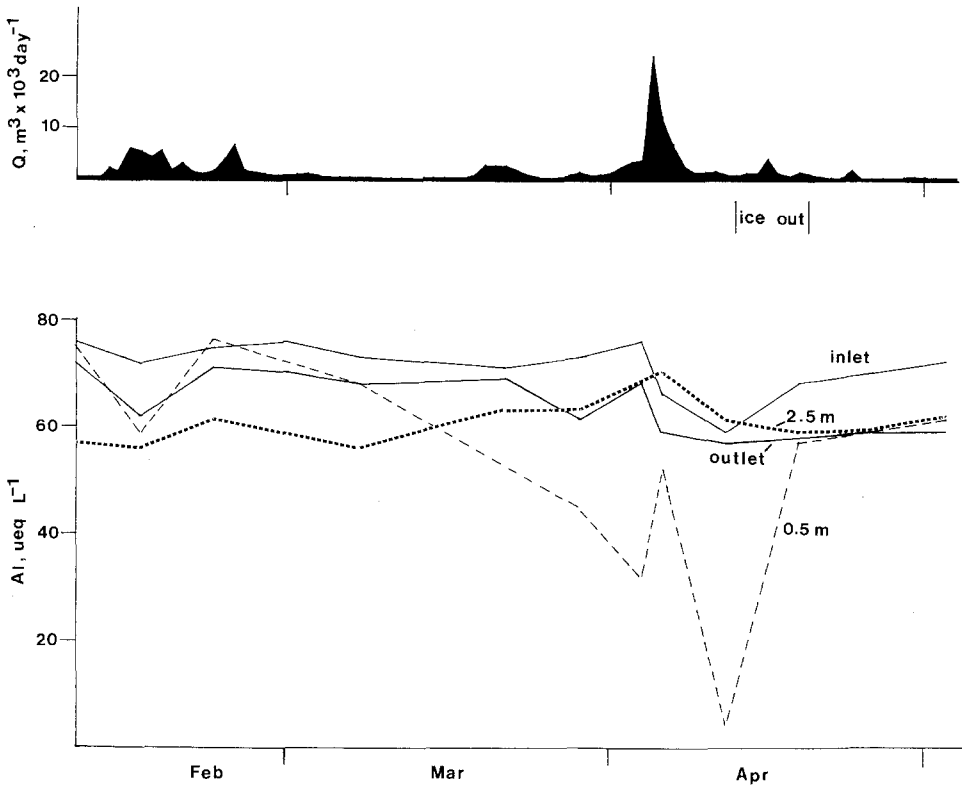


Fig. 6. Monomeric Al concentration, $\mu\text{eq L}^{-1}$, at inlet, outlet, 0.5 and 2.5 m, February 10 to May 3, 1984. Note scale is compressed compared to Figure 3. Upper graph shows modelled streamflow.

1984 shows that over this period Cone Pond lost H^+ (-0.639 eq) and SO_4^{2-} (-3.21 eq) but gained Al (0.523 eq). By comparing measured loads in the water column, it was possible to evaluate storage changes between November and February, a period when weekly measurements were not made. Based on these measured storage changes, November–February was a period of recovery for Cone Pond. Volume-weighted pH rose from 4.65 in November to 4.90 in February, and then decreased to 4.80 in April.

The loss of SO_4^{2-} and H^+ seen in Cone Pond over the winter could be explained by SO_4^{2-} reduction in the anoxic hypolimnion. It has been suggested that when lakes receiving acid deposition become anoxic, SO_4^{2-} reduction is favored because there is abundant SO_4^{2-} in such lakes (Kelly *et al.*, 1982; Kilham, 1982a; Cook *et al.*, 1986). Alkalinity production by biological activity has been noted in Precambrian Shield lakes, including the experimentally acidified Lake 223 (Schindler *et al.*, 1986), with higher rates of SO_4^{2-} reduction seen with increased SO_4^{2-} loading. At Hubbard Brook, the longterm average value reported for S loading is $12.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in bulk precipitation and $6.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ as gaseous or aerosol input (Likens *et al.*, 1977). However, at Cone Pond the coniferous forest may provide a more efficient aerosol trap than the hardwood forest at Hubbard Brook, so that the Hubbard Brook value for S loading may

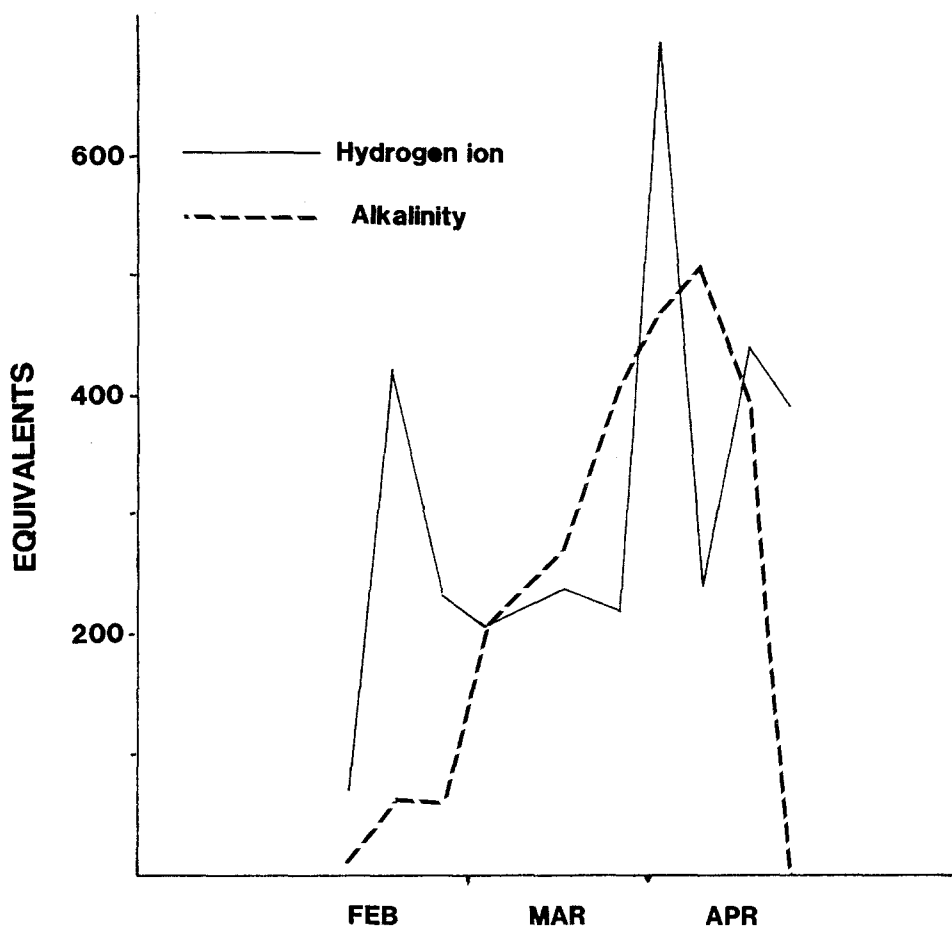


Fig. 7. Stored mass of H^+ in 0–1 m stratum (solid line) compared to alkalinity in 3–9 m stratum (dashed line), Cone Pond, February 10–May 3, 1984.

underestimate aerosol inputs at Cone Pond. Cone Pond's inlet stream often has very high SO_4^{2-} concentrations; Buso *et al.* (1984) report concentrations as high as 12 mg L^{-1} at the inlet (February 1980), and found that the pond itself has high SO_4^{2-} concentrations compared with five similarly sized ponds in the area which were also studied.

A comparison of the mass of alkalinity present in Cone Pond with the mass of H^+ in the top stratum (Figure 7) shows that additions of H^+ during thaws were of the same magnitude as the steady increase in alkalinity in the bottom waters, i.e., the addition of H^+ in acid pulses between February and May 1984 was balanced by internal alkalinity production. This is surprising in light of the relatively small volume of the anoxic hypolimnion, about 4000 m^3 compared with 27000 m^3 for the top stratum. However, the alkalinity produced by SO_4^{2-} reduction in lakes during anoxic periods is permanent only if the sulfide produced is precipitated in the form of FeS (Kelly *et al.*, 1982). H_2S

is rapidly reoxidized to H_2SO_4 in the aerobic part of the water column, or when it is recirculated through a lake during turnover. High Fe concentrations are required for H_2S to precipitate as FeS ; measured iron from anoxic Cone Pond bottom waters ranged from 1 to 6 mg L^{-1} .

4. Discussion

Acid pulses can profoundly affect streams, but their effects were limited to pond surface waters in this study. Based on our results, the deeper waters of ponds could provide shelter for stream organisms that cannot tolerate acid pulse conditions. Despite the short-term nature of this study, our observations at Cone Pond can be generalized to other water bodies because of physical factors that limit the mixing of acid pulses and pond water. Because of the high volume of water in the final snowmelt, the highest loading of solutes from the snowpack to water bodies will come during the final snowmelt in early spring. However, at this time ice cover and stratification are still present. The time period between snowmelt and ice-out will vary from year to year, but snowmelt will always precede ice-out because the water equivalent of lake ice is generally higher than that of the snowpack. The strong temperature stratification seen under ice cover will tend to prevent mixing between cold streamwater and warmer lakewater, as has been demonstrated in arctic lakes (Bergmann and Welch, 1985). In contrast, autumn rains during turnover provide stream inputs that can readily mix with pond-water, and may be more important in permanently changing water chemistry, as was seen in Norway (Henricksen and Wright, 1977).

The importance of ice cover in maintaining a strong temperature stratification suggests that in regions where ice cover is short in duration or where lakes circulate throughout the winter, loading from acid pulses could substantially change whole-lake chemistry. Climatic or meteorological effects which influence the length of the turnover period in fall may vary from year to year, and will also be important determinants of the susceptibility of lakes to acid pulses. The extent of mixing during thaws will also be related to residence time of the water body, so that lakes with short residence times would be more likely to show changes in chemistry due to acid pulses. At the same time, a short residence time would imply a relatively fast recovery for the lake after an acid pulse event.

Our intensive sampling suggests strategies for evaluating acid pulse effects in lakes and ponds. The vertical extent of acid pulses was related to temperature stratification, and the horizontal extent was related to location and chemistry of inlet streams. The effects and severity of acid pulses during thaws will be overestimated if only surface samples are collected, particularly at stations near acidic inlet streams. Alkalinity production was strikingly apparent from our results, and was an unexpected finding because Cone Pond is so acidic.

The study of acid environments such as Cone Pond can warn us of what might be expected from acidification that results from human activities, and may shed light on regional effects of acid deposition by relating pond chemistry to the chemistry of

precipitation. However, it should be noted that Cone Pond is anomalous in several ways. Its chemistry is dominated by mineral acids now, but paleolimnologic studies suggest that it has been an acid lake for thousands of years (Ford, 1984). This demonstrates the inadvisability of relying on a single chemical parameter, pH, as an indicator of acidification from human activities. The watershed experienced a major fire in the early 1800s, so that although it is now completely forested and free of human habitation, it cannot be regarded as having a disturbance-free history. The absence of NO_3^- in the inlet stream was unexpected given that nearby Hubbard Brook streams are high in NO_3^- in early spring, and suggests unusually efficient N cycling or denitrification in the Cone Pond watershed. There are a number of *Sphagnum* bogs in the watershed, and the pond itself is fringed by *Sphagnum* and ericaceous shrubs. *Sphagnum* prefers poorly drained, acidic environments, and once established it keeps its surroundings acid by releasing organic acids (Kilham, 1982b). Thus acidification here is a complex interaction of terrestrial and aquatic ecology along with acid deposition.

Acknowledgments

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