EFFECTS OF NITRATE ON THE ACIDIFICATION OF THE AQUATIC SYSTEM

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1 Introduction

The occurrence of precipitation that is more acidic than expected from the atmospheric carbon dioxide equilibrium has now been well documented (1). The ionic composition of acid precipitation has been documented by Galloway et al. (2), Schneider et al (3), and Barrie (4), among others. The complex relationships of the precipitation composition to emission sources, however, are not treated in this paper. For purposes of this discussion, the estimates of Galloway and Dillon (5) that, in the northeastern United States and Canada, SO_4^{2-} contributes 65 percent to the precipitation acidity while NO_3^- contributes most of the balance have been used. The pH of the precipitation may be modified by basic cations, including NH_4^+, but the purpose of this report is to examine the importance of the NO_3^- deposition in relation to the acidifying effects on the aquatic regime.

2 Nitrogen Utilization by the Biosystem

As indicated above, SO_4^{2-} and NO_3^- in precipitation contribute the primary acidifying anions. NH_4^+ may also be present in significant amounts and this nitrogen species also enters the reactions that affect the acidity of water systems. Each of these ions may undergo assimilation and consequent reactions in the biosystem. It is the ability of the biosystem to reduce the sulphur and nitrogen previously oxidized by combustion processes that determines the relative importance of these substances in acidification processes. Reuss (6) has provided an exhaustive treatment of the interactions that may be expected to affect the alkalinity or acidity of the system.

Deposited SO_4^{2-} may undergo reduction in either the terrestrial or aquatic systems. Assimilation of SO_4^{2-} by plants would generate OH^- that would, in part, neutralize the acidity contributed by deposition of H_2SO_4. While Johnson et al. (7), cited cases where SO_4^{2-} is retained and presumably reduced in significant amounts, Thompson (8) has shown that in a gross sense, the SO_4^{2-} deposited by precipitation shows a high degree of agreement with the load carried by the waters of eastern Canada. Thus, while

Kerekes et al. (9) found that the organic regimes of Nova Scotia may be reducing some portion of the SO_4^{2-}, it appears generally valid to assume that the SO_4^{2-} deposited represents a direct alkalinity demand on the aquatic system.

The relative nitrogen reaction within the terrestrial aquatic systems has been well presented by Galloway and Dillon (5). Their adaptation of a schematic reaction from Reuss (6) is a convenient illustration of the simplified reactions that may be important (Figure 1). Because NH_4^+ is not a product of automobile emissions, it will not be considered further here except to note that most NH_4^+ contained in precipitation is retained and presumed to be assimilated in the terrestrial system. It therefore contributes to the acidification of the terrestrial regime and may, in some cases, make small contributions to acidification of the aquatic regime.

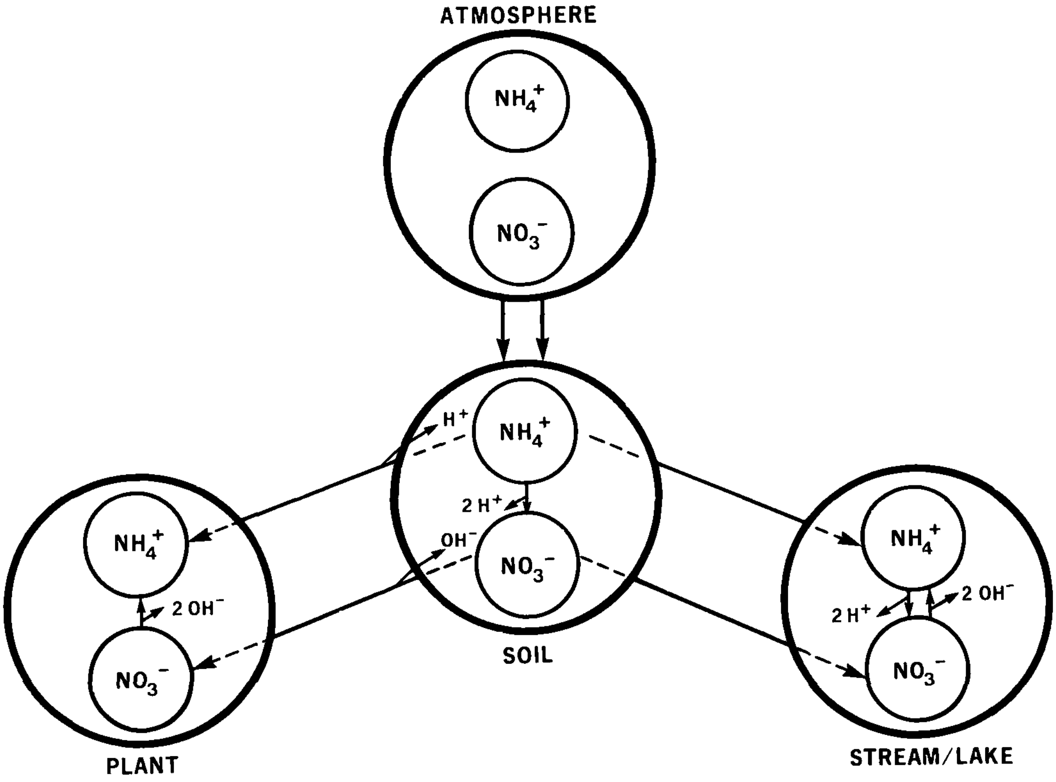

FIGURE 1 SIMPLIFIED NITROGEN CYCLE (6)

NO_3^- may undergo assimilative uptake and reduction by either terrestrial or aquatic plants as an essential plant nutrient. Such assimilation produces one equivalent of alkalinity for each equivalent of NO_3^- assimilated and may serve to neutralize the acidity related to the HNO_3 deposition. Decay of plant growth may reverse this reaction or may result in partial production of organic acids (10). However, for the period over which biomass is accumulating and for biosystems that are nitrogen limited, it may be expected that the major portion of the available NO_3^- will be assimilated. In the forestry practice of eastern Canada, forest harvest removes biomass prior to forest maturity so that continued uptake of nutrients may be expected to prevail.

In biosystems that have reached maturity, are limited in growth by disease or insect predation or are growth limited by other nutrient deficiency, it may be found that all available NO_3^- is not utilized. A special case of short duration is the inactive growth period in winter. An example of an aquatic system limited by availability of phosphorus is Lake Superior, where nitrate is accumulating apparently in response to an increase in atmospheric deposition (11). Specific cases of mature forest may also be observed where all of the available nitrate cannot be utilized.

3 Nitrate Contribution to Long-term Acidification of Waters

Nitrate that is deposited on a drainage basin may reach the waters of lakes or streams either by direct surface deposition or by deposition on the terrestrial portion of the basin and subsequent interaction with the soils and biosystem during transport to the surface waters. In basins of the sensitive regions of Canada, direct deposition to the water surface constitutes less than about 10 percent of the total deposition and the surface water chemistry is controlled primarily by flow from the basin.

The nitrate retention and assimilation by the biota of the terrestrial system is dependent upon the state of activity of the biosystem, upon the length of time of transit and on the degree of soil penetration. Thus the effects of the nitrate on the waters of lakes and streams are expected to be related to the biosystem activity (season or temperature) and to the terrestrial residence time (rate of flow) in addition to the terrestrial basin properties.

If NO_3^- is not delivered to the waters from the terrestrial basin, there is no contribution to the water acidity. If NO_3^- is a significant anion in the waters it may be associated with a cation from the soils or may remain as nitric acid to contribute acidity to the waters. By examining the relationship between the NO_3^- deposited to a basin and that delivered to the waters, the maximum potential contribution to the water acidity may be estimated. The annual average nitrogen budgets of several watersheds are shown in Table 1 (12). On a mean annual basis, a large portion of the nitrogen (including NO_3^-) deposited on a basin is retained and only a small portion reaches the waters. Thus the larger portion of the NO_3^- is not available to contribute to the acidity of the waters and

TABLE 1 NITROGEN BUDGETS (kg/ha/annum) FOR VARIOUS TERRESTRIAL ECOSYSTEMS OF THE WORLD (12)

Climate	Location	Precipitation input	Streamwater output	Net gain or loss
TEMPERATE: mostly angiosperm and deciduous forest	Coshocton, OH, U.S.	20	2.5	+ 17.5
	Hubbard Brook, U.S.	20.7	4.0	+ 16.7
	Southeast U.S.	2	1	+ 1
	Silverstream, New Zealand	2.2	1.8	+ 0.4
	Taughannock Creek, NY, U.S.	9.7	5.6	+ 4.1
	Walker Branch, TE, U.S.	8.7	1.8	+ 6.9
TEMPERATE: mostly coniferous and evergreen forest	Birkenes Watershed, Norway	14.5	2.2	+ 12.3
	Carnation Creek, Vancouver, Canada	2.7	1.1	+ 1.6
	Cedar River, WA, U.S.	1.1	0.6	+ 0.5
	ELA, Ontario, Canada	6.4	0.9	+ 5.5
	Finland	6	2	+ 4
	Storsjon, Sweden	10.0	2.3	+ 7.7
	Velen, Sweden	5.9	0.4	+ 5.5
	Western Cascades Range, OR, U.S.	2.5	1.2	+ 1.3
TEMPERATE: bog vegetation	Rough Spike Catchment, England	8.2	3.0	+ 5.2
TROPICAL: angiosperm mostly evergreen forest	Rio Negro, Brazil	5.6	4.7	+ 0.9
TUNDRA: low shrub vegetation	Kuokkel area, Sweden	1.15	0.97	+ 0.18

some portion of that deposited to the basin may have contributed alkalinity to the system through assimilation by the biota. Further convincing evidence that NO_3^- deposition is not significantly related to long-term surface water acidification has been provided by studies in the Muskoka-Haliburton Lakes which show the variations of the H^+/NO_3^- and H^+/SO_4^{2-} for several lakes having a pH ranging from 4.08 to 6.18 (13,14). These observations (Table 2) indicate that the H^+ concentration, or acidity, of the waters has no relation to the NO_3^- concentrations. pH values less than 5.5 could not be explained on the basis of nitric acid. In these lakes, SO_4^{2-} is always present in concentrations sufficient to explain the observed acidity.

These observations give strong evidence that NO_3^- deposited on sensitive basins is, on a mean annual basis, largely utilized by the basin biota and is not a significant factor in acidification of surface waters on that time scale. However, in short episode events with emphasis on periods of inactive biological growth, terrestrial utilization of the NO_3^- as a nutrient may be restricted.

4 Nitrate Contribution to Short-Term Episodic Acidification

In the climatic conditions of eastern Canada, the primary hydrologic event that produces strong peaks in surface water runoff is the snow-melt episode. The accumulation of precipitation in the snow pack continues for up to several weeks during which time the surface discharge is reduced to nearly base-flow. The water accumulation, with the associated ionic content, is released to the basin in a few days of spring melt, often accompanied by rain. This melt occurs frequently during the winter in the Atlantic provinces but most often only in the spring in Québec and Ontario. In all cases, it occurs during biologically inactive periods. The rapid increase in water supply greatly reduces terrestrial contact time. In some cases, the surface soils are frozen, further restricting infiltration.

During snow-melt the surface waters are subjected to a rapid change in water supply often associated with large change in ionic composition. A net increase in H^+ content (pH depression) of surface waters has been documented during the snow-melt period in northern Europe, northeastern United States and eastern Canada.

Measurements of the ionic content of the snow pack in the Algoma area of Ontario have illustrated the processes that produce the rapid change in surface water composition at the time of snow-melt (15). Figure 2 shows the cumulative snow pack water and ionic content during the winter of 1981. The water content accumulates gradually and there is a general proportional increase in ionic content. The H^+ content

TABLE 2 MEAN AND RANGE OF pH VALUES, MEAN H^+/NO_3^-, H^+/SO_4^{2-} AND SO_4^{2-}/NO_3^- RATIOS (Calculated as μeq/L) FOR 21 HEADWATER STREAMS IN MUSKOKA-HALIBURTON, ONTARIO 1976-1980.
Data is from an ongoing study, methods and study areas as described in Jeffries *et al.* (13) and Scheider *et al.* (14)

Stream	Mean pH	Range pH	H^+/NO_3^- (μeq/L)	H^+/SO_4^{2-} (μeq/L)	SO_4^{2-}/NO_3^- (μeq/L)
Dickie 11	4.08	3.53 - 5.61	93.60	0.457	245
Red Chalk 2	4.30	3.68 - 4.81	60.00	0.188	265
Dickie 5	4.34	3.71 - 4.76	58.30	0.318	233
Dickie 6	4.35	3.74 - 5.05	60.20	0.297	247
Dickie 10	4.59	3.92 - 5.10	25.90	0.119	170
Chub 2	4.82	4.12 - 6.08	23.90	0.071	236
Dickie 8	5.03	4.04 - 5.87	12.60	0.049	284
Harp 6A	5.19	4.34 - 6.39	9.57	0.028	337
Harp 5	5.34	4.66 - 6.60	2.49	0.017	145
Chub 1	5.41	4.48 - 6.61	5.49	0.019	232
Harp 3	5.64	4.89 - 6.39	1.05	0.009	156
Harp 6	5.77	5.20 - 6.90	0.83	0.007	130
Red Chalk 1	5.81	5.19 - 6.69	1.74	0.009	174
Red Chalk 3	5.95	5.17 - 6.65	0.21	0.006	34
Harp 3A	5.95	5.30 - 7.30	0.29	0.004	100
Red Chalk 4	5.96	5.28 - 6.71	0.24	0.006	37
Jerry 3	5.98	5.27 - 6.67	0.51	0.004	134
Jerry 4	6.07	5.49 - 6.55	0.46	0.003	118
Harp 4	6.08	5.29 - 6.90	0.15	0.003	57
Blue Chalk 1	6.16	5.71 - 6.62	0.67	0.003	198
Jerry 1	6.18	5.58 - 6.74	0.04	0.003	14

reaches a maximum before melting begins but remains high. SO_4^{2-} always exceeds NO_3^- on an equivalent basis.

It is significant that the ionic content decreases more rapidly than the water content when melt occurs. The differential loss of ions produces a discharge of early meltwater from the snow pack having higher ionic concentrations and lower pH than the

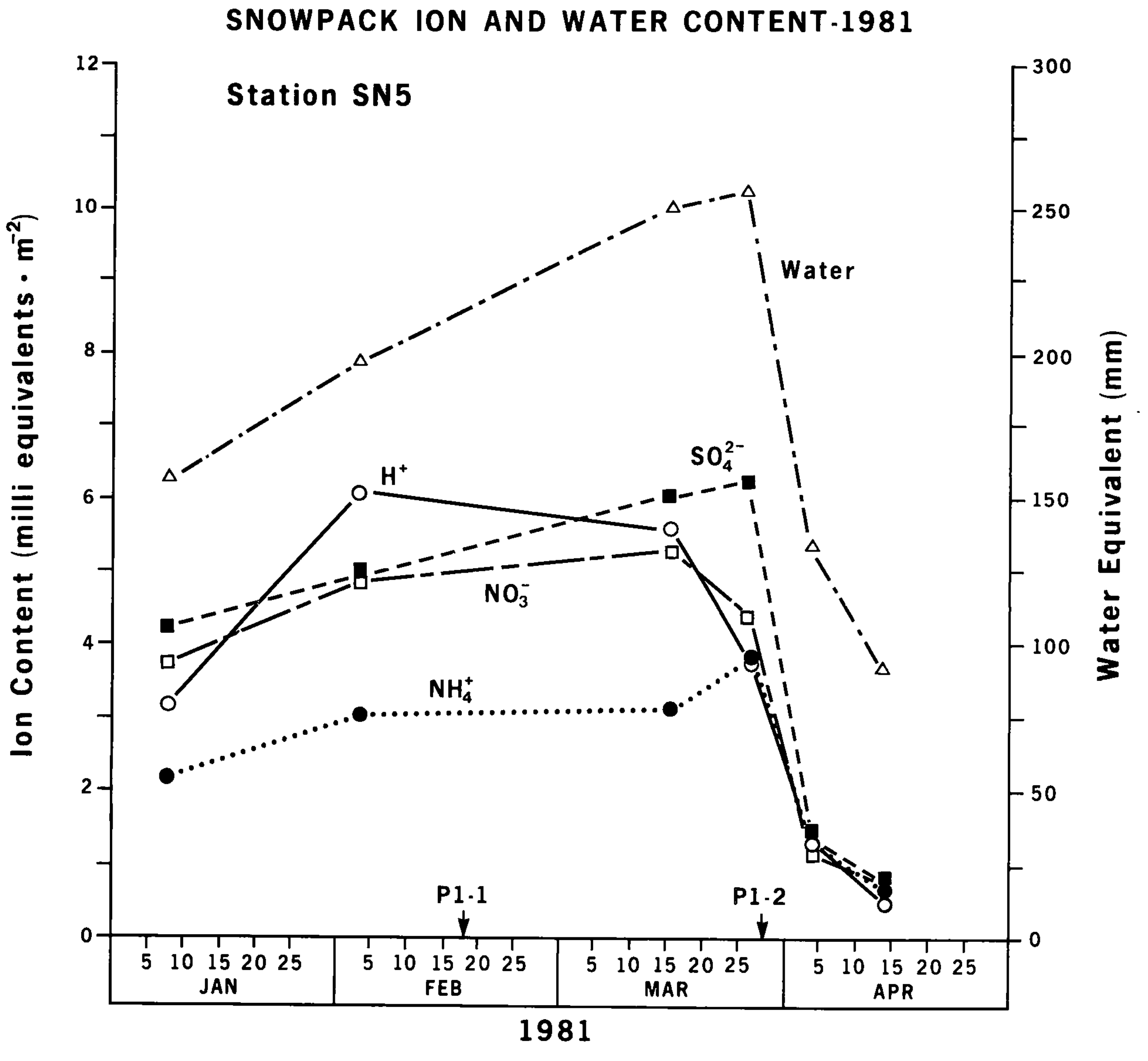

FIGURE 2 HYDROGEN ION, SO_4^{2-}, NO_3^-, NH_4^+, AND WATER CONTENT OF SNOWPACK, JANUARY TO APRIL 1981 (15)

mean of the snow pack or the winter snow. The late snow-melt produces water of very low ionic strength approaching that of distilled water.

The water discharge from the snow-melt causes a decrease in alkalinity of the surface waters by a) dilution of the waters and a decrease in the basic cation concentration, b) an increase in the NO_3^- concentration, and c) a possible change in the SO_4^{2-} concentration. These changes in major ion concentration result in a significant increase in H^+ to retain an ionic balance (Figure 3).

Actual measurements of such short-term changes in surface water ionic concentrations have been carried out at a few locations for several years (5,13,15,16,17). The observed changes have been highly dependent upon the meteorological events that determine the surface water hydrograph in addition to the chemistry of the precipitation that forms the snow pack. One year may have a very heavy snow cover that melts quickly and is possibly associated with rain. This type of a melt episode gives rise to a short but severe pulse in the watershed. Another year may have an equal or lesser snow pack but have large losses by sublimation and a gradual melt over a longer period resulting in a time-broadened and less intense pulse. Data do not yet exist to define an "average", "typical" or "extreme" event for any location.

Galloway and Dillon (5) used the relative contribution of cation dilution, NO_3^- and SO_4^{2-} concentration to the alkalinity decrease observed during the spring snow-melt as a measure of relative importance of each factor. Data from Panther Lake and Woods Lake in New York are shown in Table 3. Additional data for the Turkey Lake basin (15), and for Lake Laflame (17) are included. These examples illustrate that the alkalinity decrease and associated pH depression is the result of dilution by melt waters of low basic cation concentration. However, increases in NO_3^- concentration may often be of sufficient amounts to produce a total loss of alkalinity or acidified conditions.

The changes in SO_4^{2-} concentration during the melt episode and the concentrations relative to NO_3^- are important to note. Sulphate has not appeared to undergo the changes in concentration in the melt waters that would have been expected from the ionic content of the snow pack. Actual decreases in concentration have been observed. While this relative constancy in discharge concentration appears to remain unexplained, it is highly important to note that SO_4^{2-} concentrations in all cases have remained substantially greater than NO_3^-. Thus, SO_4^{2-} remains the primary acidic anion of the waters even during the peak of the melt episodes and may be considered the baseline on which the further pH depression due to NO_3^- is imposed. While it is clear that the NO_3^- contribution may be as great as 40 μeq/L, this is imposed on an already existing alkalinity

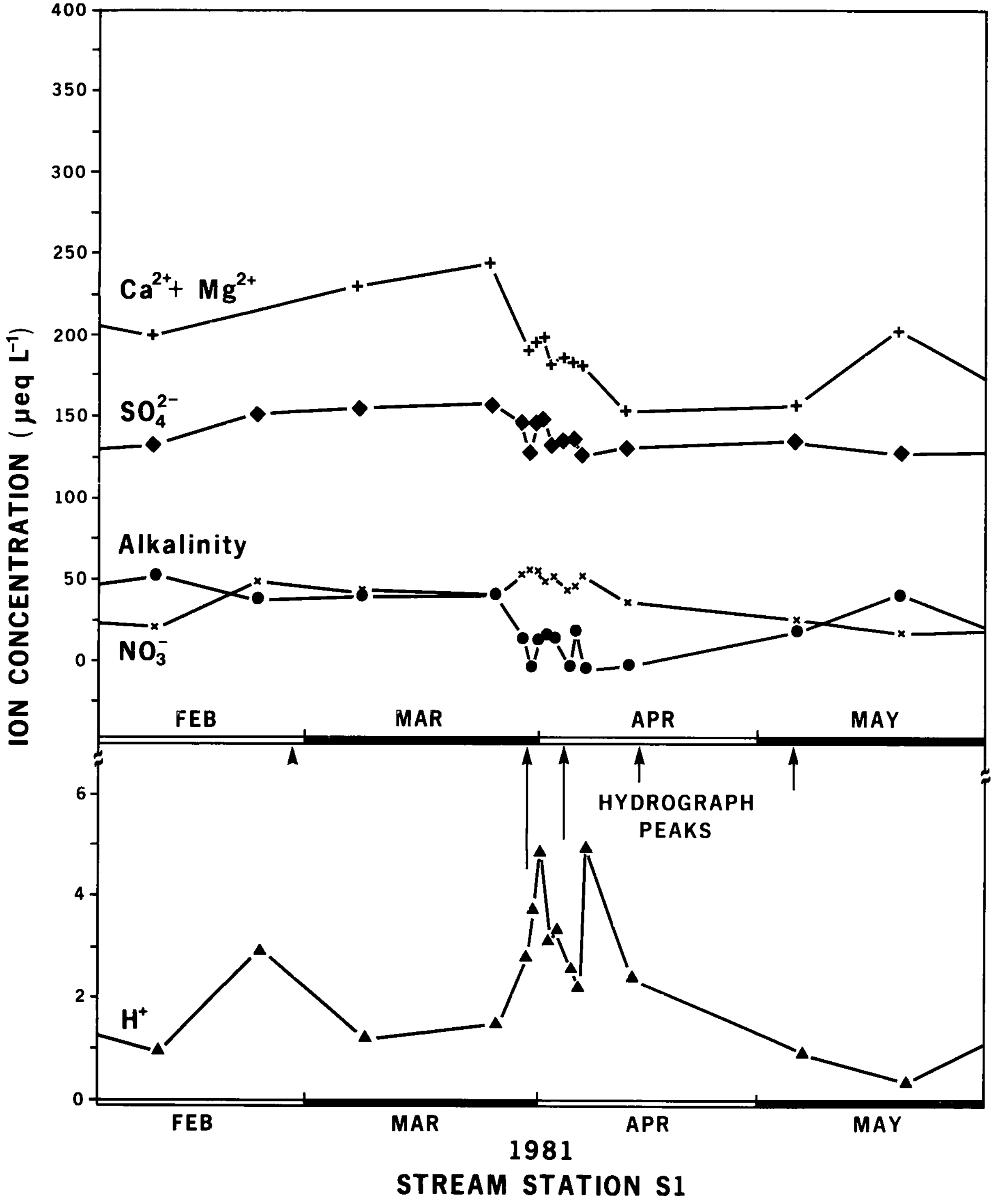

FIGURE 3 VARIATION IN THE CONCENTRATION OF CA^{2+} + Mg^{2+}, SO_4^{2-}, ALKALINITY, NO_3^- AND H^+, TURKEY LAKE OUTFLOW, FEBRUARY TO MAY 1981 (15)

TABLE 3 CONTRIBUTION OF SO_4^{2-}, NO_3^- AND CATION DILUTION TO THE DECREASE IN ALKALINITY DURING SPRING SNOW MELT

Location	Alkalinity Decrease	Cation Dilution	NO_3^- Change	SO_4^{2-} Change
Panther Lake[a] N.Y.	170 µeq/L	125 µeq/L	31 µeq/L	8 µeq/L
Woods Lake[a] N.Y.	41 µeq/L	10 µeq/L	31 mg/L	0 µeq/L
Turkey Lake[b] Ontario	43 µeq/L	38 µeq/L	14 µeq/L	-35
Lac Laflame[c] Quebec			40 µeq/L	Small

a Data from Galloway and Dillon (5).
b Data from Jeffries and Semkin (15).
c Data from Charette (17).

deficit of greater than 100 µeq/L due to the SO_4^{2-}. In the presence of the high SO_4^{2-} excess, the additional pH depression due to the NO_3^- will produce critical acidic levels where the levels due to SO_4^{2-} alone may only have been marginal. In the counter sense, a reduction in the baseline SO_4^{2-} levels may be expected to raise the alkalinity on which the pH depression of the NO_3^- pulse is imposed. Fewer critical situations would be expected to occur.

5 Summary

Most of the evidence available from drainage basins of northeastern United States and eastern Canada indicate that nearly all of the atmospheric deposited NO_3^- is being retained by the terrestrial system on a long-term average basis. This appears to indicate that the nitrogen is being assimilated by the biosystem which would imply biomass accumulation (forest growth) and associated alkalinity production. Local exceptions such as Lake Superior where phosphorus limitation prevents biosystem utilization of nitrate or cases of mature or disease limited systems likely occur. Under the forest management practices of Canada these conditions are not likely to be of importance.

The primary concern for atmospheric deposited NO_3^- remains with its contribution to the pH depression associated with the snow pack melt episode. This depression, when imposed on the surface waters where alkalinity has been depressed due to excess SO_4^{2-}, results in levels of acidity that may be critical even though the long-term average acidity remains acceptable for biological habitats. Such spring snow-melt pH depression episodes occur at sensitive life stages of many aquatic organisms (18). Because such events are the result of hydrologic circumstances, as discussed previously, in addition to the levels of atmospheric deposition, their occurrence may be irregular or even infrequent. The frequency and severity is determined by meteorological factors independent of the atmospheric deposition.

There is not sufficient monitoring information on surface waters of Canada to permit a quantitative estimate of the portion of the Canadian resources subject to critical levels of pH depression episodes. However, a rough approximation may be obtained by examining the profiles of alkalinity observed in waters of sensitive areas. Figure 4 shows the distribution of alkalinity observed in surveys of several districts of Ontario (19). Only three districts have a small percentage of lakes with negative alkalinity (acidified) on an annual basis. However, these districts and one other have a much greater percentage (up to 20 percent) of lakes having alkalinity less than 40 µeq/L. As shown above, the alkalinity demand of the acidic NO_3^- in the melt episode may, under critical hydrologic conditions, be as great as 40 µeq/L.

From this analysis, the critical spring pH depression episode due to present levels of NO_3^- deposition imposed on present levels of SO_4^{2-} deposition may increase the numbers of lakes experiencing critical conditions by up to 20 percent in sensitive regions. A reduction in NO_3^- deposition would likely reduce the number of lakes experiencing critical melt expisodes but it must be observed that a reduction in SO_4^{2-} deposition would accomplish the same purpose and would also reduce the chronic long-term acidification. It is unclear how the reduction of NO_3^- deposition would influence the long-term acidification if biomass accumulation and associated alkalinity production were influenced. If the biological assimilation and production of alkalinity are significant, a loss of NO_3^- could cause some small net increase in system acidity.

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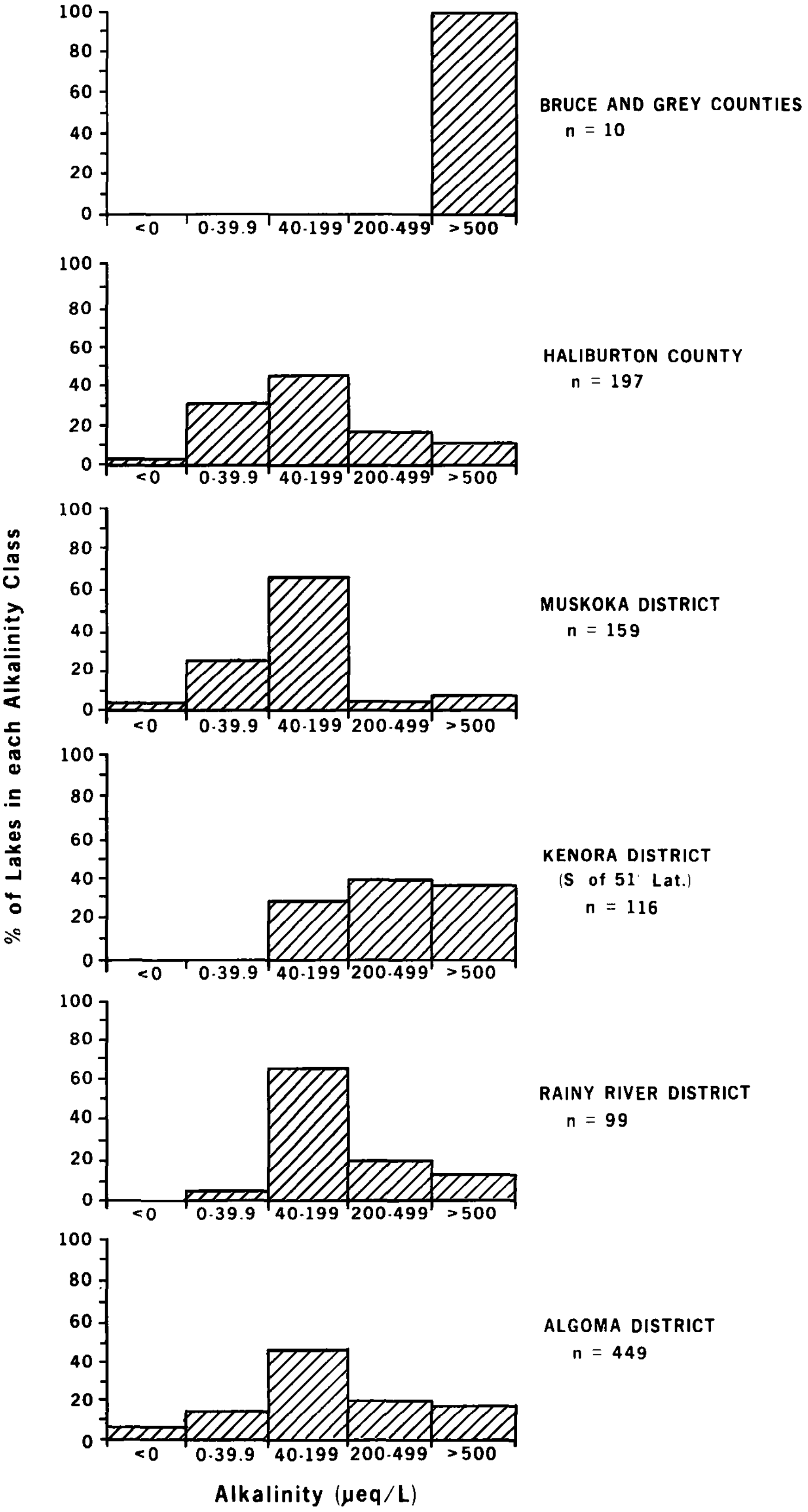

FIGURE 4 DISTRIBUTION OF ALKALINITY VALUES FOR LAKES IN SIX REGIONS OF ONTARIO (19)

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