

TEMPORAL VARIATIONS IN SOLUTE CONCENTRATIONS OF MELTWATER AND FOREST
FLOOR LEACHATE AT A FORESTED SITE IN THE ADIRONDACKS, NEW YORK

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ABSTRACT

During winter 1984-85, the chemical quality of snowpack meltwater was compared with that of forest floor leachate to evaluate the chemical transformations that occur to meltwater as it moves through the forest floor. Meltwater and forest floor leachate were collected from 2.9-m² stainless-steel pan lysimeters in a hardwood forest in the west-central Adirondack Mountains, New York. Fractionation of solutes from the melting snowpack produced the highest solute concentrations in meltwater at the onset of melting and was followed by a progressive decrease in concentrations. Sulfate was eluted preferentially from the snowpack during the major melt in February. Concentrations of sodium, chloride, and sulfate in the first meltwater sample collected for the major melt in February were 5.5 to 9 times greater than those in the snowpack, and were comparable throughout the melt to those of the corresponding forest floor leachate. However, hydrogen, potassium, ammonium, and nitrate were enriched in the meltwater as it passed through the forest floor; for February and March, enrichment of these constituents in leachate averaged 2.1, 4.9, 3.4, and 2.6, respectively. Nitrification and decomposition of organic matter in the unfrozen soils probably caused the solute enrichment.

INTRODUCTION

Acidification of surface waters during snowmelt has been observed in the northeastern United States (Galloway et al., 1980; Driscoll and Schafran, 1984; Driscoll et al., 1987) and in Eastern Canada (Jefferies et al., 1979). In the Adirondack Mountains, New York, this acidification is accompanied by an increase in nitrate concentration whereas sulfate concentration remains relatively constant, as is shown for streamwater draining a small forested catchment in the west-central Adirondacks in figure 1. Solute concentrations in melting snow have been observed to fractionate, which produces the highest concentrations in meltwater at the onset of snowmelt (Johannessen et al., 1977; Johannes et al., 1980). Increased stream acidity during snowmelt has been attributed to the concentrated release of nitric acid from the snowpack

in northeastern North America (Galloway et al., 1980; Semkin and Jeffries, 1986; Galloway et al., 1987) and, in general, to the elution of nitric and sulfuric acids from the snowpack in other areas (Jacks et al., 1986; Tranter et al., 1988).

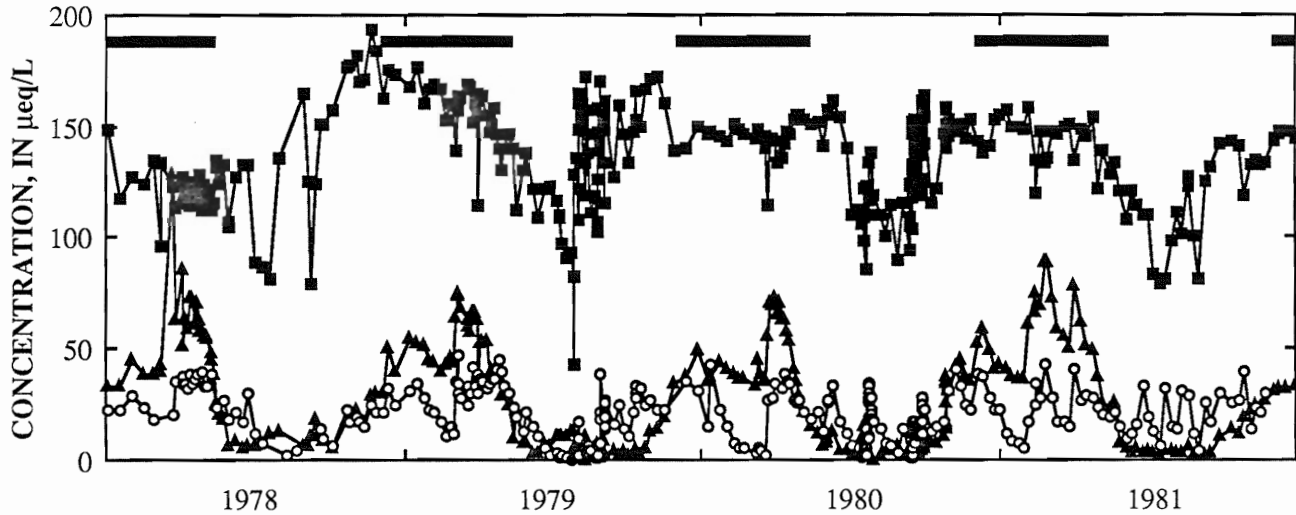


Figure 1 Solute concentrations of Woods Lake tributary in the west-central Adirondack Mountains, New York for the winters of 1978-81. Solid bars denote the winter periods from December through April; sulfate is shown as squares; nitrate is shown as triangles; and hydrogen is shown as circles.

Any chemical alteration of meltwater along its flow path to a stream obscures the degree to which the chemical composition of meltwater can be associated with that of streamwater. Therefore, to link the composition of meltwater to that of streamwater, it is important to investigate the chemical transformations that may occur along the hydrologic pathways taken to the stream. In forested ecosystems in the northeastern United States, it is probable that a high percentage of the water released from snowmelt infiltrates the forest floor, particularly in areas where the floor is unfrozen. For many of these systems, water may infiltrate the forest floor and move vertically into the mineral soil, but some water may move laterally across the forest floor (Peters and Driscoll, 1987). Interactions of meltwater with the forest floor can produce large changes in meltwater composition. For example, in a study of temporal variations in the chemical composition of snowmelt and runoff in northern Michigan, Cadle et al. (1987) observed much higher sulfate concentrations in runoff than in meltwater, which was attributed to watershed release of the sulfate. They also noted that nitrate was much lower in runoff than in meltwater, which indicated watershed retention of the nitrate. In this paper, results from a field study of snowmelt at a northern hardwood site in the west-central Adirondack Mountains, New York, are presented. The purpose of the study was to assess the effect of the forest floor on the chemical composition of meltwater as it relates to the sources of streamwater acidity, mainly nitric acid, during the snowmelt period.

METHODS

The chemical composition of snowpack, meltwater, and forest floor leachate were monitored during the 1984-85 winter in a northern hardwood forest at the south end of Twitchell Lake in the west-central Adirondack Mountains, New York (figure 2). In addition, the quality and quantity of atmospheric deposition was monitored 3 km southeast of the study site by the Electric Power Research Institute (EPRI). The forest at the study site is dominated by beech, red maple, and sugar maple, and soils are spodosols developed on till, which is underlain by a granitic gneiss.

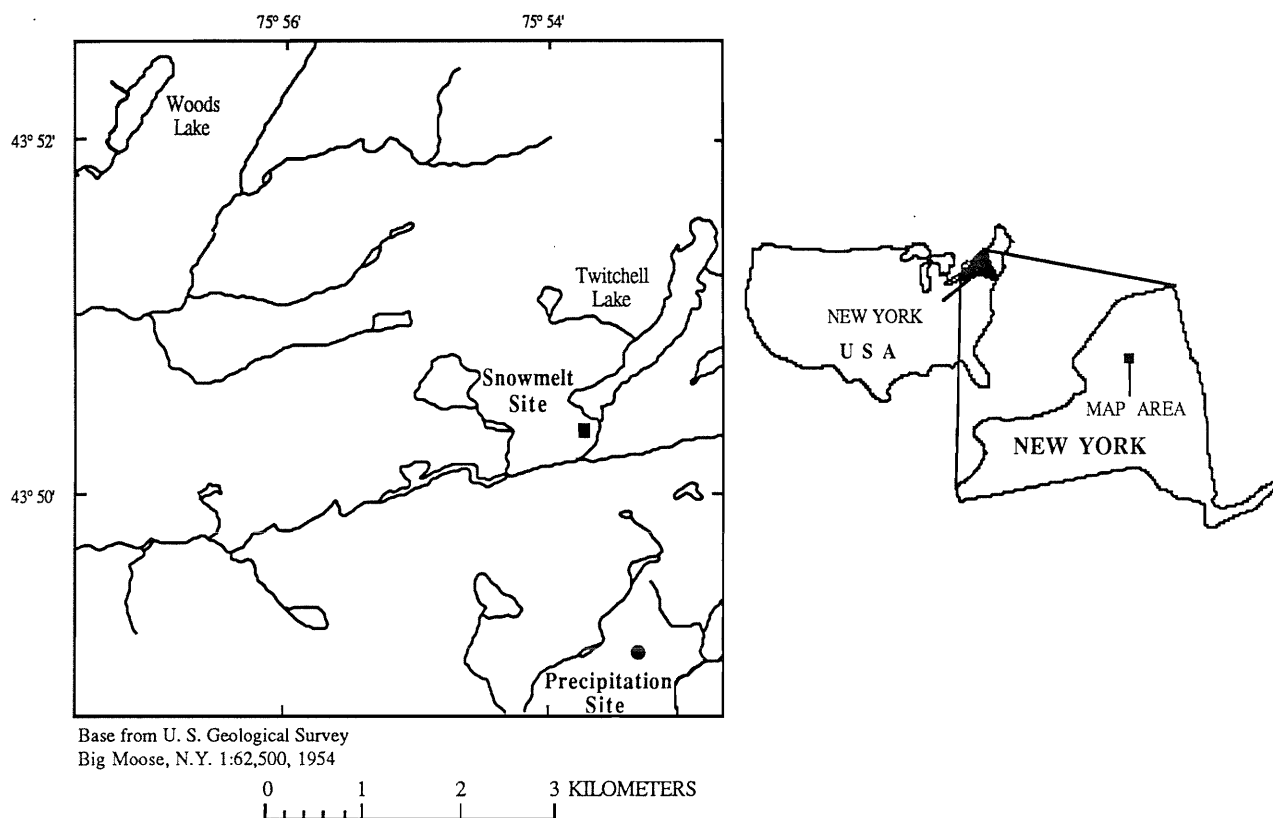


Figure 2 Location of snowmelt experiment.

The depth and water equivalent of the snowpack were recorded weekly for a 10-station snow course by using a depth-graduated, fiberglass Adirondack snow tube and spring scale. Additionally, more frequent measurements of depth and water equivalent were made during snowmelt periods at four 9-m² plots; at each plot, snowcores were collected with the fiberglass tube and placed in polyethylene bags for chemical analysis.

In October 1983, stainless-steel pan lysimeters were installed to collect meltwater and forest floor leachate. Paired 2.9-m² lysimeters, one for meltwater and one for leachate, were installed at two of the snowcore plots which were 250 m apart. One lysimeter was installed on top of the forest floor for meltwater collection. The second lysimeter was installed by excavating the forest floor to the top of the mineral horizon (10-20 cm) in 0.5-m² blocks, and setting the lysimeter on top of the mineral horizon. The blocks of forest floor were then placed in the lysimeter. A pit, which

housed a 20-L collection vessel, was excavated downslope and partially below the 5-cm drain in each lysimeter; an insulated plywood enclosure was built around the pit. One of the two lysimeter sites was designated as a primary site from which samples (snowpack, meltwater, and forest floor leachate) were collected as often as daily during major melt periods. Samples were collected less often at the second lysimeter site because these data primarily provided a check on the spatial variability of the quantity and quality of the snowpack, and the quality of the meltwater and forest floor leachate. Comparisons of data between sites indicate no statistically significant differences in the chemistry for all constituents except potassium and chloride. In addition, there was some concern that the excavation of the forest floor may have induced mineralization/oxidation reactions which would cause hydrogen and nitrate concentrations to be elevated (Vitousek et al., 1979). Therefore, sampling was conducted in the first winter (1983-84) as reported by Rascher et al. (1987) and again the following winter, as reported herein for comparison. The same solutes enriched in leachates collected during the winter 1984-85 also were enriched in leachates collected during winter 1983-84 (Rascher et al., 1987). The similarity of results from 1983-84 to those herein indicate that the forest floor had equilibrated prior to sampling in the first year. Data are missing for the leachate during the melts at the end of March and the beginning of April because a dead mouse was found in the drain of the lysimeter. The mouse caused rather dramatic increases in some of the major solute concentrations such as sodium, chloride, ammonium, and potassium.

Samples of snowpack, meltwater, and forest floor leachate were analyzed on the same day for pH and specific conductance. Samples were kept chilled and, generally, processed within a few days for analysis of all major chemical solutes by using: ion chromatography for sulfate, nitrate, and chloride; atomic absorption spectrophotometry for calcium, magnesium, potassium and sodium; and the alkaline phenol method for ammonium (for specific information concerning analytical methods, see Rascher et al., 1987).

RESULTS

Hydrologic characteristics of 1984-85 snowmelt

Five major melt periods occurred during the 1984-85 winter, and each was initiated by rainfall or mixed precipitation, or atmospheric warming. The snowpack aggraded to a depth of 30-cm and a water equivalent of 9-cm on December 28 and it eroded to a depth of 8-cm and a water equivalent of 2-cm in response to about 14 cm of rain on December 28-29. In 1985, the snowpack progressively aggraded through January and early February (figure 3). From February 22 through 24, 4 cm of rain produced the second major melt which resulted in higher stream discharges than any of the subsequent melt periods, except the final melt which began in the middle of April. Prior to the February melt, the snowpack depth was 80 cm and the snowpack water equivalent was 16.5 cm. The melt caused the snowpack to decrease to less than half of its premelt depth and it caused the snowpack water equivalent to decrease to 13.7 cm. A minor melt occurred in mid-March and three more major melts similar to the February melt occurred in April.

Chemical variations in meltwater and forest floor leachate

The concentration of all solutes in meltwater or forest floor leachate were highest at the onset of snowmelt and declined as melting continued (figure 4). The decrease in solute concentrations was most pronounced for the February melt. For the sequence of five samples collected during the minor melt in March, meltwater solute concentrations increased in the second sample coincident with the melt and decreased thereafter, except for chloride. The high meltwater chloride concentrations occurred at the end of the sequence after the melt had ceased. They coincided with high chloride concentrations in snowfall, and may have resulted from the leaching of chloride from the new snow. Changes in sulfate concentrations in meltwater during this minor melt were similar to those of the leachate, but generally were much higher. The effect of the forest floor on the sulfate concentrations in the meltwater was greater during this melt than for the melt in February.

For the last major melt, which occurred in April, all solute concentrations in meltwater generally were lower than in the corresponding leachate. At this time, most of the solutes had been depleted from the snowpack and the higher concentrations in the leachate were the result of releases from the forest floor. The variability in meltwater solute concentrations were caused by the variability in solute concentrations in the concurrent precipitation.

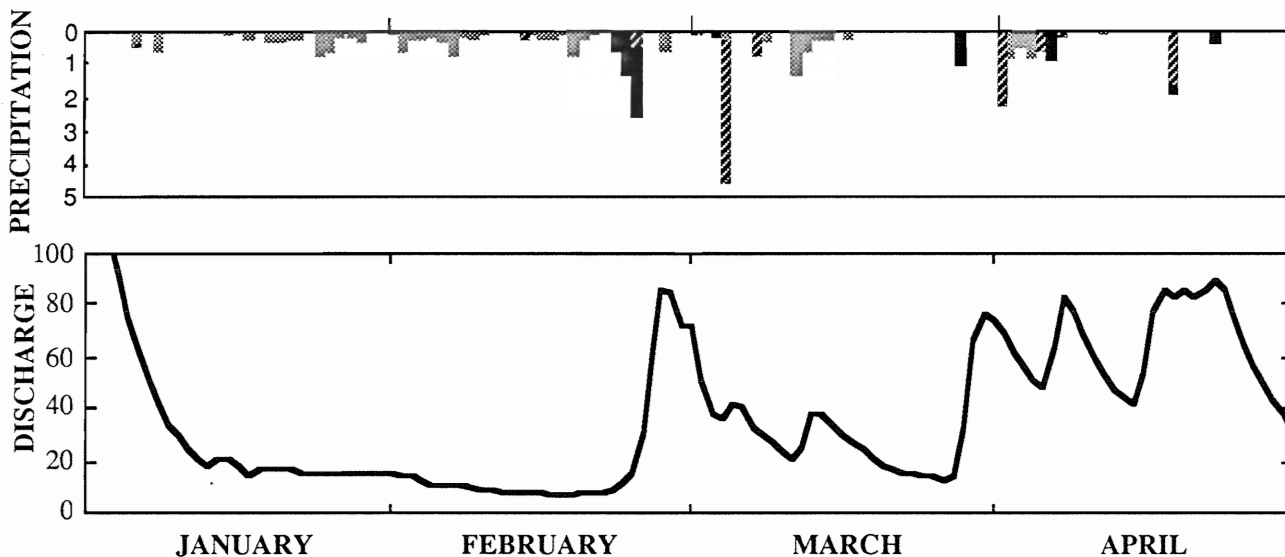


Figure 3 Precipitation quantity at the EPRI precipitation site for 1985, in centimeters per day, and mean daily discharge from Woods Lake, in liters per second per square kilometer. Gray bars are for snowfall; striped bars are for mixed precipitation; and solid bars are for rainfall.

Solutes were fractionated from the snowpack during melting. Meltwater concentrations of sulfate, nitrate, and chloride were 9, 6, and 5.5 times higher than in the corresponding snowpack at the onset of the melt in February (figure 5). For the February melt, 52 %, 41 %, 38 %, and 35 % hydrogen, nitrate, sulfate, and chloride, respectively, were released from the the snowpack in 5 days while the water equivalent of the snowpack decreased by 17 %. The fractionation or concentrated release of solutes from

the snowpack at the onset of the melt is consistent with those of other studies (e. g. Johannessen and Henriksen, 1978; Johannes et al., 1980).

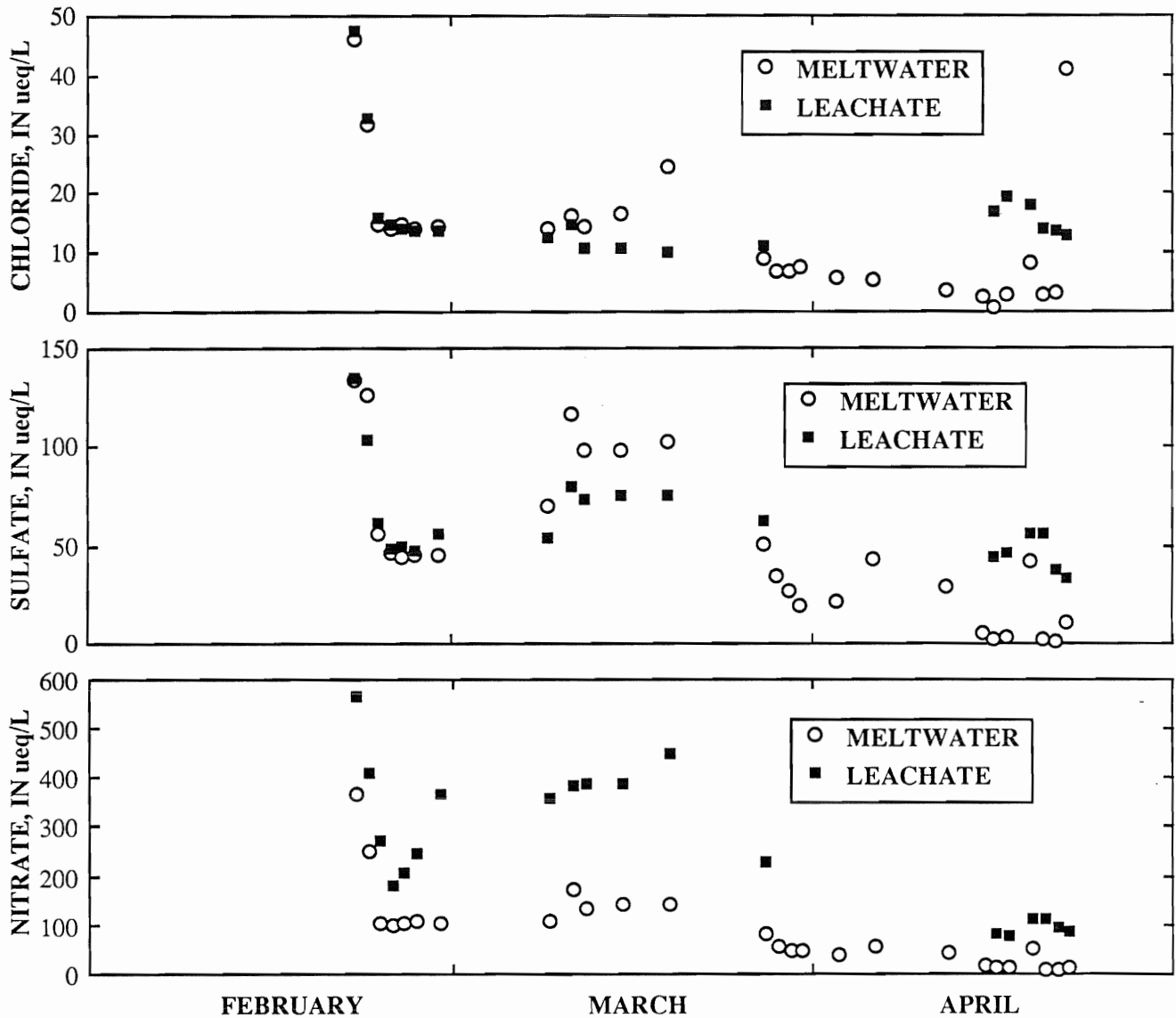


Figure 4 Concentrations of chloride, sulfate, and nitrate in meltwater and forest floor leachate during the 1984-85 winter.

Recent investigations of solute release from melting snow and ice indicate that solutes are not only fractionated in the meltwater, but they also are eluted preferentially; the rates of release of the major anions are as follows sulfate > nitrate > chloride (Brimblecombe et al., 1988). The results herein indicate that sulfate is released preferentially from the snowpack compared with nitrate and chloride (figure 5). However, the greater enrichment of sulfate compared to nitrate and chloride, in part, may result from the throughput of solutes from rainfall, which was much more enriched in sulfate compared to nitrate (2:1, concentrations in $\mu\text{eq/L}$). In contrast, solutes were not preferentially released from a physically similar type of snowpack in Michigan (Cadle et al., 1984). Also, the similarity in

concentration ratios of meltwater to snowpack for nitrate and chloride (figure 5) indicate that nitrate was not preferentially released from the snowpack as compared to chloride.

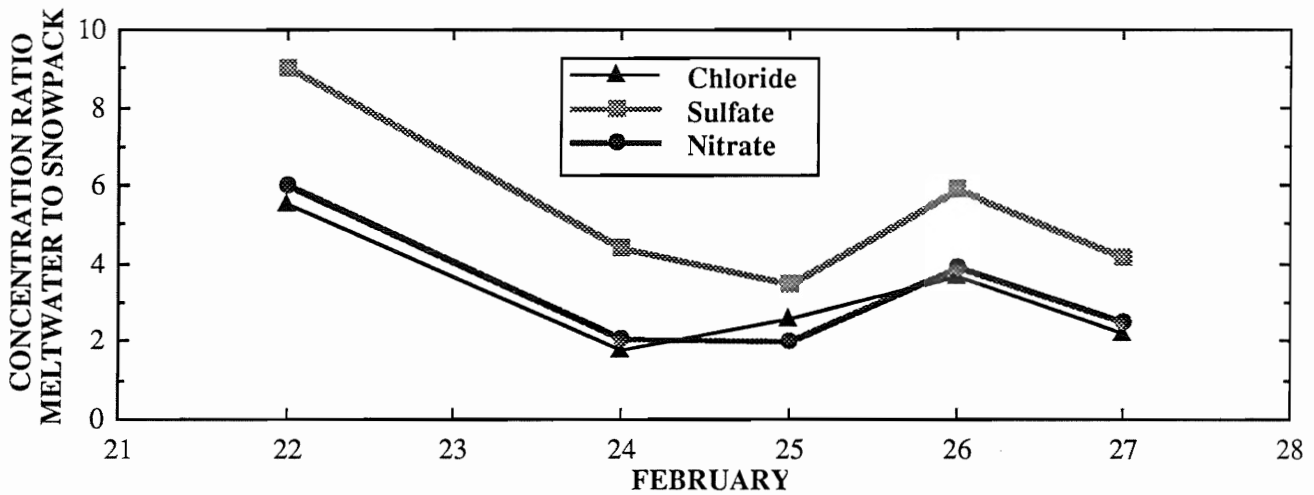


Figure 5 Ratios for the major anion concentrations in meltwater to those in the snowpack for the February 1985 melt.

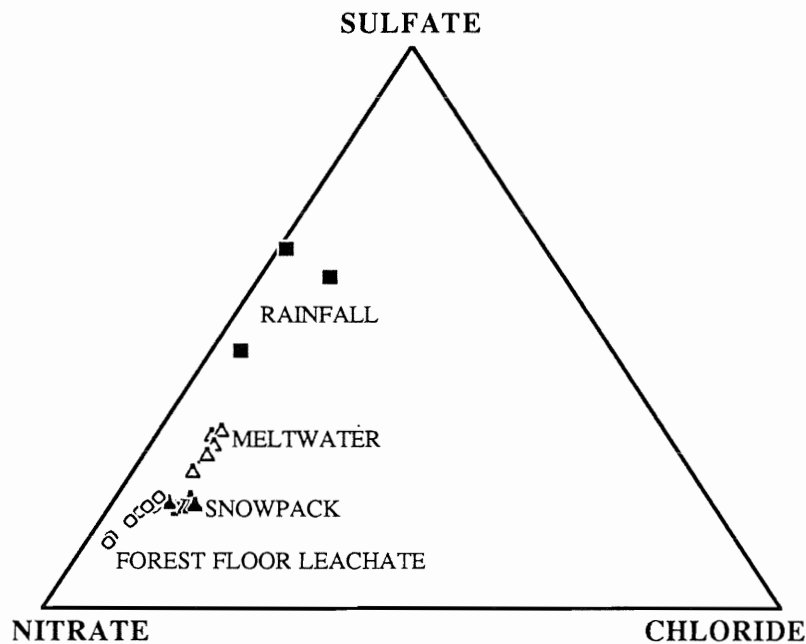


Figure 6 The major anion composition of precipitation, snowpack, meltwater, and forest floor leachate during snowmelt in February 1985.

The changes in the relative anion composition (RAC) of snowpack, meltwater, and forest floor leachate during the major melt in February show some notable patterns (figure 6). The RAC of meltwater for the first sample collected was most similar to that of the snowpack, and the next sample was most similar to that of the rainfall; the RAC of successive samples tracked back toward that

DISCUSSION

Alteration of meltwater composition by the forest floor

In general, the forest floor has little effect on the sodium, chloride, or sulfate concentrations of the meltwater. When compared to sodium or chloride, however, sulfate concentrations were slightly less variable in forest floor leachate than in meltwater. The forest floor, to some extent, must regulate the concentration of sulfate. As the snowpack becomes depleted in solutes from successive melts, the forest floor has a greater effect on the concentration of all solutes, as was the case for the last major melt in April (figure 4).

Throughout the winter, the forest floor is a source for biologically active constituents such as hydrogen, potassium, and the nitrogen species. Processes that occurred in the forest floor under the snowpack at the Adirondack site also have been observed at a hardwood site in Canada (Foster et al., 1989). As observed in 1980-81 at a site nearby (Peters, 1984), the forest floor remained unfrozen, a result of heat generation from biological processes within the forest floor and insulation by the overlying snowpack. Nitrification and decomposition of organic material in the forest floor are probable mechanisms for the generation of "nitric acid," potassium, and ammonium observed in leachate.

Linkage between meltwater and streamwater

The chemical transformations in meltwater as it infiltrates the forest floor tend to obscure a simple relation between meltwater and streamwater composition. For some watersheds, variations in streamwater composition seem to be controlled by the release of solutes from the snowpack. Cooper et al. (1987) investigated the variations in streamwater chemistry at Ciste Mhearad, a small high-altitude (1250 m) catchment in Scotland. They observed increased streamwater conductivity during snowmelt and decreased conductivity during heavy rainstorms. They concluded that the cause of the conductivity increase during snowmelt was a direct consequence of fractionation of solutes from the snowpack. Results of additional analyses of snowmelt in the same watershed by Tranter et al. (1988) indicated that the individual solute concentrations in streamwater coincided closely with the release of solutes from the snowpack. Likewise, at watersheds in Norway, increases in stream sulfate concentrations at the onset of snowmelt were attributed to the fractionation of solutes from the melting snowpack (Christophersen et al., 1984).

In nearby Adirondack watersheds, concentrations of hydrogen and the major mineral acid anions, nitrate and sulfate, were comparable from year to year and display similar temporal variations over several years prior to this snowmelt experiment (Galloway et al., 1980; Schofield et al., 1985; Driscoll and Schafran, 1984; Driscoll et al., 1987; Galloway et al., 1987), as is shown for 1978-81 at one nearby site in figure 1. From these other studies, an increase in streamwater sulfate concentration was not observed during snowmelt (figure 1), although fractionation of sulfate did occur from the melting snowpack as reported herein and by Johannes et al. (1980). Furthermore, sulfate concentrations in streamwaters remain relatively constant during winter, as also observed in Michigan (Cadle et al., 1987), and decrease during summer after the snowpack has melted. The decreases in

of the snowpack. Although the RAC of the snowpack remained relatively constant, the first sample was the most enriched in chloride, which is consistent with a preferential release of sulfate. The RAC of the leachate was much more enriched in nitrate than either the snowpack or the rainfall, but the RAC of the first leachate sample was highest in sulfate, and successive samples were more enriched in nitrate which likewise is consistent with the preferential flushing of meltwater sulfate through the forest floor.

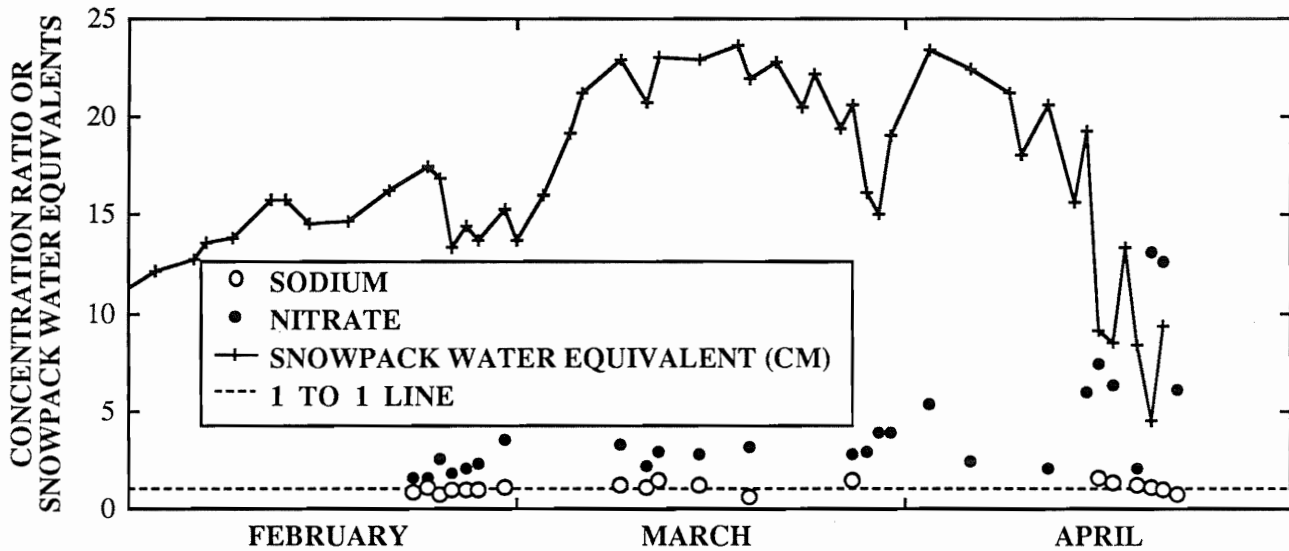


Figure 7 The ratio of solute concentration in forest floor leachate to that in meltwater for sodium and nitrate and the snowpack water equivalent for the 1984-85 winter.

Some solutes were conserved as the meltwater travelled through the forest floor and others were released from the forest floor. The transformation of solutes by the forest floor was determined by comparing the solute concentrations. This comparison is valid provided the forest floor does not store or release meltwater, which is consistent with the relative volumes observed in the collection vessels of the meltwater and forest floor lysimeters during major melt periods. Sodium, chloride, and sulfate concentrations in leachate were similar to those found in the corresponding meltwater; concentration ratios of leachate to meltwater were approximately 1.0 (see figure 7 for sodium), which suggests that the forest floor has little effect on these solutes. In contrast, hydrogen, potassium, ammonium, and nitrate concentrations were considerably higher in the forest floor leachate than in the corresponding meltwater as shown for nitrate in figures 6 and 7. The average ratios for all pairs of meltwater and leachate samples collected in February and March 1985 were 2.1, 4.9, 3.4, and 2.6 for hydrogen, potassium, ammonium, and nitrate, respectively. In contrast, the average ratios of the more conservative constituents for the same period were 1.1, 1.0, and 1.0 for sodium, chloride, and sulfate, respectively.

summer coincide with the seasonally high concentrations in rainfall (Altwicker and Johannes, 1987). These temporal patterns in sulfate concentrations of streamwater and precipitation also were reported for areas in western Pennsylvania (Lynch and Corbett, 1989).

In addition, the sulfate concentrations of forest floor leachate throughout the winter for the Adirondack snowmelt experiment were lower than those observed in streamwaters (figure 1 and 4), which indicates that the organic horizon was not the source of the high streamwater sulfate concentrations. Galloway et al. (1980) attributed the high and relatively constant sulfate concentrations in Adirondack streamwaters to the accumulation of sulfate in soils during summer and the subsequent flushing of sulfate during snowmelt. Sulfate is assumed to be stored somewhere below the forest floor, thus the relatively constant sulfate concentrations found in streamwater may result from the regulation of sulfate concentrations by the mineral soils (Christophersen and Wright, 1980; Fuller et al., 1985). An alternate hypothesis is that mineral soils store the sulfate during summer because the soil-moisture deficits are sufficient to prevent saturated flow, which would transport the sulfate out of the upper soils to the stream (Lynch and Corbett, 1989). In fall and winter as soil moisture is replenished, saturated flow is more prevalent and results in the transport of the previously stored sulfate (Lynch and Corbett, 1989).

Sources and sinks of mineral acids

In the study area, sulfuric acid is the dominant component of rainfall and nitric acid the dominant component of snowfall. Meltwater at the onset of snowmelt is dominated by nitric acid, but sulfuric acid becomes more dominant as the solutes in the rainfall that caused the melt are flushed through the snowpack (figure 7). The streamwaters are relatively enriched with sulfate as compared with either meltwater or forest floor leachate, but the source of the streamwater sulfate has yet to be identified. In addition, the concentrations of the most conservative constituents, sodium and chloride, peak at the onset of melting in both the meltwater and forest floor leachate. However, this pattern has not been observed in streamwaters during melt periods. These results indicate that understanding the nature of water pathways, mixing patterns, and residence times of the water may be key factors in evaluating the processes controlling the mobility of strong mineral acids within these forested ecosystems. Therefore, the increases in nitrate and hydrogen concentrations in streamwaters during major melt periods cannot simply be associated with a particular source, whether it be the snowpack or the forest floor. However, the forest floor, which can release at least twice as much nitric acid as derived from the snowpack, may be a major source of nitric acid in streamwater.

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Agency's review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

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