

IMPORTANCE OF THE CHEMICAL COMPOSITION OF THE SNOWPACK

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ABSTRACT

The chemical composition of the snowpack was determined throughout the winter of 1972-73 in the Hubbard Brook Experimental Forest, New Hampshire. The importance of the snowpack was evaluated in relation to chemical inputs to the forest ecosystem and to chemical outputs in streamflow. The snowpack was slightly less acid and had about the same or lower concentrations of calcium, nitrate, and sulfate than incident precipitation. Potassium occurred in higher concentrations in the snowpack than in precipitation, possibly as a result of potassium leaching from organic matter incorporated in the snowpack. Just before spring melt the snowpack contained about 50 percent of the total calcium and 25 percent of the total nitrate and sulfate input to the ecosystem in winter precipitation. Potassium in the snowpack just before melt was nearly twice the amount of input by winter precipitation. For all four ions the amount stored in the snowpack was small in relation to the amount lost in streamflow. The study indicated that the ecosystem concept is readily adaptable for determining the importance of the chemical composition of snow.

INTRODUCTION

At the Hubbard Brook Experimental Forest in the White Mountains of New Hampshire, the ecosystem concept is being used to investigate nutrient and hydrologic budgets of forest ecosystems (Bormann and Likens, 1967). The ecosystems being studied are small gaged watersheds (12 to 43 ha) completely forested with deciduous hardwood species. As a recent addition to the ecosystem studies, we have been sampling chemical composition of the winter snowpack on the watershed.

Studies as far back as 1852 have shown that snowfall contains measurable amounts of a variety of chemicals (Feth et al., 1964). Sources of these chemicals in freshly fallen snow include oceanic air masses, terrestrial dusts, atmospheric gases, and industrial pollution. As snow accumulates and ages, the chemical composition may be changed further by atmospheric fallout and by biologic activity above, within, and beneath the snowpack. The chemistry of the meltwater from the snowpack may be important in chemical weathering and as a source of nutrients for vegetation, soils, streams, and lakes.

The Hubbard Brook ecosystem studies offer an ideal opportunity to learn more about the importance of the chemistry of snow. Since 1965, quantity and chemistry of precipitation and streamflow have been measured on six adjacent watersheds at Hubbard Brook. From these data, input and output budgets of both water and chemical nutrients have been determined for the forest ecosystems that comprise the watersheds (Likens et al., 1967, 1971; Fisher et al., 1968; Johnson et al., 1969).

We know from our studies that snow is an important factor in both the hydrologic and the nutrient budgets for these ecosystems. By the end of an average winter the snowpack represents several months of precipitation and has a water equivalent of 200 to 300 mm. Spring melt is rapid, and it is common for the snowpack to disappear completely within a period of 1 to 3 weeks. Thus a large volume of water passes through the soil to the stream channel and leaves the ecosystem in a very short time. Because of snowmelt, April runoff accounts for 35 to 40 percent of the average annual streamflow of 710 mm. In contrast, less than 5 percent of annual streamflow occurs in the combined growing season months, June through September.

The large volume of snowmelt runoff takes with it a corresponding proportion of the annual nutrient output from the ecosystem. As an example, for calcium, which occurs in our streams at fairly constant concentrations of just over 1 mg/l (Likens *et al.*, 1967; Johnson *et al.*, 1969), 33 percent of the average annual output in streamflow occurs in April and 60 percent occurs in the combined snowmelt runoff months of March, April, and May (Figure 1). Input of calcium in precipitation is evenly distributed throughout the year (Figure 1), so snow and snowmelt play an important part in the uneven output of calcium in streamflow.

As part of our study we want to find out the importance of the winter snow accumulation as a source of nutrients and how this relates to outputs such as discussed above. Also we want to see if snow undergoes any important changes in chemical composition while stored in the snowpack. We can examine these findings in light of our input and output data and better evaluate the impact of snow both on our forested ecosystems and on downstream ecosystems.

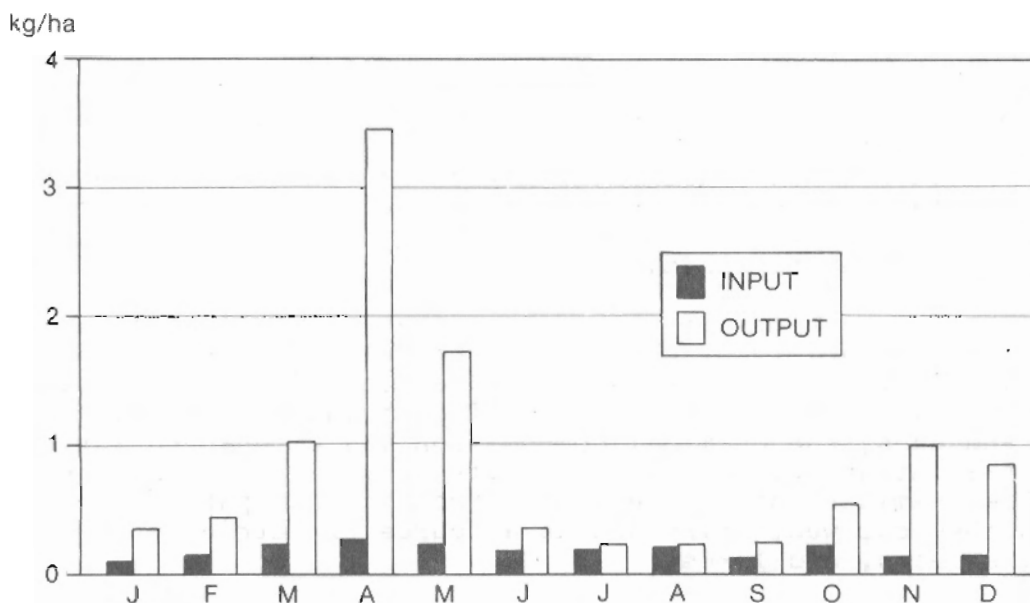


Figure 1. Average monthly input and output of calcium in precipitation and streamflow, 1966 to 1972.

STUDY AREA AND METHODS

The Hubbard Brook Experimental Forest is typical of much of central New England in that the rugged terrain has relatively steep slopes of 20 to 30 percent and is forested with northern hardwood species. Mean annual precipitation is about 1,220 mm, of which one-fourth to one-third occurs as snow. Snow cover usually persists from mid-December to mid-April, the peak snow depth in late March averaging 900 to 1,250 mm, equivalent to 200 to 300 mm of water. The continuous snow cover and forest humus insulate the soil against freezing. Thus infiltration capacities remain high throughout the year, and practically all water reaching the stream channel does so as subsurface flow.

Our snow-chemistry study is being conducted on Hubbard Brook watershed 1, which is centrally located among six adjacent gaged watersheds. The watershed is south-facing and is 12 ha in area. Snow samples for chemical analysis are collected at two previously established snow courses located at elevations of 520 and 705 m.

Each snow course has 10 moving stations, which are measured weekly with a Mt. Rose sampler for snow depth and water equivalent. At the same time, snow cores for chemical analysis are extracted, using a fiberglass tube with an inside diameter of 7 cm. Samples from each of the snow courses are composited in polyethylene jugs until enough sample is obtained to give at least 1,000 ml of meltwater.

Upon melting, the samples are analyzed for pH, electrical conductivity, dissolved silica, calcium, magnesium, potassium, sodium, sulfate, ammonium, nitrate, molybdate-reactive phosphate, and chloride. Ionic determinations are made either by atomic absorption spectrophotometry or automated colorimetric analysis. Values for mass per unit area are obtained for individual ions found in the snowpack by using the ionic concentrations and water-equivalent data. Procedures for obtaining inputs and outputs of ions in precipitation and streamflow are given in Likens et al. (1967) and Fisher et al. (1968).

RESULTS AND DISCUSSION

Continuous snow cover for the winter of 1972-73 began in mid-November. We started weekly measurements of snow depth and water equivalent on 4 December, and weekly collection of samples for chemical analyses on 11 December. The 1972-73 snowpack was unusual in that by mid-January it had built to a water equivalent of about 200 mm (Figure 2). From that point, the water equivalent remained fairly uniform until melting in mid-March. Under more usual conditions, the snowpack builds more gradually to a maximum water equivalent of about 300 mm by mid to late March, and the majority of melt occurs in April.

The 1972-73 winter was also unique in that a sizable portion of precipitation occurred as rain or rain-snow mixtures rather than as snow. As a result, the snowpack that developed through the winter contained a smaller than usual proportion of the 520 mm of precipitation that occurred from mid-November through mid-March.

Although we measured 12 chemical parameters of the snowpack, we have chosen to limit major discussion here to pH and four ions: calcium, potassium, sulfate, and nitrate. These ions are ecologically important at Hubbard Brook and also cover the ranges of patterns and concentrations of most of the ions being studied. Variations in chemical data between the two snow courses were generally small, so we report only averages of the weekly samples.

pH. Precipitation in the Hubbard Brook area is decidedly acid (Likens et al., 1972; Johnson et al., 1972; Fisher et al., 1968). Since 1965, annual average pH of precipitation has ranged between 4.0 and 4.2, and individual weekly samples have had a pH as low as 3.0.

During the period of our snow-chemistry study, pH ranged from 4.0 to 4.7 for weekly precipitation and from 4.4 to 5.2 for weekly samples from the snowpack (Figure 3). pH of the snowpack showed considerable week-to-week variation and twice declined by 0.5 pH unit in the interval between weekly sampling. pH of the snowpack is apparently responsive to pH of precipitation occurring over the previous 1 to 2 weeks (Figure 3).

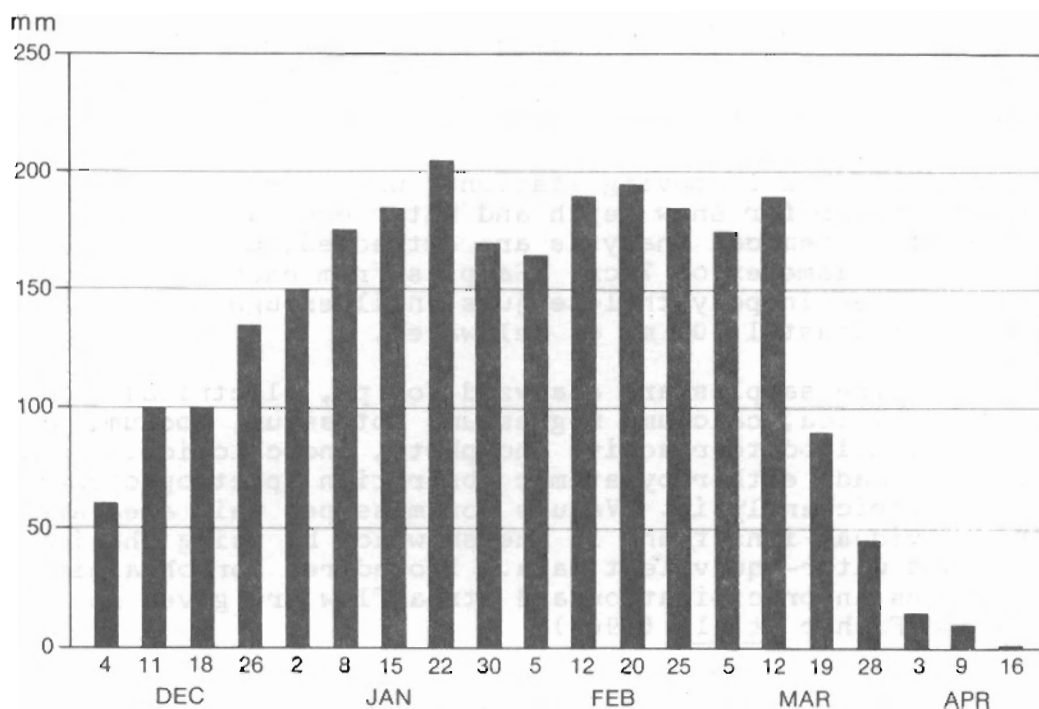


Figure 2. Water equivalent of snowpack at weekly intervals during the winter of 1972-73. The values are averages for the two snow courses being studied.

Our data also showed that the snowpack is generally less acid than incident precipitation. This finding is in line with an earlier study in Wyoming (Clement, 1966), which showed that, as snow ages and becomes less pure, it becomes less acid. The decrease in acidity while precipitation is stored in the snowpack may be of significance to chemical weathering and to acidity of snowmelt runoff. In this regard, streamflow during the major snowmelt period of 1973 had an average pH of 4.6.

Calcium. Concentrations of calcium in the snowpack averaged about 0.09 mg/l over the 1972-73 winter (Figure 3). A general trend of decreasing calcium concentration persisted from initial sampling in December through about mid-February. Concentrations then increased through mid-March.

The decline in calcium may be the result of two things. First, the concentration of calcium in precipitation decreased during the latter half of the winter. Second, the decline may be the result of rain. The low concentrations observed on 22 January and 12 February were preceded by winter rains. On both occasions the snowpack was unable to absorb much additional water, and calcium may have leached from the snowpack.

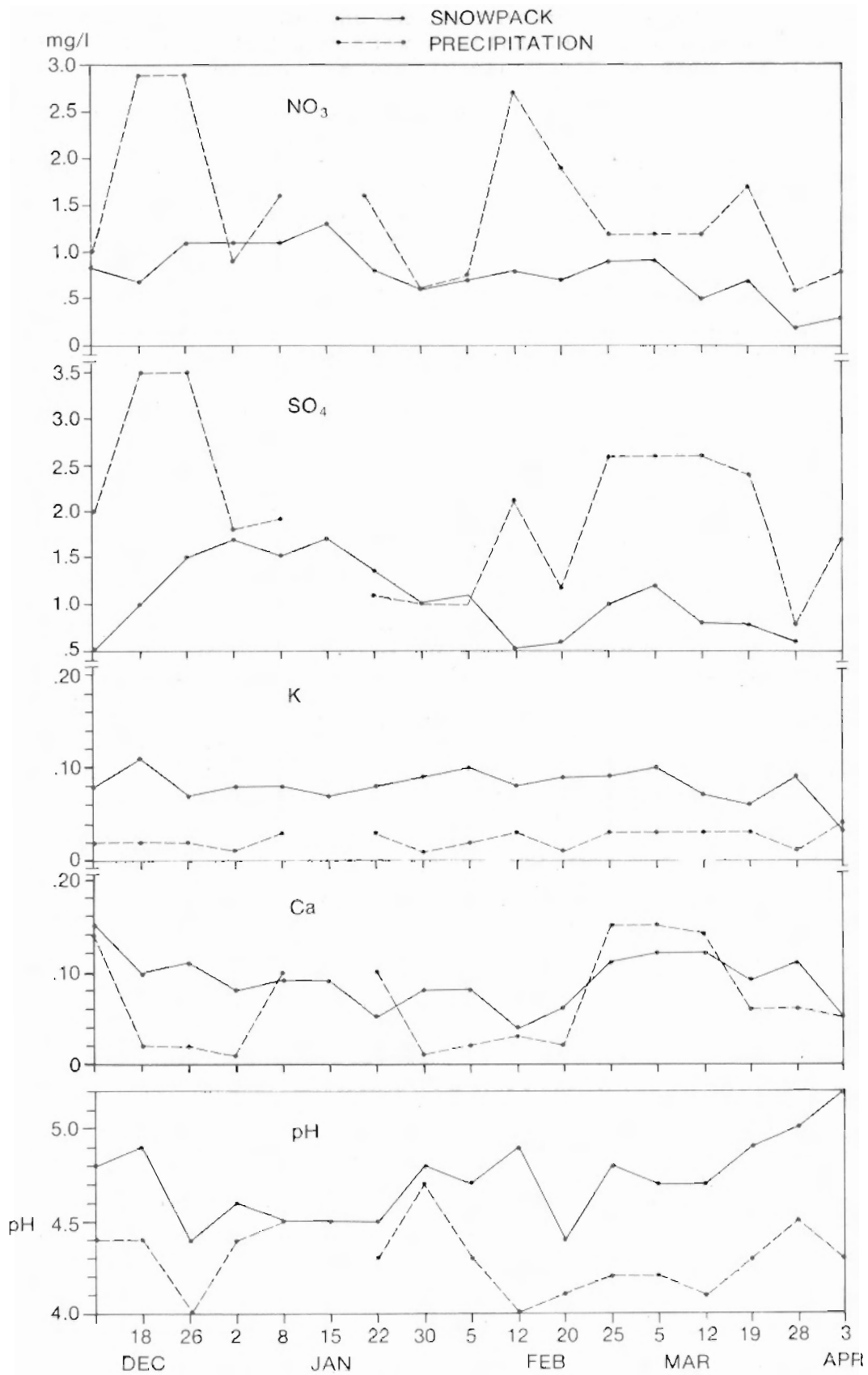


Figure 3. pH and concentrations of ions in weekly samples of incident precipitation and the snowpack. Missing data points indicate weeks without precipitation.

Potassium. Potassium concentrations showed less tendency to fluctuate than did calcium. Mean concentrations were relatively uniform between 0.07 and 0.10 mg/l for most of the winter (Figure 3).

The potassium found in snow apparently stems from two main sources: precipitation and leaching of plant organic materials incorporated in the snowpack. The organic sources may help to dampen some of the fluctuations that might otherwise have resulted from amounts and form of precipitation. And the organic matter source may also account for potassium concentrations in the snowpack being consistently higher than concentrations in precipitation (Figure 3).

Sulfate. Sulfate is the dominant anion in precipitation at Hubbard Brook, and during the winter months the concentration averages between 1 and 4 mg/l (Fisher et al., 1968). For our period of study, concentrations in weekly precipitation ranged from 0.6 to 3.5 mg/l. In the snowpack, mean sulfate concentrations reached a maximum of 1.7 mg/l in early January (Figure 3); concentrations then declined to 0.5 mg/l in mid-February and rose to over 1.0 mg/l in early March.

Unlike calcium and potassium, the mean sulfate concentration of the snowpack is considerably less than the sulfate concentration in precipitation. The reason for this is not clear, but leaching by winter rains may be important.

Nitrate. Nitrate is also an important constituent of precipitation at Hubbard Brook. During our study, nitrate concentrations in weekly precipitation had a maximum value of 2.9 mg/l and a minimum of 0.6 mg/l (Figure 3). For the snowpack, the nitrate pattern showed a resemblance to the pattern for sulfate. A maximum concentration of 1.3 mg/l occurred by mid-January and was then followed by a gradual decline through mid-February. A slight increase occurred again before the start of melt in March. As with sulfate, nitrate in the snowpack seems responsive to form and ionic concentration of precipitation.

Other ions. We found that magnesium was present in relatively low and constant concentrations of 0.01 to 0.03 mg/l. Sodium ranged from 0.02 to 0.07 mg/l and followed a pattern similar to that for calcium. Ammonium was unique in that it showed a continuous increase in concentration through the winter, rising from 0.02 to about 0.08 mg/l. Chloride showed a wide range of values from 0.1 to 1.3 mg/l and was the only ion to show sizable differences between sampling locations. Mean concentration was 0.25 mg/l at the 520-m elevation and 0.40 mg/l at the 705-m elevation. Molybdate-reactive phosphate occurred in very low and constant concentrations of about 0.01 to 0.02 mg/l.

Nutrient content of the snowpack. By using concentration and water-equivalent data, we could obtain an estimate of the content or mass per unit area of nutrients in the snowpack at the time of each weekly sampling (Figure 4). These values could in turn be compared with cumulative input of nutrients in winter precipitation to evaluate how the snowpack performs as a storage for nutrients.

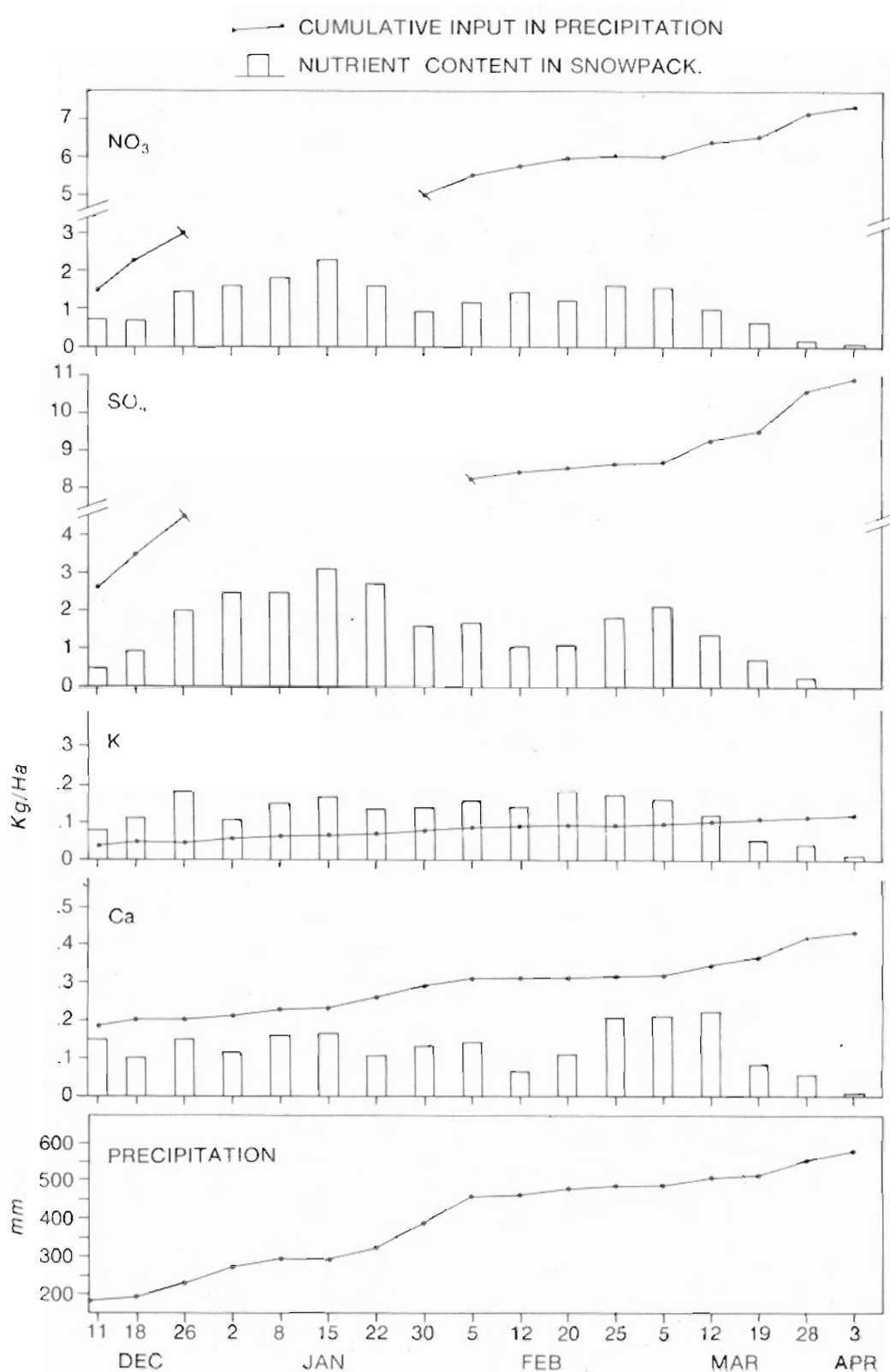


Figure 4. Average nutrient content (kg/ha) at each sampling date and cumulative input in precipitation. The cumulative values for precipitation were started on 15 November to coincide with the start of continuous winter snow cover.

Before making the comparisons, we should mention again that the snow-pack did not store a large portion of the winter precipitation. On 5 March (just before the start of the melt season) the snowpack held 175 mm of water (Figure 2). This compared with a total input in winter precipitation from 15 November (start of continuous snow cover) to 5 March of 480 mm (Figure 4). Thus about 62 percent of the winter precipitation was not stored by the snowpack.

Our data showed that amounts of sulfate and nitrate found in the snow-pack were also considerably less than the total input in winter precipitation. As an example, on 5 March the snowpack held an average 2.2 kg/ha of sulfate (Figure 4). In contrast, cumulative input of sulfate in precipitation from 15 November through 5 March was 8.6 kg/ha. The difference, 6.4 kg/ha or 74 percent of the winter input of sulfate, was not stored by the snowpack. Nitrate showed a similar trend. On 5 March there was an average 1.6 kg/ha of nitrate in the snowpack as compared to a 6.0 kg/ha cumulative input in precipitation. Thus 73 percent of the nitrate input was not retained by the snowpack.

The snowpack seemed more efficient at storing calcium, and especially potassium. For calcium the cumulative input in precipitation for the entire winter was 0.4 kg/ha. As late as 12 March the snowpack held an average 0.2 kg/ha of calcium, about half of the precipitation input.

Potassium presented a different situation in that the snowpack held more than input in precipitation. Total input of potassium for the entire winter was 0.12 kg/ha. Potassium in the snowpack exceeded this value on nearly every sampling date (Figure 4). As mentioned earlier, the additional potassium was thought to come from the leaching of organic material incorporated in the snowpack. This organic material, which is transported to the snowpack by wind or intercepted precipitation, occurred in surprisingly large quantities, primarily in the form of birch cone scales and seeds, leaves, twigs, and bark fragments.

Within this organic plant material, potassium occurred as soluble inorganic salts (Gilbert, 1957). Our data indicated that potassium from this source is readily solubilized by water moving within the snowpack. Laboratory results of an earlier Hubbard Brook study tend to confirm this (Gosz *et al.*, 1969).

Most other ions we are studying occurred in relatively small volumes in the snowpack. Maximum values in the course of the winter for some individual ions included: 0.05 kg/ha for magnesium; 0.14 kg/ha for sodium; 1.3 kg/ha for chloride; 0.10 kg/ha for ammonium; and 0.03 kg/ha for phosphate. We have not yet compared these values with inputs in precipitation.

Comparison with streamflow outputs. As with precipitation, we make routine chemical analyses of streamflow as a part of our ecosystem studies. Thus it was possible to evaluate the volume of nutrients in the snowpack in relation to nutrient loss in streamflow.

Figure 5 shows the cumulative loss in streamflow for calcium, potassium, nitrate, and sulfate for the time period in which snow and snowmelt have the most effect on streamflow. All the curves show a similar pattern. There was a gradual loss of nutrients until about mid-January, when winter rains caused the output to be increased. A more rapid loss also began about 10 March due to increased volume of runoff from snowmelt.

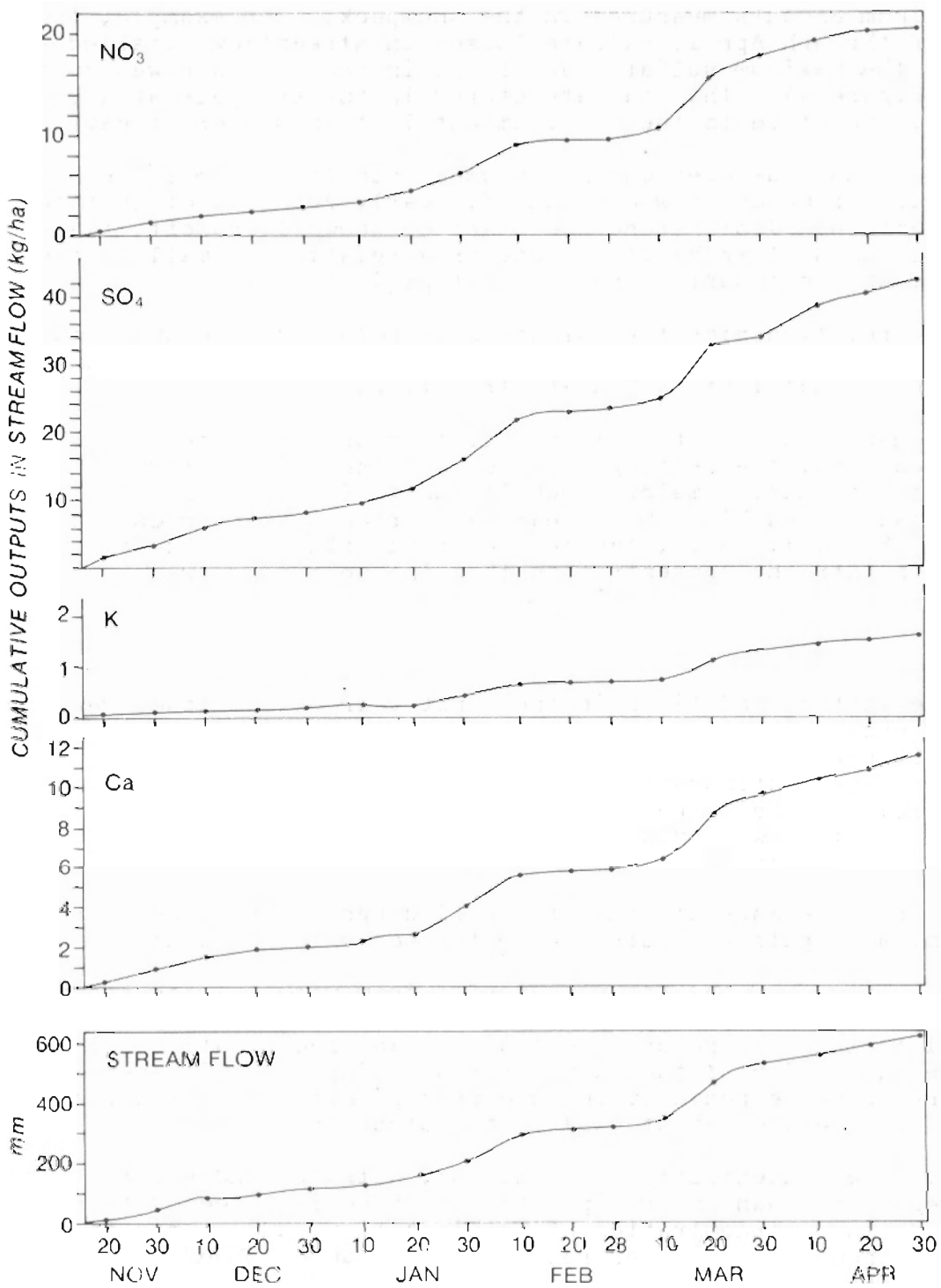


Figure 5. Cumulative outputs of nutrients in streamflow.

The cumulative losses for all four ions in streamflow greatly exceeded the maximum amounts measured in the snowpack. For example, from mid-November through April, sulfate losses in streamflow totalled about 42 kg/ha. The maximum sulfate ever found in the snowpack was just over 3 kg/ha (Figure 4). Thus sulfate stored in the snowpack at any given time was small relative to the total amount lost in winter streamflow.

This was true even during snowmelt runoff. From 1 March to 20 March, the period of major snowmelt runoff, nearly 20 kg/ha of sulfate were lost in streamflow. Just before the start of snowmelt runoff, the snowpack held only about 1 kg/ha of sulfate or a relatively small portion of the total amount lost during the snowmelt period.

The relationships for sulfate also hold for calcium, potassium, and nitrate. The snowpack stored only a small amount of these nutrients in relation to that lost in winter streamflow.

Though it does not seem important as an immediate source of nutrients for streamflow, the melting snowpack was the trigger for the increased nutrient loss during major snowmelt runoff (1 to 20 March). Apparently the meltwater reaching the stream was enriched in nutrients during passage through the soil. Also, the meltwater may flush stored soil water that is higher in nutrient concentration than the melting snow.

SUMMARY

The winter conditions in the first year of our study were not typical in that snow accumulation and melt occurred earlier than usual. Also, an unusually high proportion of winter precipitation occurred as rain. The study will be continued to obtain data under more typical winter conditions. Meanwhile, our preliminary findings indicated that an evaluation of the importance of snow chemistry is greatly enhanced when studied in the context of an ecosystem.

A brief summary of some of our findings on snow chemistry as related to chemical inputs and outputs for the ecosystem showed:

1. The pH of the snowpack varied from week to week, seemingly in response to form and pH of precipitation. But the snowpack was usually several tenths of a pH unit less acid than precipitation. The slight decline in acidity of the snowpack may be important in chemical weathering and streamflow, especially because precipitation was of a decidedly acid nature (pH averages about 4.0) on the study area.

2. The concentrations of calcium, nitrate, and sulfate in the snowpack were less than in precipitation. These ions seemed to respond to form and ionic concentration of precipitation, and seemed to be leached from the snowpack by winter rains. Potassium occurred at higher concentrations in the snowpack than in precipitation, and at relatively consistent levels throughout the winter. The different pattern for potassium in relation to the other ions was thought to be the result of potassium leaching from organic materials incorporated in the snowpack.

3. The masses per unit area of sulfate and nitrate found in the snowpack were considerably less than input in winter precipitation. Just before start of melt, the snowpack held only about 25 percent of the total sulfate or nitrate occurring in winter precipitation. About one-half of the calcium input was held by the snowpack while potassium in the snowpack exceeded the input in precipitation.

4. The amount of nutrients stored in the snowpack was generally small in relation to the amount lost from the ecosystem in streamflow. This was true even for the 3-week interval when snowmelt was at a maximum.

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