Snowpack Storage and Release of Nitrogen in the Emerald Lake Watershed, Sierra Nevada

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ABSTRACT

Interactions between the storage and release of nitrogen (N) from the seasonal snowpack and basin processes were evaluated from 1985 through 1987 at the Emerald Lake watershed, located at 2800 m in the southern Sierra Nevada, California. The volume-weighted mean annual concentrations of NH_4^+ and NO_3^- in winter snow were $\leq 5.0\,\mu$eq L^{-1} and are among the most dilute recorded in the northern hemisphere. However about 90% of the annual flux of NH_4^+ and NO_3^- in wet deposition was supplied during the period of snowmelt runoff, due to the large percentage of annual precipitation that occurred as snow. Dry deposition of N to the seasonal snowpack was not significant relative to wet deposition. Concentrations of NH_4^+ and NO_3^- in the first fraction of meltwater were 3-6-fold greater than bulk concentrations measured in co-located snowpits, an ionic pulse. Elution of NO_3^- from the snowpack in the form of an ionic pulse appeared to be the cause of seasonal maxima in NO_3^- concentrations in streamwaters. In contrast to the export of NO_3^- during snowpack runoff, more than 99% of the ammonium stored in the seasonal snowpack was retained in the basin. The retention of NH_4^+ in the basin during snowpack runoff indicates that much of snowpack meltwater infiltrates soils before becoming stream water and that soil processes with relatively fast kinetics must be active at this time.

INTRODUCTION

Until recently, concern about atmospheric deposition has focused largely on sulfur and subsequent effects associated with accelerated leaching of cations and acidification of soils and drainage waters. It is now evident that elevated inputs of N are an additional stress on both terrestrial and aquatic ecosystems. Recent research suggests that forested ecosystems may be much closer to N saturation, soil acidification, and altered N-cycling than previous thought [Kahl et al,. 1993]. To date, little attention has been focused on the role of N-cycling in high-elevation catchments. There is reason to believe that aquatic and terrestrial biota in high-elevation systems of North America may be more sensitive to continued or increased atmospheric deposition of anthropogenic compounds than are forested ecosystems [Barmuta et al, 1990, Baron, 1991; Williams et al., 1993].

A confounding factor in evaluating the role of N in high-elevation catchments is the presence of a seasonal snowpack. Atmospheric deposition of wet and dry species of N is stored in the seasonal snowpack and then released in a relatively short period during spring runoff. Nitrogen eluted from the snowpack has the capacity to both enhance the growth of biota that are N limited [Bowman et al., 1993] and degrade biota through acidification processes [Stoddard, 1992]. Emphasizing the need to understand the role of N storage and release from the snowpack is the fact that concentrations of anthropogenic N in the ambient air of high-elevation areas in the U.S. have increased as much as 30-fold in the last several decades [Fahey et al., 1986].

Here I present information on the sources, transformations and outputs of inorganic N from the Emerald Lake watershed (ELW), a headwater basin located in Sequoia National Park, southern Sierra Nevada. Data from 1985 through 1987 are presented, with an emphasis on the period of snowpack runoff in 1986 and 1987. Statistical analyses of data from the Western Lakes survey conducted by the EPA show that ELW is representative of granitic basins in the Sierra Nevada [Melack and Stoddard, 1991]. Therefore knowledge of the processes that control N flux at the ELW can be applied to the broader region of granitic basins in the Sierra Nevada.

STUDY AREA

The Emerald Lake basin is a north-facing granitic cirque located on the upper Marble Fork of the Kaweah River drainage, in the southern Sierra Nevada of California, USA (36°35'49"N, 118°40'30"W). Basin area is 120 ha; elevation ranges from 2800 m at the lake outlet to 3416 m at the summit of Alta Peak (Figure 1). Emerald Lake is a 2.72 ha cirque lake at the bottom of the basin, fed by two main inflows and six intermittent streams, and drained by a single outflow. Emerald Lake and the streams in its watershed are weakly buffered, calcium-bicarbonate waters which are typical of high-altitude Sierran surface waters [Melack et al., 1985].
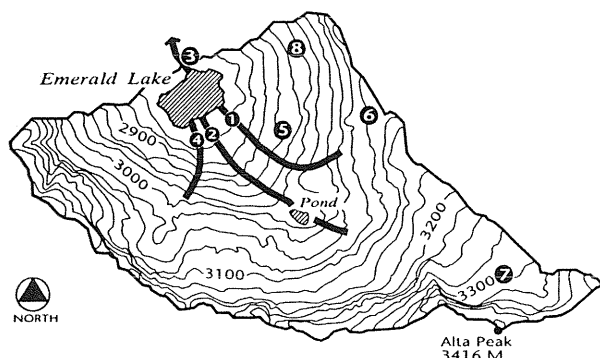

Fig 1. Topographic map of Emerald Lake and sampling sites.

Exposed rocks comprise 33 percent of the basin area; unconsolidated sand, gravels, and talus cover about 47 percent. Poorly developed soils cover about 20 percent of the basin, and these are acidic and weakly buffered. The major soils of the basin are Umbrepts and Orthents. This analysis focuses on a Lithic Cryumbrept located at the ridge site at an elevation of 3100 m (Figure 1). Vegetation in the basin is sparse, including only scattered coniferous trees, although low woody shrubs are often abundant where soils occur.

METHODS

Wet deposition (snow and rain) was collected on an event basis in 1986 and the snowpack was sampled at the period of maximum snow accumulation in each year, 1985 through 1987. Solutes in rain were collected after each event with a wet-only Aerochem Metrics model 301 sampler at the inlet site (site 1, Figure 1). The chemical content of snowfall was sampled using two techniques: (1) on an event basis at 1-4 sites using snowboards, and

Table 1. Comparison of N-species in Wet Deposition (μeq L^{-1}) at ELW to Other Sites in the United States, by Precipitation Type

	ELW	Alaska	NWT	NE USA
Snow				
NH$_4^+$	1.7	2.8	7.1	10
NO$_3^-$	2.3	2.4	11.0	30
Rain				
NH$_4^+$	55.3	2.8	29.4	20
NO$_3^-$	42.8	2.4	22.4	50

ELW: VWM concentrations, 1985-1987.

Alaska: Galloway et al. [1982].

NWT: Niwot Ridge, Colorado [LTER report].

NE USA: Stoddard [1992].

(2) at three to six snowpits during the period of maximum accumulation [Williams and Melack, 1991a] (sites 1, 5, 6, and 7, Figure 1). Meltwater draining from the snowpack in 1987 was collected in lysimeters before contact with the ground in an open, acid-washed, polyethylene container with dimensions of 10×10×50-cm, a surface area of 0.05 m² and a volume of 5 liters. The lysimeter was placed in a 20-cm tall snow cave excavated at the bottom of the snowpack; the sampling interval was approximately weekly [Williams and Melack, 1991b]. A tension lysimeter was installed at the ridge site in July of 1985 to sample the soil solution; soil solution samples were collected at depths of 100 and 300 mm in 1987 [Brown et al., 1990]. Surface water samples of all inflows, Emerald Lake, and the lake outflow were collected in acid-washed polyethylene bottles for chemical analyses approximately weekly beginning in spring and through the summer months, and monthly during the winter period. All water samples were analyzed for major inorganic ions, silica, and acid neutralizing capacity (ANC). Information on sample storage and analysis are as reported in Williams and Melack [1991a]. Hydrologic processes were monitored for two complete water years (October 1985 to September 1987). Stage height in the outflow and two main inflows was measured with a Montedero-Whitney pressure transducer and recorded on an Omnidata data logger. Stage-discharge relationship were developed using the salt dilution technique [Dozier et al., 1987].

RESULTS AND DISCUSSION

Wet Deposition

Concentrations in winter snow are among some of the most dilute measurements of N recorded in wet precipitation, yet N concentrations in rainfall are comparable to areas with large anthropogenic sources of N. Nitrogen concentrations in snow of about 2 μeq L^{-1} each for NH$_4^+$ and

Table 2. Nitrogen Concentrations and Loading in Wet Deposition, 1986

	Concentration†	Loading‡
NH₄⁺		
Snow	1.4	79
Rain	23.4	8
NO₃⁻		
Snow	1.8	74
Rain	22.2	7

†Volume-weighted mean concentration (μeq L^{-1}).

‡Volume-weighted mean concentration times precipitation amount (eq ha^{-1}).

NO_3^- (Table 1) are comparable to mean concentrations of 2.8 μeq L^{-1} for NH_4^+ and 2.4 μeq L^{-1} for NO_3^- reported by Galloway et al. [1982] for a site in central Alaska. Kennedy et al. [1979] report similar values from the sparsely populated coastal region of the Mattole River in northern California. However, mean concentrations in rainwater at the ELW of about 55.3 μeq L^{-1} for NH_4^+ and 42.8 μeq L^{-1} for NO_3^- (Table 1) are comparable to N concentrations in rainfall in areas which are considered to have considerable anthropogenic sources of N, such as the Adirondack and Catskill Mountains of New York [Stoddard, 1992]. The volume-weighted mean annual concentrations in wet deposition for 1985-1987 were 4.5 μeq L^{-1} for NH_4^+ and 5.0 μeq L^{-1} for NO_3^-, reflecting the importance of snow as the primary mechanism for wet deposition input to the basin.

Snowfall accounted for about 90% of the loading of N from wet deposition to the ELW. Loading of NH_4^+ and NO_3^- in 1986 was about 80 eq ha^{-1} from snow compared to about 8 eq ha^{-1} from rain (Table 2) Snowfall accounted for about 99% of the precipitation input and rain only 1% in 1986 [Williams and Melack, 1991a]. Consequently, while N concentrations in snow are among the lowest in the world, the large percentage of precipitation that falls as snow results in snow being the primary mechanism for wet deposition loading of N to high-elevation catchments in the Sierra Nevada.

Snowpack Storage

Solute storage in the winter snowpack was investigated in water year 1986 by comparing the chemical content of cumulative snowfalls measured on snowboards with the chemical content of the snowpack at the same site, during midwinter (January 9), at maximum snow accumulation (March 5) and after spring runoff had started (May 5). Volume weighted mean concentrations and loading (equivalents m^{-2}) in cumulative snowfalls and in the

snowpack were similar for H^+, SO_4^{2-}, and Cl^- prior to snowpack runoff. Snow water equivalent was also similar in cumulative loading and in snowpits. Nitrate had a small but persistent decrease (20%) in snowpits compared to cumulative events. For example, on both January 9 and March 5, SWE and loading of SO_4^{2-} in the snowpit were within 10% of cumulative event totals (Figure 2).
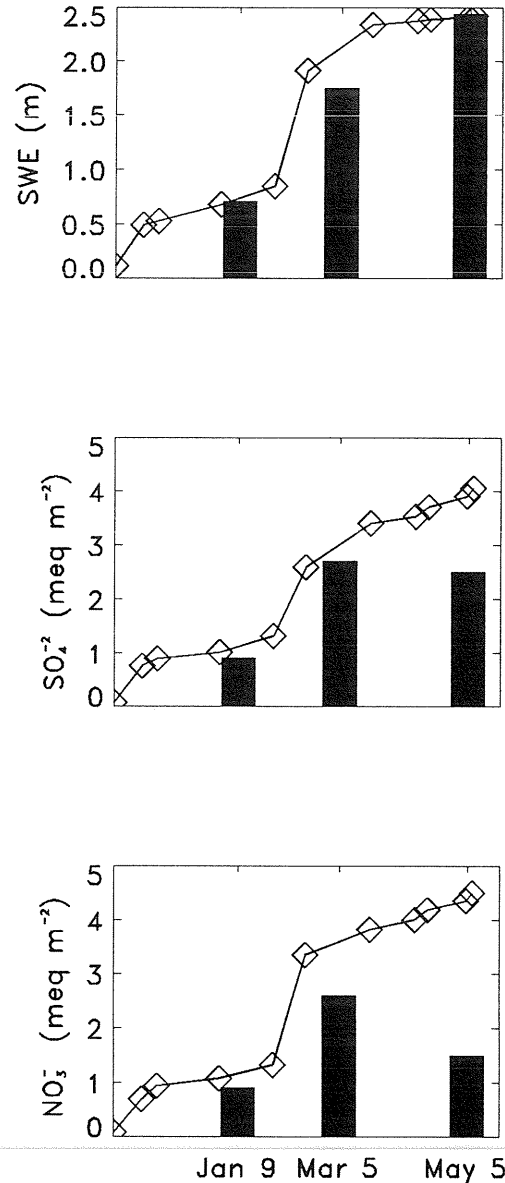

Fig 2. Comparison of cumulative snowfall loading to snowpack loading, 1986.

In contrast, NO_3^- loading in the snowpack, on the same dates was about 80% of cumulative deposition. After the onset of snowmelt in early April,

anions were released from the snowpack at a much faster rate than water.

The storage and release of NH_4^+ and NO_3^- in snowmelt runoff from deposition of snow accounted for 90% of the annual wet deposition of NH_4^+ and 91% of the annual wet deposition of NO_3^- in water years 1985 and 1986.

Dry Deposition

The role of dry deposition of N to the seasonal snowpack can be evaluated by comparing cumulative event totals to storage in the snowpack at similar dates. The equivalence between cumulative snowfall and snowpack loading indicates that dry deposition was not an important contributor of ions to solute loading in the winter snowpack. Solute loading in the snowpack was less than or equal to solute loading from cumulative snowfalls, for H^+, SO_4^{2-}, NO_3^-, and Cl^-, in water year 1986 (Figure 2). The possibility that ionic losses from the snowpack were matched by dry deposition cannot be discounted, but is unlikely. However, nitric acid (HNO_3) is soluble in water and may have contributed significant deposition after the initiation of snowmelt runoff.

Ionic Pulse

About 80% of the NO_3^- and NH_4^+ stored in the seasonal snowpack was eluted in the first 20% of snow melt, an ionic pulse. Maximum concentrations of NO_3^- measured in the first fraction of snowpack meltwater were 26 μeq L^{-1}, or about six times that of the bulk snowpack concentrations from the same site at the same time. The magnitude and loading of N in meltwater varied throughout the basin as a function of snow depth, rate of snowmelt, and melt-freeze cycles within the basin [Williams and Melack, 1991b]. For example on April 22, 1987, NO_3^- concentrations in meltwater at the cirque (26 μeq L^{-1}) were eight-fold higher than at the bench (3 μeq L^{-1}). In turn the spatial variation in the chemistry of meltwater caused spatial variation in the ionic loading from snowpack meltwater to soil and rock surfaces. For the date above, NO_3^- loading from snowpack meltwater was 330 μeq m^{-2} at the bench, 3.5 μeq m^{-2} at the inlet, and 1,540 μeq m^{-2} at the cirque.

Streamflow

Nitrate concentrations in stream waters varied seasonally. Maximum concentrations occurred during the first part of snowmelt runoff (Figure 3). Maximum concentrations in inflow 2 were about 20 μeq L^{-1}, four times the wet deposition mean (5.0 μeq L^{-1}) for the period of 1985-1987. Highest concentrations of NO_3^- coincided with the first fraction of snowpack runoff in April of each year (Figure 3). During the summer months concentrations of NO_3^- decreased to near detection limits (0.2 μeq L^{-1})

at maximum discharge and remained low as discharge decreased through the summer months. Concentrations of NO_3^- slowly increased during the fall and winter months to about 6 μeq L^{-1}, reflecting the contribution of groundwater to streamflow. Nitrate concentrations in inflow 2 exceeded the atmospheric mean value for about 20 days in 1986 and 60 days in 1987. The annual maximum NO_3^- concentrations always occurred during the first stages of snowmelt runoff. A five year time series of NO_3^- concentrations measured at the lake outlet shows that maximum concentrations here were about 2.5x mean annual concentrations and always occurred about May 1 when the first stages of snowmelt runoff reached the lake outlet (Figure 4).

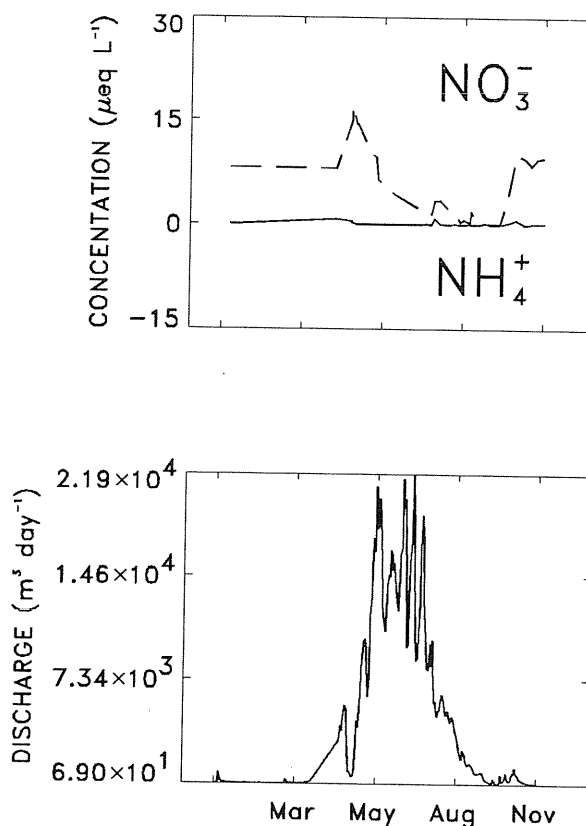*Fig 3. Stream water concentrations of* NO_3^- *and* NH_4^+, *inflow 2, 1986.*

In contrast to NO_3^-, NH_4^+ concentrations were always near or below detection limits and showed no seasonal trends (Figure 3). It is interesting to note that NH_4^+ concentrations in stream waters showed little variation between water years 1986 and 1987, which differed in amount of snowfall, the duration and extent of snow cover, air temperation and other parameters [Williams and Melack, 1991b]. The low concentrations of NH_4^+ in stream

waters relative to the higher concentrations of NH_4^+ in snow and rain strongly indicates that snowmelt runoff and rainfall interact with the basin in some manner and that NH_4^+ in precipitation is removed during this interaction.
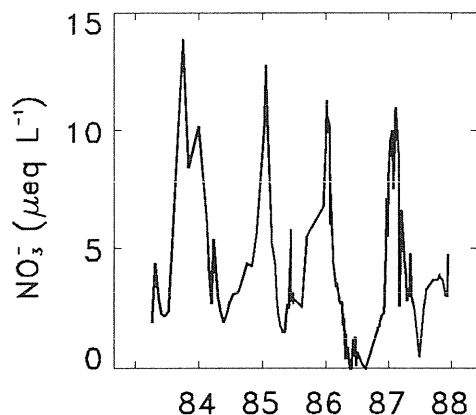

Fig 4. Time series of NO_3^- concentrations in the outlet stream, 1983-1988.

Nitrate export in streamflow occurred primarily during the period of snowpack runoff (Figure 5). About 90% of the annual NO_3^- export in streamwaters in water years 1986 and 1987 occurred during the 100 days of snowmelt runoff in each of those years. Maximum NO_3^- loading in streamflow always occurred during the period of snowpack runoff.

Soils

The high concentrations and loading of NO_3^- in stream waters measured during the period of snowpack runoff may be from several sources or a combination of sources. The high concentrations of about $20\,\mu eq\ L^{-1}$ in streamflow are consistent with maximum concentrations of NO_3^- measured in meltwater draining from the snowpack. Alternatively, these high NO_3^- concentrations measured in stream waters may be from NO_3^- mineralized and then stored in the soil solution over the winter [e.g. Rascher et al., 1987]. Infiltrating meltwater may then force out the NO_3^- from the soil solution and into streamflow, so called piston pumping [Sklash and Farvolden, 1979].

Nitrate concentrations in soil reservoirs at the start of spring melt should be high enough to combine with the more dilute waters of snowpack runoff to produce the elevated NO_3^- concentrations observed in surface waters if mineralization and nitrification processes in soils prior to snowpack
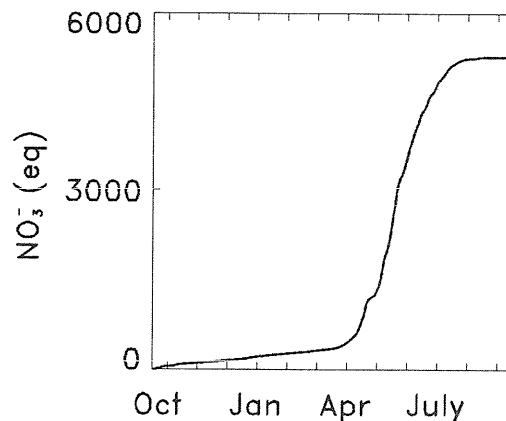

Fig 5. Cumulative export of NO_3^- (eq) in inflow 2, 1986. About 90% of the annual export of NO_3^- occurred during snowpack runoff, from April through June.

runoff are the source of NO_3^- in stream water. Soils were not frozen and free water was present in the soils at the initiation of snowmelt runoff, indicating that piston pumping of soil water was a possible source of streamflow [Williams et al., 1993]. Nitrate concentrations in the soil solution were dynamic, increasing from below detection limits ($0.2\,\mu eq\ L^{-1}$) at the initiation of snowpack runoff to $87\,\mu eq\ L^{-1}$ in late May and early June (Figure 6). Ammonium concentrations in the soil solution showed a similar pattern to NO_3^- but were much more static, with concentrations near detection limits at the start of snowpack runoff and increasing to a maximum of $11\,\mu eq\ L^{-1}$ at the ridge site (Figure 6). The absence of NO_3^- and NH_4^+ in soil solution at the onset of snowpack runoff indicates that mineralization and nitrification processes prior to snowpack runoff were most likely not an important source of N in streamwaters.

Mass Balance

Mass balance calculations for the sum of NO_3^- and NH_4^+ released from the snowpack and the yield of NO_3^- in all inflowing waters confirm that NO_3^- becomes a mobile anion and that NH_4^+ is retained within the basin during the period of snowpack runoff. The basin was a source of about 20% of the NO_3^- in stream waters in 1987, and a large sink (40%) for the NO_3^- in wet deposition in 1987 (Table 3). Conversely, little of the NH_4^+ released from storage in the snowpack reached Emerald Lake as NH_4^+. More than 99% of the NH_4^+ released from the snowpack did not leave the basin as NH_4^+ in 1986 or 1987. Confidence limits are
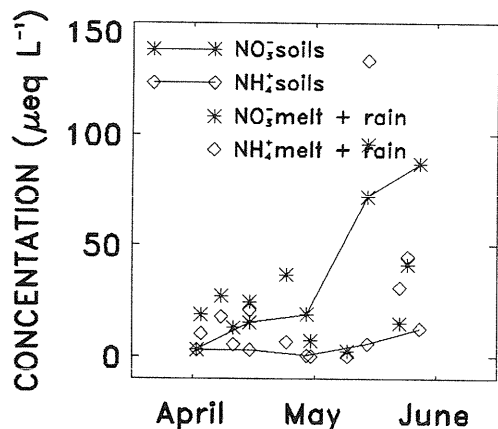
Fig 6. Time series of NO_3^- *and* NH_4^+ *concentrations in the soil solution, ridge site (site 6, Figure 1).*

always difficult to assign to such mass balance calculations. We can state with confidence that NH_4^+ is retained in the basin and that NO_3^- is a mobile anion for all of the year except the summer growing season.

Table 3. N Loading (10^3 eq) in the Snowpack and Stream Inflows to Emerald Lake, Spring Runoff 1986 and 1987

	Year	NO_3^-	NH_4^+
Snowpack	1986	6.0	5.9
	1987	11.2	12.9
Streams	1986	7.3	<0.1
	1987	6.4	<0.1
Fraction*	1986	1.21	0.015
	1987	0.57	<0.01

*Fraction is the ratio of loading in streams to loading in the snowpack.

CONCLUSIONS

The storage and release of inorganic N from the seasonal snowpack at the ELW is an important source of NO_3^- and NH_4^+ to the basin. My results show that the volume-weighted mean annual concentrations of NH_4^+ and NO_3^- in winter snow were ≤ 5.0 µeq L^{-1} and are among the most dilute measurements of N recorded in the northern hemisphere. However about 90% of the annual flux of NH_4^+ and NO_3^- in wet deposition was supplied during the period of snowmelt runoff, due to the large percen-

tage of annual precipitation that occurred as snow. Dry deposition to the seasonal snowpack was evaluated by comparing cumulative event totals with co-located snowpits and indicates that dry deposition of N was not significant relative to wet deposition of N. Inorganic N was eluted from the snowpack in the form of an ionic pulse. Concentrations of NH_4^+ and NO_3^- in the first fraction of meltwater were 3-6-fold greater than bulk concentrations measured in co-located snowpits. The annual seasonal maximum concentrations of NO_3^- in streamwaters occurred during the first stages of snowpack runoff and were 4x the annual mean concentrations in wet deposition in inflowing streams and 2.5x wet deposition concentrations in the lake outflow. Elution of NO_3^- from the snowpack in the form of an ionic pulse appeared to be the cause of seasonal maxima in NO_3^- concentrations in streamwaters. Analysis of inorganic N in soil waters further indicates that snowpack release of N and not mineralization processes and subsequent piston-pumping was the source of the high NO_3^- concentrations in streamwaters. Concentrations of NO_3^- and NH_4^+ in soil waters were both near 0 µeq L^{-1} at the initiation of snowmelt runoff and then increased in concentration in tandem with the release of NO_3^- and NH_4^+ from the snowpack and in rain events. In contrast to the export of NO_3^- during snowpack runoff, more than 99% of the ammonium stored in the seasonal snowpack was retained in the basin. The retention of NH_4^+ in the basin during snowpack runoff indicates that much of snowpack meltwater infiltrates soils before becoming stream water and that soil processes with relatively fast kinetics must be active at this time.

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