Biogeochemistry **55:** 219–245, 2001.

Nutrient fluxes in a snow-dominated, semi-arid forest: Spatial and temporal patterns

D.W. JOHNSON[1,*], R.B. SUSFALK[2], R.A. DAHLGREN[3],
T.G. CALDWELL[4] & W.W. MILLER[1]
[1]*Environmental and Resource Science, College of Agriculture, University of Nevada, Reno, Reno, NV 89512 U.S.A.;*[2]*Environmental Studies, University of California, Santa Cruz, CA 95064 U.S.A.;* [3]*Soils and Biogeochemistry, University of California, Davis, CA 95616-8627 U.S.A.;* [4]*Pacific Northwest National Labs, Richland, WA 99352 U.S.A. (*e-mail: dwj@unr.edu)*

Key words: base cations, nitrogen, Sierra Nevada, snowmelt, soil solution, sulfur

Abstract. We tested five hypotheses regarding the potential effects of precipitation change on spatial and temporal patterns of water flux, ion flux, and ion concentration in a semiarid, snowmelt-dominated forest in Little Valley, Nevada. Variations in data collected from 1995 to 1999 were used to examine the potential effects of snowpack amount and duration on ion concentrations and fluxes. Soil solution NO_3^-, NH_4^+, and ortho-phosphate concentrations and fluxes were uniformly low, and the variations in concentration bore no relationship to snowmelt water flux inputs of these ions. Weathering and cation exchange largely controlled the concentrations and fluxes of base cations from soils in these systems; however, soil solution base cation concentrations were affected by cation concentrations during snowmelt episodes. Soil solution Cl^- and SO_4^{2-} concentrations closely followed the patterns in snowmelt water, suggesting minimal buffering of either ion by soils. In contrast to other studies, the highest concentration and the majority of ion flux from the snowpack in Little Valley occurred in the later phases of snowmelt. Possible reasons for this include sublimation of the snowpack and dry deposition of organic matter during the later stages of snowmelt. Our comparison of interannual and spatial patterns revealed that variation in ion concentration rather than water flux is the most important driver of variation in ion flux. Thus, it is not safe to assume that changes in total precipitation amount will cause concomitant changes in ion inputs to this system.

Introduction

Nutrient fluxes in snow-dominated, semi-arid forests are characterized by a high degree of spatial and temporal variability. These systems often do not have fully closed canopies, leading to a high degree of regular, spatial heterogeneity on a 2–4 m scale due to the presence or absence of trees

(McDaniel & Graham 1992; Stark 1973; Thran & Everett 1987). In addition to the local variation in litterfall contributing to these so-called "islands of fertility", there are also large variations in local snowpack accumulation and rate of melting due to the presence or absence of trees. Stark (1973) noted that more than 80% of total litter decomposition occurred beneath snowpack in a jeffrey pine (*Pinus jeffreyii* [Grev. and Balf.]) forest in Little Valley, Nevada. Decomposition during the snow-free season was limited by severe summer drought as well as by litter and soil hydrophobicity. Stark (1973) also noted that snowpack duration and, consequently, decomposition rate, were much lower in the "tree wells" – areas near tree boles where snow melts early because of radiant heat from the boles. The early snowmelt in the tree wells exposes O horizons to drying and large air temperature fluctuations, slowing decomposition. Thus, the O horizons at the bases of trees are substantially thicker than at further distances from the trees. This observation suggests that factors affecting snowpack duration (whether they are related to total precipitation or to spring temperature) will have a greater effect than temperature *per se* on decomposition rates in these systems.

In addition to substantial spatial variability, semi-arid forests also display a high degree of temporal variability in nutrient fluxes, both interannually and seasonally. The inorganic solute chemistry of streams draining snow-dominated ecosystems may be strongly controlled by snow chemistry during snowmelt, with rapid peaks in the concentrations of some solutes and rapid declines in the concentrations of other solutes during distillation of the snowpack. At Emerald Lake on the western slope of the Sierra Nevada Mountains, Williams and Melack (1991) found up to 100% increases in NO_3^- and Cl^- concentrations in stream water inflow during spring runoff. Given that stream discharge increased by at least ten fold during these periods, the mass flux of NO_3^- during spring runoff dominates the total yearly flux. Recent work in the eastern Sierra Nevada also suggests that organic colloids play an important role in nutrient discharge (Rhea 1993; Ryan & Gschwend 1990; Chin & Gschwend 1991).

The importance of decomposition beneath the snowpack in semi-arid forests also contributes to the high degree of temporal variability by creating the potential for a buildup of mineralized nutrients which could be flushed down to the rooting zone during snowmelt (Stark 1973; Taylor & Jones 1990; Brooks et al. 1996). Lewis and Grant (1980) found that nitrate pulsing through soils in a Rocky Mountain watershed was inversely proportional to snowpack amount and duration. They speculated that soil freezing in low snow years caused increased N mineralization and nitrification, resulting in increased NO_3^- flushing during snowmelt. Denning et al. (1991) postulated that this is an explanation for the NO_3^- pulses observed during snowmelt in

Loch Vale, a Rocky Mountain alpine watershed. In contrast, Brooks et al. (1996) postulated that microbial immobilization accounted for the retention of N released from snowpacks at Niwot Ridge in the Colorado Rockies. They found high rates of respiration and N mineralization beneath the snowpack but very low rates of N leaching from the terrestrial system (NH_4^+ and NO_3^- concentrations in streamwaters remained at trace levels). Similarly, Zak et al. (1990) found that microbes took up more N than a spring ephemeral plant during early spring in a northern hardwood system in Michigan. Preston et al. (1990) found that soil rather than vegetation was the major sink for both NH_4^+ and NO_3^- fertilizer applied to snow in lodgepole pine (*Pinus contorta*) and Douglas-fir (*Pseudotsuga menziesii*) forests in British Columbia.

The high degree of spatial and temporal variability in snow-dominated, semi-arid forests may allow assessment of the potential effects of climate change on these systems. Reduced total precipitation (due to either the vagaries of snowdrift on a spatial level or interannual variation) should cause reduced soil water flux, which should in turn result in increases in the concentration of conservative, weakly adsorbed ions (such as Cl^-) in soil solution. Concentrations of non-conservative ions in soil solutions may be buffered by soil chemical processes or biological uptake and, therefore, may not be sensitive to changes in precipitation. For example, biological processes exert a dominant control over N fluxes, and these controls operate in unique ways in snow-dominated, semi-arid forests. On the other hand, adsorption by Fe and Al (hydr)oxides may exert major control over soil solution $H_2PO_4^-$ and SO_4^{2-} concentrations and fluxes. The effects of changing precipitation on soil solution cation concentrations will be a function of changes in total ion concentration and the degree to which individual cations are adsorbed to exchange sites. As noted by Reuss and Johnson (1986), increased ionic strength will cause trivalent cations to increase disproportionately to di- and monovalent cations (to the 1.5 and 3rd power, respectively) and divalent cations to increase as the square of monovalent cations.

In previous papers, we have described some of the general features of nutrient cycling in two semi-arid forests of the Sierra Nevada Mountains: a lodgepole pine forest in Little Valley, Nevada and a jeffrey pine forest in Sagehen Creek Basin, California (Johnson 1995; Johnson et al. 1997). In comparison to more humid forest ecosystems, these Sierran sites have very low N, S, and H^+ fluxes, but high base cation fluxes transported with the bicarbonate ion. These patterns reflect the relatively low levels of air pollution in the area and the probable input of dry deposition of base cations from nearby arid and semi-arid soils. These Sierran sites also have considerably lower S and N deposition than the more polluted, Mediterranean-climate forests in the San Bernardino mountains of southern California studied by

Fenn and Bytnerowicz (1993). As in most snow-dominated systems, pulses of NO_3^- are released from the melting snowpack each spring in the Sierran systems. Nitrogen released from melting snowpack was retained in the soil in most cases, but substantial pulses of NO_3^- were noted in streamwaters during the snowmelt period of dry years (Johnson et al. 1997). Reasons for the latter are unclear but may include the soil freezing hypothesis of Lewis and Grant (1980) and lower denitrification in riparian areas, early release of NO_3^- from snowpack or soils (prior to the period of maximum plant and microbial uptake).

Simulations of the effects of changing precipitation and temperature at the Little Valley site (and five other forest sites) were recently conducted using the Nutrient Cycling Model (NuCM) (Johnson et al. 2001). The results suggested that soil water flux would change disproportionately with changes in precipitation: results showed an increase of 61% with a 33% increase in precipitation and decrease by 48% with a 33% decrease in precipitaiton (Johnson et al. 2001). This occurred because simulated evapotranspiration changed very little in response to increases and decreases in precipitation (+9 and –12%, respectively). The results also suggested that total N deposition would be less affected by changing precipitation than total water flux would; increasing precipitation by 33% caused only an 8% increase in simulated N deposition and decreasing precipitation by 33% resulted in only a 7% decrease in N deposition. This was due to the relative importance of simulated dry deposition at this site even though total N deposition was very low. Similarly, changes in precipitation caused little change in simulated N leaching in Little Valley because N leaching was strongly regulated by biological uptake in all cases. Changing precipitation caused roughly proportional changes in simulated deposition and leaching of K, Ca, and Mg, however.

The purpose of this paper is to examine the spatial and temporal variation in water and ion flux using five years of data on snowmelt, soil solution, and stream chemistry at the Little Valley site. Variations in the data were used to examine the potential effects of snowpack amount and duration in regulating ion concentrations and fluxes. Based on the above discussion we hypothesized that decreasing snowfall amount would cause the following:

1. Decreased deposition of all ions via snowfall
2. Higher concentrations and increased leaching of NH_4^+ and NO_3^- in soil solutions (because of more freezing and thawing of litter and because of the earlier release of N from snowpack)
3. No change in soil solution base cation concentrations but decreased base cation leaching (because of buffering by cation exchange and weathering)
4. No change in soil solution SO_4^{2-} or $H_2PO_4^-$ concentrations but decreased SO_4^{2-} or $H_2PO_4^-$ leaching (because of buffering by anion adsorption)

5. Increased soil solution concentrations of Cl^- because of concentration (because Cl^- is a conservative ion)

Site and methods

The Little Valley site is located approximately 30 km southwest of Reno, Nevada in the eastern Sierra Nevada mountains. The valley itself is is approximately 2000 ha in size and is defined on the east and west by parallel ridges which reach elevations of 2100 and 2680 m, respectively. Elevation in the valley floor ranges from 1950 to 1980 m. The climate is characterized by warm, dry summers and cold winters; and the major hydrologic event is snowmelt. Mean annual air temperature near the valley floor is 5 °C and mean annual precipitation is 550 mm, approximately 50% of which falls as snow. More than 90% of total precipitation falls between October and July, and snowpack generally persists from mid November until May. Vegetation is dominated by jeffrey pine (*Pinus jeffreyii* [Grev. and Balf.]) and lodgepole pine (*Pinus contorta* Dougl.) at lower elevations and white fir (*Abies concolor* [Gord and Glend.] Lindl.) at higher elevations. The study site is at an elevation of 2015 m, with a slope of less than 3% and with an overstory vegetation dominated by 110-120-year-old lodgepole pine with occasional jeffrey pine. Overstory stocking is 230 stems ha^{-1}, and basal area is 61 m^2 ha^{-1}. Understory vegetation consists of bitterbrush (*Purshia tridentata* D.C.), and various grasses and forbs. Soils at the study site are the Marla soil series, sandy, mixed Aquic Cryumbrepts derived from colluvium of decomposed granite. Some basic chemical and physical data for the soil at the site are provided in Table 1.

Two snowmelt collectors were installed in an opening near the meterological station in Little Valley, and six snowmelt collectors and six tube-type tension lysimeters were randomly located within the 0.10 ha plot. Snowmelt collectors consisted of two 4 L polypropylene bottles attached end-to-end with tygon tubing. The bottom was removed from one of the bottles, creating a 178 cm^2 snowmelt collector which is partially buried and drained to the buried collection bottle. These devices collect rain or throughfall (depending upon their location) during the snow-free seasons and snowmelt during the snow season. The collection bottle was fitted with tubing attached to poles so that collections of snowmelt solutions were possible from beneath the snowpack without disturbance. The snowmelt collectors were in place from October through June; it was impossible to maintain the collectors during later summer and early fall months because of animal (bear) damage. Soil solutions were collected with falling-head, porous cup lysimeters (Soil Moisture Corp., Santa Barbara, CA). The lysimeters were fitted with an extra tube

Table 1. Bulk density (Db), concentrations of C, N, extractable P, cation exchange capacity (CEC), and base saturation (%BS) in soils from Little Valley (standard deviations are given; n = 6.) (concentration data adapted from Johnson et al. 1997)

Horizon and	Db	C	N	C/N	Extr. P	CEC^1_{sum}	CEC^2_{eff}	$\%BS^1_{sum}$	$\%BS^2_{eff}$
Depth (cm)	$g\ cm^{-3}$	%			$\mu g\ g^{-1}$	$cmol_c\ kg^{-1}$		%	
Little Valley, NV									
A (0–5)	1.22 ± 0.04	3.17 ± 2.54	0.11 ± 0.09	32 ± 13	10.0 ± 3.2	8.76 ± 3.79	6.72 ± 3.03	95 ± 4	130 ± 26
BA (5–20)	1.19 ± 0.06	0.58 ± 0.17	0.01 ± 0.01	60 ± 24	7.8 ± 2.9	3.95 ± 0.46	2.73 ± 0.60	96 ± 2	143 ± 29
BC (20–50)	1.26 ± 0.02	0.26 ± 0.05	0.01 ± 0.01	30 ± 15	5.6 ± 2.3	3.44 ± 0.55	2.11 ± 0.40	97 ± 9	164 ± 45
C (50+)	N.D.	0.20 ± 0.04	0.01 ± 0.01	25 ± 11	3.6 ± 2.3	3.59 ± 0.74	2.34 ± 0.15	98 ± 2	149 ± 22

[1] Sum of cations method.

[2] Neutral salt (NH_4Cl) method.

which extended to the bottom of the lysimeter, which, along with the vent tube, allowed removal of soil solutions and re-establishment of vacuum under snowpack without disturbance. Lysimeters were installed at the 15 and 30 cm depths in the soil. Tension was set at –50 kPa at each collection date.

Snowmelt and soil solutions were sampled according the weather conditions (specifically, with regard to how rapidly snow was melting) and varied from approximately two to five weeks during the snowmelt season. Further details on methodology of collecting snowmelt and soil solutions from beneath the snowpack are given by Johnson (1995) and Johnson et al. (1997).

Solutions were filtered (0.2 μm membrane filter) and analyzed for electrical conductivity, pH, alkalinity (titration to pH 4.5), cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+) by Dionex ion chromatography, and anions (Cl^-, NO_3^-, ortho-phosphate, SO_4^{2-}) by Dionex ion chromatography. In some cases, solution volumes were too low for the determination of pH and alkalinity, especially in soil solution. Thus, the data set for pH and alkalinity is incomplete and is not presented here. Grab samples were taken from Franktown Creek, which runs through Little Valley about 0.5 km from the study site, whenever snowmelt and soil solutions were collected and on approximately a monthly basis at other times.

We used the chloride balance method (Lindberg & Johnson 1989) to estimate nutrient fluxes. Chloride fluxes were measured directly from water volumes and concentrations in the snowmelt collectors beneath the forest canopy. We used snowmelt collectors under canopy rather than the open collectors in order to better incorporate dry deposition of Cl^- into the calculations. It was assumed that Cl^- fluxes through the soil were equal to inputs via snowmelt (i.e., that Cl^- was a conservative tracer), and soil water fluxes (SWF, cm) were calculated as the product of snowmelt water flux (SMF, cm) times the ratio of the volume-weighted average Cl^- concentration in snowmelt (CLSM, μmol_c L^{-1}) to volume-weighted average Cl^- concentration in soil solution (CLSS, μmol_c L^{-1}): SWF = (SMF)(CLSM/CLSS). Evapotranspiration values calculated as the difference between snowmelt and soil solution flux at 30 cm averaged 22 cm. These calculated soil water fluxes were then multiplied by volume-weighted average soil solution concentrations to calculate soil leaching rates for the various ions. Because of many uncertainties and assumptions involved in these calculations, the soil solution fluxes presented here must be regarded with some caution. However, they are useful as a means of integrated data to make inter-annual comparisons and for the purpose of making “ball-park” comparisons with measured snowmelt fluxes (e.g., are the calculated soil solution fluxes so much larger or smaller than snowmelt fluxes that even large errors would not change the net balance?)

Results and discussion

Inter-annual trends in annual fluxes and ion concentrations

Total precipitation during the sampling period was above average. This is illustrated by data from nearby Marlette Lake (courtesy of the Western Regional Climate Center at DRI) in Figure 1. During the 1995–1999 water years, total precipitation at Marlette was greater and less variable than the long-term average. Snowmelt volumes collected at Little Valley were somewhat lower than those at Marlette Lake. This was largely due to the lower elevation of Little Valley (2010 m) as compared to Marlette (2440 m) and, to a lesser degree, to the fact that no summertime precipitation was collected at Little Valley. The snowmelt collections at Little Valley included all over-snow precipitation and snowmelt collected between October and July of each year, however, and are estimated to have included at least 90% of total precipitation.

The average annual fluxes are summarized in Table 2 and the annual fluxes by year of water and ions are presented in Figure 1 for the winters of 1994–1995 through 1998–1999. As reported previously (Johnson et al. 1997), this system has very low fluxes of N and S and high fluxes of base cations compared to most forest ecosystems. Average annual fluxes of water appear to be somewhat greater in snowmelt under canopy (SMC) than in snowmelt in the open (SMO). This contrasts with many studies which have shown that small clearings normally cause enhanced snowpack accumulation (Troendle 1983). We suspect that this reflects the vagaries of snow drifting at the site rather than a deviation from the theories of snowpack accumulation; further aspects of the spatial patterns in snowmelt are discussed below.

The interannual variations in ion flux were driven primarily by variations in concentration rather than water flux. The inter-annual patterns in volume-weighted, average ion concentrations (Figure 3) were nearly identical to those in ion flux (Figure 2). There were statistically significant, positive correlations between NH_4^+ Cl^-, NO_3^-, ortho-phosphate (*o*-PO_4), and snowmelt water flux among years (Table 3). These correlations were largely spurious, however: there were also significant, positive correlations between water flux and volume-weighted average concentrations of NH_4^+ Cl^-, NO_3^-, and *o*-PO_4 (Table 3). Only in the case of *o*-PO_4 in SMC was the correlation between water flux and volume-weighted, average concentration not significant. No correlations between Ca^{2+}, Mg^{2+}, K^+, Na^+, or SO_4^{2-} and water flux were found. Thus, it is quite clear that variations in concentration rather than water flux were the dominant cause of inter-annual variations in ion flux.

Inter-annual variations in snowmelt fluxes of NH_4^+, NO_3^-, and *o*-PO_4 were very large; but there were no clear trends over time. Soil solution fluxes

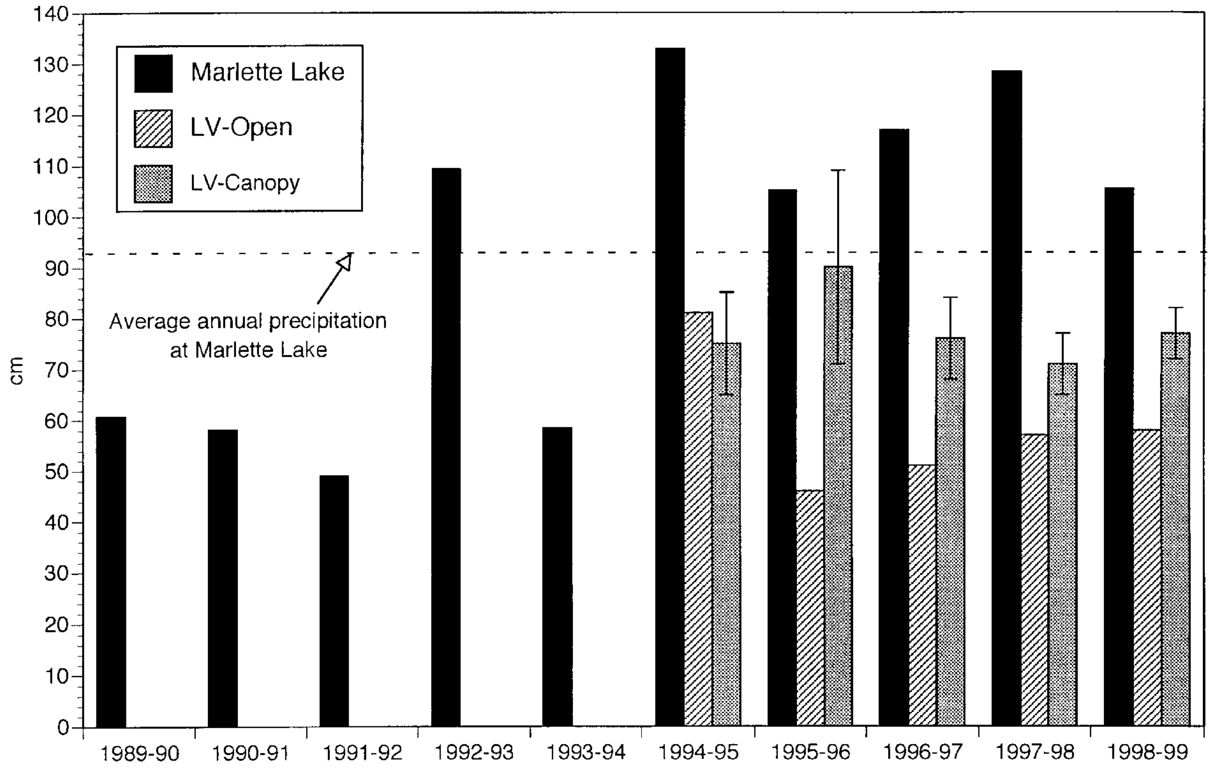

Figure 1. Total precipitation at Marlette Lake, NV from 1989 to 1999 and in open- and under-canopy snowmelt at the Little Valley site from 1994–1999. (Standard errors are shown.) Data courtesy of the Western Regional Climate Center, Desert Research Institute, Reno, Nevada.

Table 2. Water and ion fluxes in the Little Valley lodgepole pine site over a five-year period (SMO = snowmelt in the open; SMC = snowmelt under canopy; SS15 = soil solution at 15 cm; SS30 = soil solution at 30 cm) (means and standard errors)

	H_20	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	NH_4^+	NO_3^-	$H_2PO_4^-$	SO_4^{2-}
	cm	mol_c ha^{-1} yr^{-1}								
SMO	58 ± 6	656 ± 149	39 ± 10	168 ± 40	131 ± 48	554 ± 7	13 ± 5	20 ± 4	0.4 ± 0.3	35 ± 8
SMC	78 ± 3	1149 ± 51	155 ± 19	319 ± 37	346 ± 85	103 ± 13	44 ± 23	26 ± 9	4.4 ± 1.6	41 ± 9
SS15	65 ± 6	1700 ± 53	249 ± 46	397 ± 25	482 ± 91	103 ± 13	3 ± 1	3 ± 2	0.4 ± 0.4	37 ± 9
SS30	56 ± 1	1526 ± 71	148 ± 12	363 ± 19	624 ± 102	103 ± 13	2 ± 2	4 ± 3	0.2 ± 0.1	35 ± 10

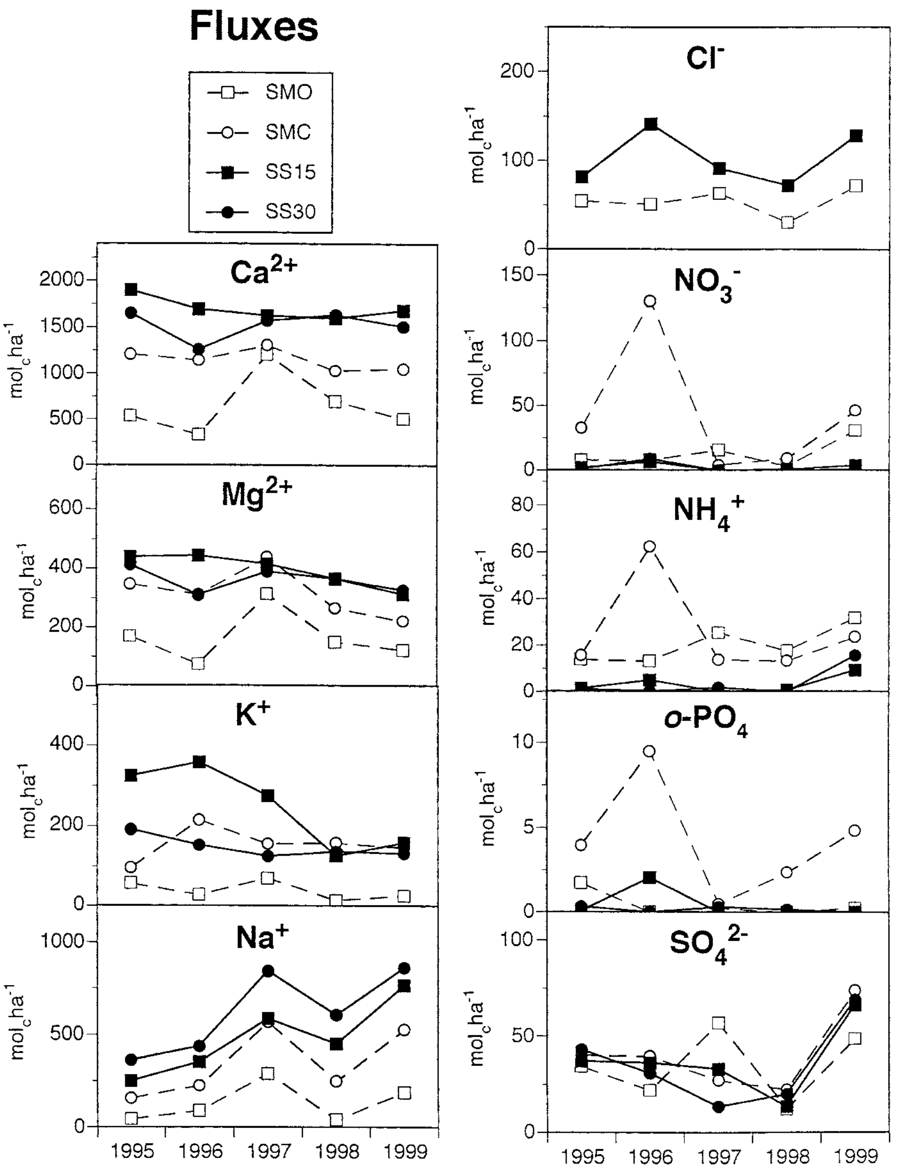

Figure 2. Inter-annual fluxes of ions in open snowmelt (SMO), snowmelt under canopy (SMC), soil solution at 15 cm (SS15), and soil solution at 30 cm (SS30) at the Little Valley site.

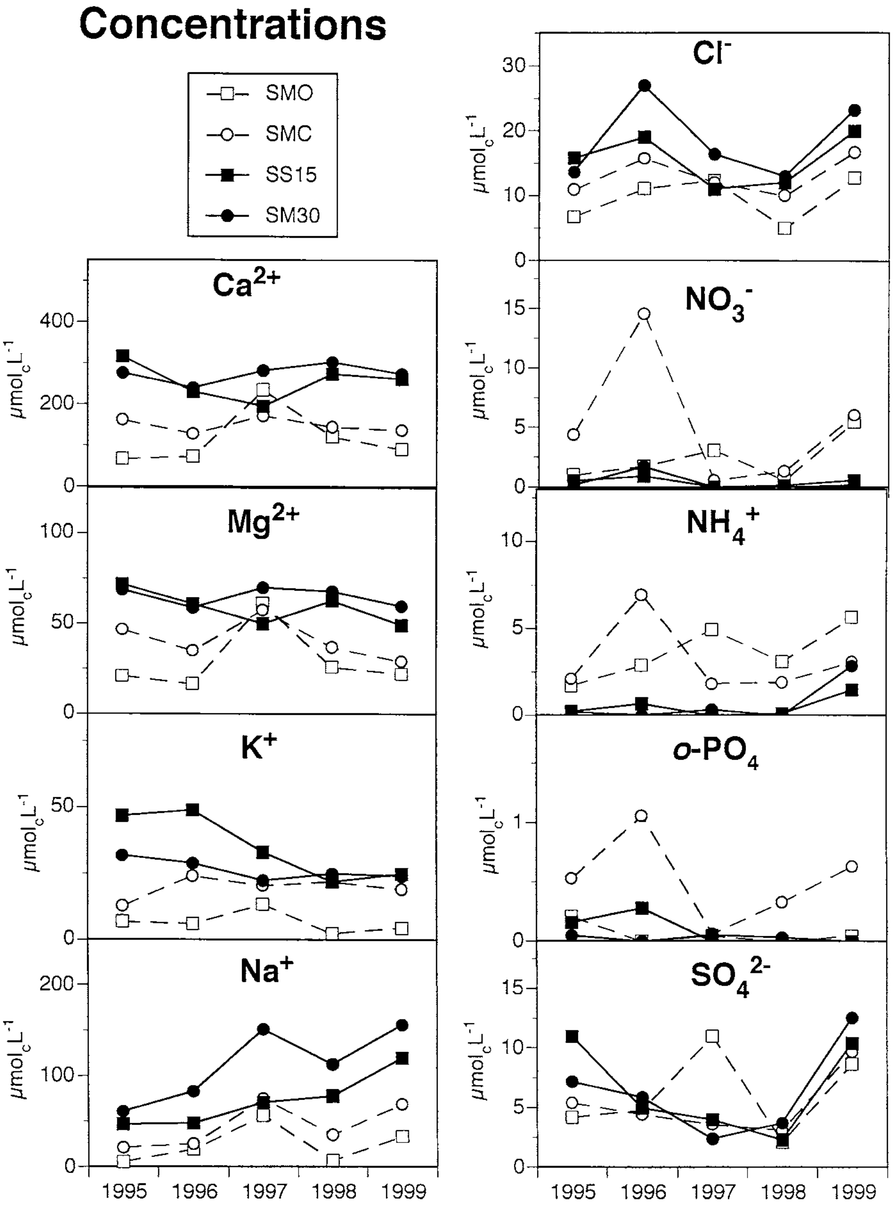

Figure 3. Inter-annual variation in volume-weighted average annual concentrations of ions in open snowmelt (SMO), snowmelt under canopy (SMC), soil solution at 15 cm (SS15), and soil solution at 30 cm (SS30) at the Little Valley site.

Table 3. Correlation coefficients (r^2), sign of slope, and significance of regressions of ion fluxes against water fluxes and of volume-weighted average concentrations against water fluxes over the five-year (1994–1999) sampling period. Only parameters for correlations with $p = 0.10$ are shown

Level*	Ion	Slope	r^2	P
Ion flux against water flux by year				
SMO	$H_2PO_4^-$	+	0.89	0.04
SMC	NH_4^+	+	0.90	0.01
SMC	$H_2PO_4^-$	+	0.74	0.06
SMC	NO_3^-	+	0.94	< 0.01
SMC	Cl^-	+	0.72	0.07
SS30	Mg^{2+}	+	0.71	0.07
Ion concentration against water flux by year				
SMO	$H_2PO_4^-$	+	0.85	0.03
SMC	NH_4^+	+	0.87	0.02
SMC	NO_3^-	+	0.93	< 0.01
SMC	Cl^-	+	0.72	< 0.01
SS15	Ca^{2+}	–	0.87	0.02

*SMO = snowmelt, open; SMC = snowmelt under canopy; SS15 = soil solution, 15 cm; SS30 = soil solution, 30 cm.

of NH_4^+, NO_3^-, and *o*-PO_4 were uniformly low, reflecting a high degree of biological and chemical control of these ions, and showed no pattern over time. Inter-annual variations in snowmelt Cl^- and SO_4^{2-} fluxes were also large and, unlike the case for NH_4^+, NO_3^-, and *o*-PO_4, appeared to strongly affect soil solution concentrations and fluxes. (Soil solution Cl^- fluxes were assumed to be equal to those in under-canopy snowmelt for the purposes of water flux calculations, as noted in the Methods section.) Snowmelt and (especially) soil solution fluxes and concentrations of Na^+ increased during the five-year sampling period; between 1994–1995 and 1998–1999, volume-weighted average soil solution concentrations of Na^+ increased by two- to three-fold ($p < 0.05$ for the 15 cm depth, $p < 0.10$ for the 30 cm depth, regressing calculated fluxes against year). Snowmelt and soil solution K^+ fluxes and concentrations decreased approximately 30% during the sampling period (but the changes were not statistically significant). Snowmelt and soil solution Ca^{2+} and Mg^{2+} fluxes and concentrations showed no consistent pattern with the exception of K^+ in the 15 cm level of soil solution, which decreased by nearly 50% during the five-year sampling period.

In nearby Franktown Creek, there were no trends in any of the base cations during the five-year sampling period (Figure 4). (Samples for the period July

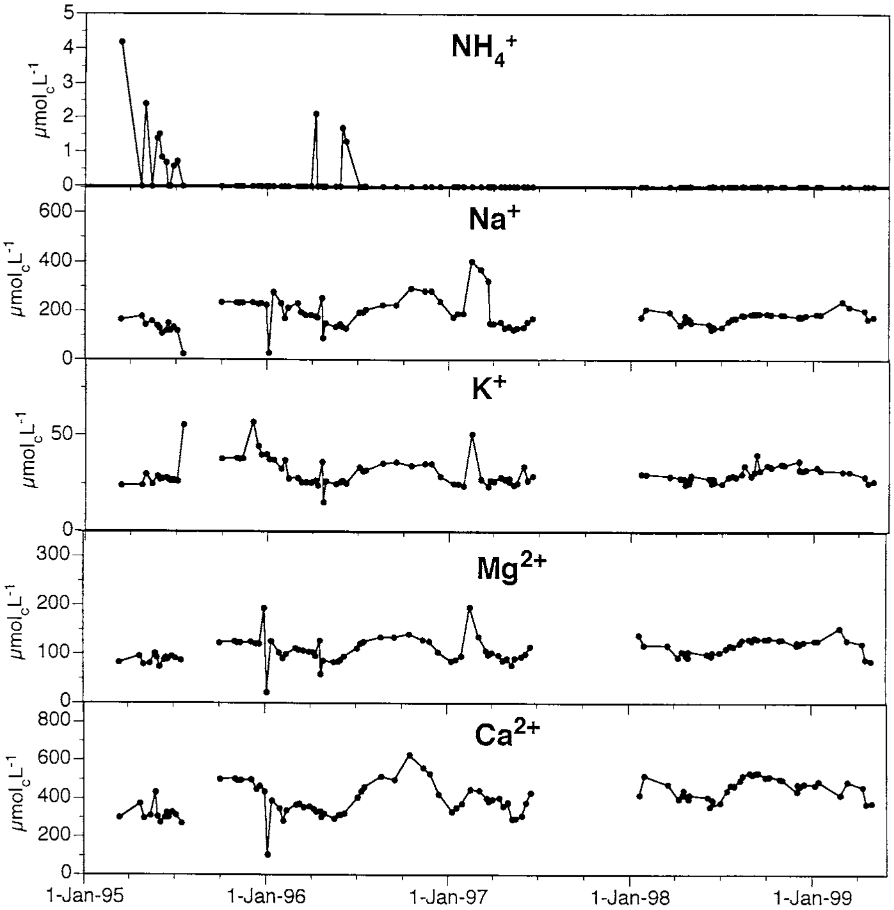

Figure 4. Ammonium and base cation concentrations in Franktown Creek in Little Valley from 1995 through 1999.

through December 1998 were lost in shipment.) There were some minor variations in NH_4^+ and NO_3^-, but no peaks of the magnitude recorded during the previous droughty period (Johnson 1995) were observed. Sulfate showed a downward trend between 1995 and 1997 ($p < 0.01$, regressing concentration against date), then an upward trend in 1998–1999 ($p < 0.01$ regressing concentration against date) (Figures 4 and 5).

Seasonal patterns in fluxes and ion concentration

Many studies have reported pulses in ion concentrations in snowmelt, soil solution, and streamwater during the snowmelt period (Fahey & Knight 1986;

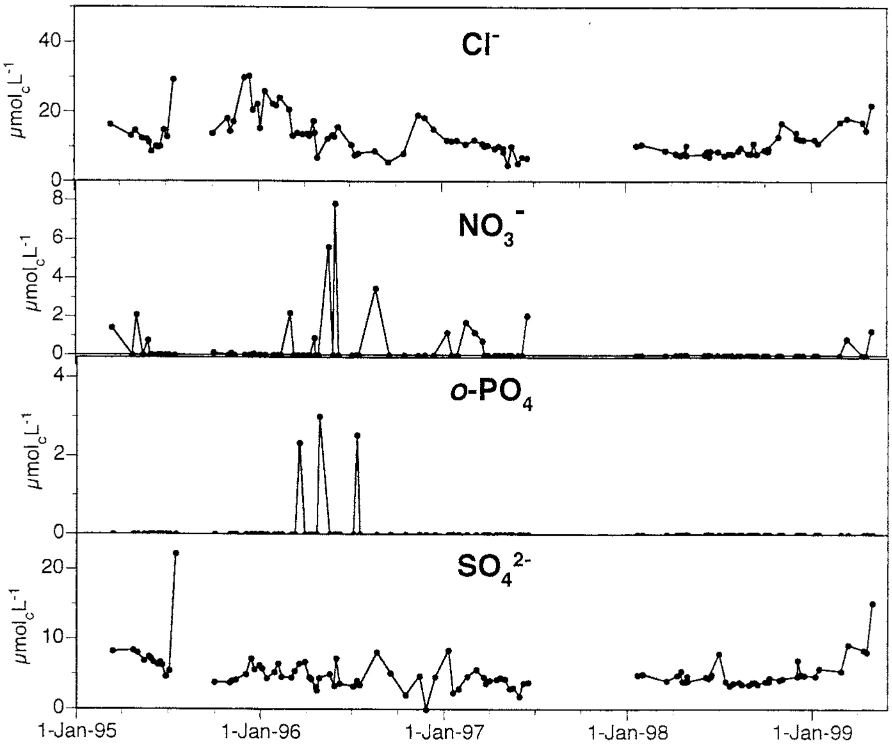

Figure 5. Chloride, NO_3^-, o-PO_4, and SO_4^{2-} concentrations in Franktown Creek in Little Valley from 1995 through 1999.

Marsh & Pomeroy 1999; Stottlemeyer 1987; Stottlemeyer & Toczydlowski 1990, 1999; Stottlemeyer & Trundle 1992; Berg 1992; Cadle et al. 1984; Denning et al. 1991; Williams & Melack 1991; Lewis & Grant 1980; Creed et al. 1996; Rascher et al. 1987; Roberge & Plamondon 1987). We have also reported such patterns for the Little Valley site and other sites in the eastern Sierra Nevada mountains (Johnson 1995; Johnson et al. 1997). In contrast to most studies (Fahey & Knight 1986; Bowman 1992; Marsh & Pomeroy 1999; Berg 1992; Williams & Melack 1991; Peters & Leavesley 1995; Williams et al. 1995), we usually found in the eastern Sierra that the highest concentrations and the bulk of the ion flux occur in the later portion rather than the earlier part of the snowmelt. This is illustrated in Figures 6 through 8, which show the patterns in water flux and ion concentration in the under-canopy snowmelt and soil solution during the 1994–1995 season. During the spring of 1995, snowmelt commenced in early March; and the bulk of the water was lost from the snowpack in March and April. Ionic concentrations during this period were substantially lower than in the subsequent period from April

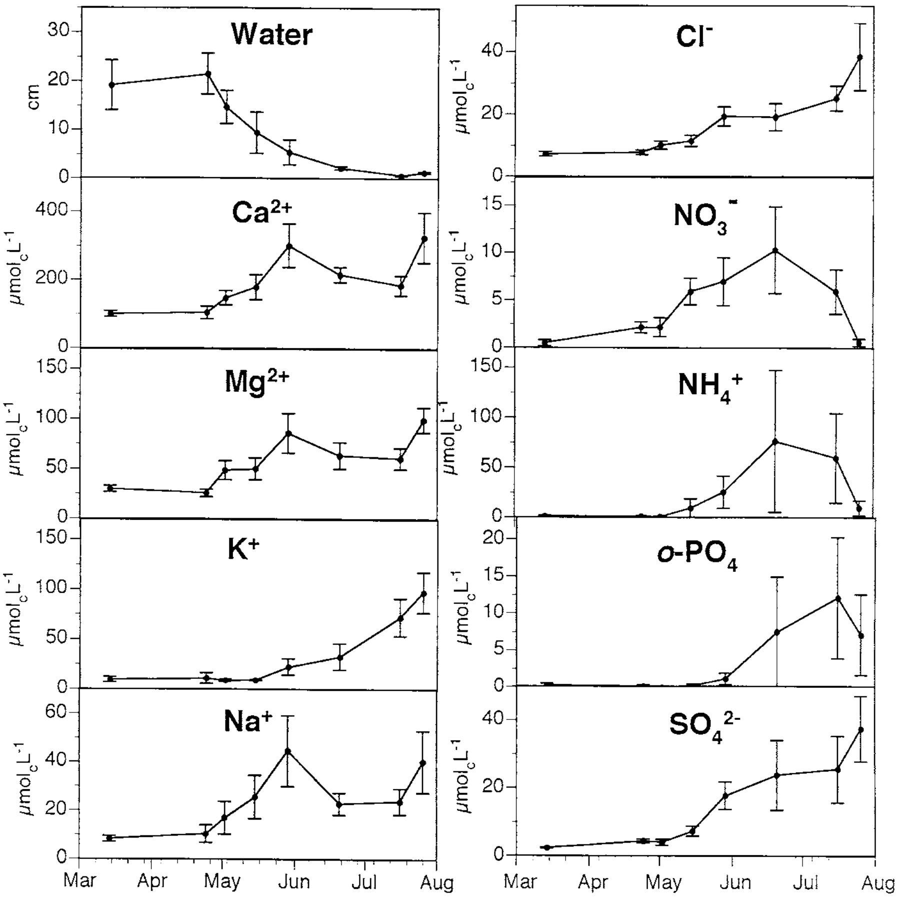

Figure 6. Water flux and ion concentrations in under-canopy snowmelt during 1995 in Little Valley.

through July when less water volume was melting from the snowpack. The only deviations from this pattern were the declines in NH_4^+, NO_3^-, and *o*-PO_4 during the very last stages of snowmelt in July. Soil solutions also showed a general pattern of increased concentrations of most ions over time, especially at the 15 cm depth (Figures 7 and 8).

The increases in ion concentration later in the snowmelt period more than counterbalanced the decline in water flux during the later part of snowmelt in the 1994–1995 season, so that the largest proportion of the ion fluxes occured later rather than earlier during snowmelt. This is illustrated in Figure 9, which shows the cumulative flux of water as a percent of total water flux in under-canopy snowmelt (top) and the cumulative fluxes of ions plotted

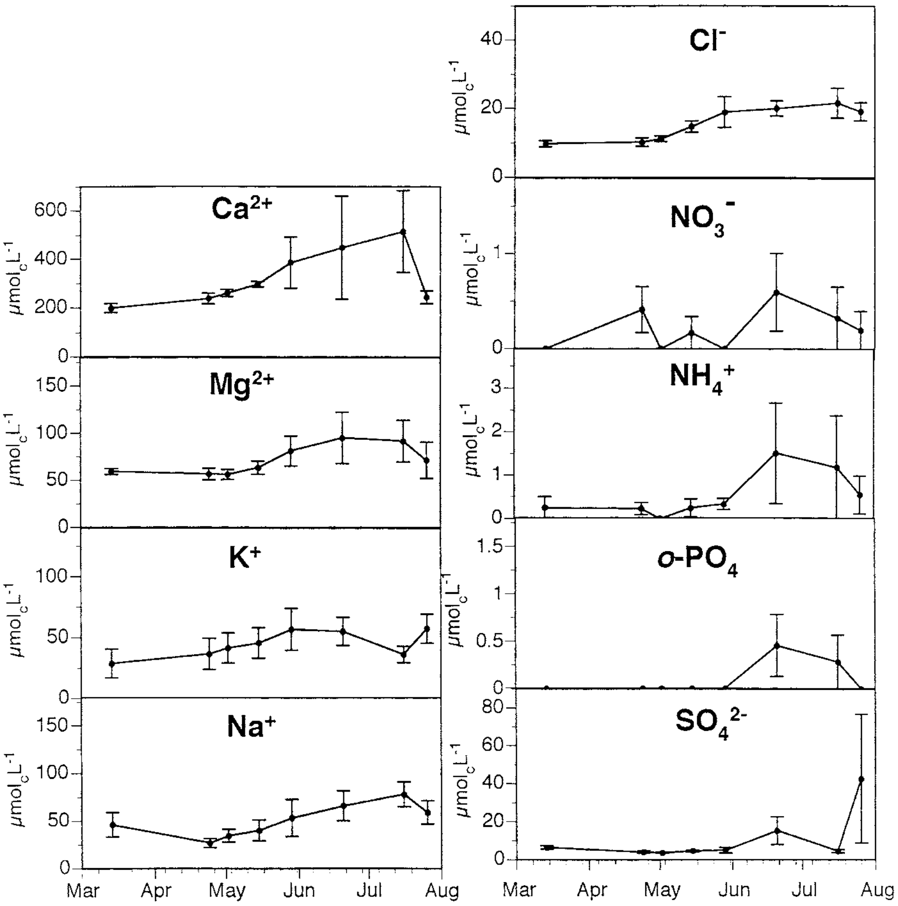

Figure 7. Ion concentrations in soil solution at 15 cm during 1995 snowmelt in Little Valley.

against percent of total water flux for the season (bottom). In contrast to the results obtained by Berg (1992) from the nearby Sierra Snow Laboratory, the plots of cumulative ion fluxes (percent of total) versus cumulative water flux (percent of total) are concave rather than convex, indicating that the bulk of ionic flux occurs later, not earlier, during snowmelt. The pattern of late release of ions from snowmelt noted above held true for each replicate collector (not shown).

The same patterns in snowmelt water and ion fluxes also appeared for most ions in most other years monitored. To illustrate this, we present in Table 3 the percent of water and ion flux at approximately the halfway point through snowmelt for each of the five monitoring years. In the 1994–1995 season, the percent of total fluxes of each ion was less than the percent of total water

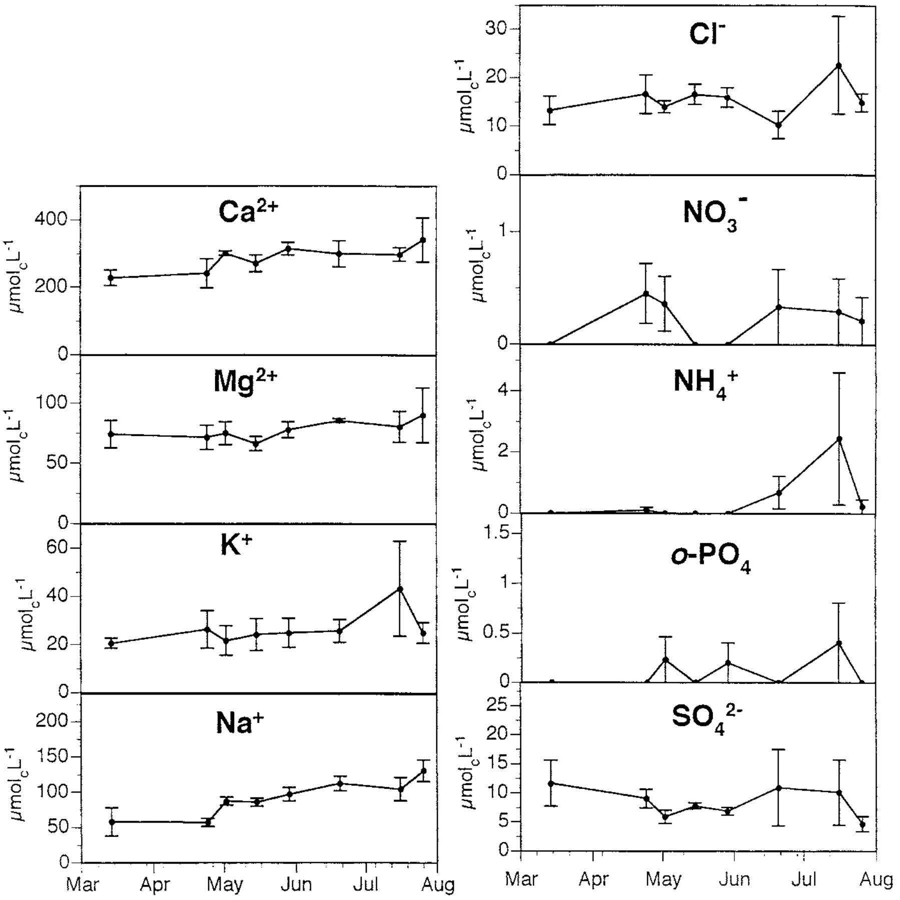

Figure 8. Ion concentrations in soil solution at 30 cm during 1995 snowmelt in Little Valley.

flux (57%) at the approximate halfway point. Similar patterns were noted in the 1996–1997 through 1998–1999 seasons. The 1995–1996 season was an exception: the percent of total ion fluxes was slightly greater than water flux at the approximate halfway point for Ca^{2+}, K^+, Mg^{2+}, Na^+, Cl^-, and NO_3^- but not for NH_4^+, o-PO_4, and SO_4^{2-} (Table 3). Thus, the patterns of water and ion release from melting snowpack varied from year to year; in most cases, however, the bulk of the flux occurred late during snowmelt.

Spatial patterns in water and ion fluxes

The spatial variation in water and ion fluxes among the SMC collectors was substantial. This pattern is illustrated in Figure 10 for the 1994–1995 season; and the volume-weighted, average concentrations for snowmelt and

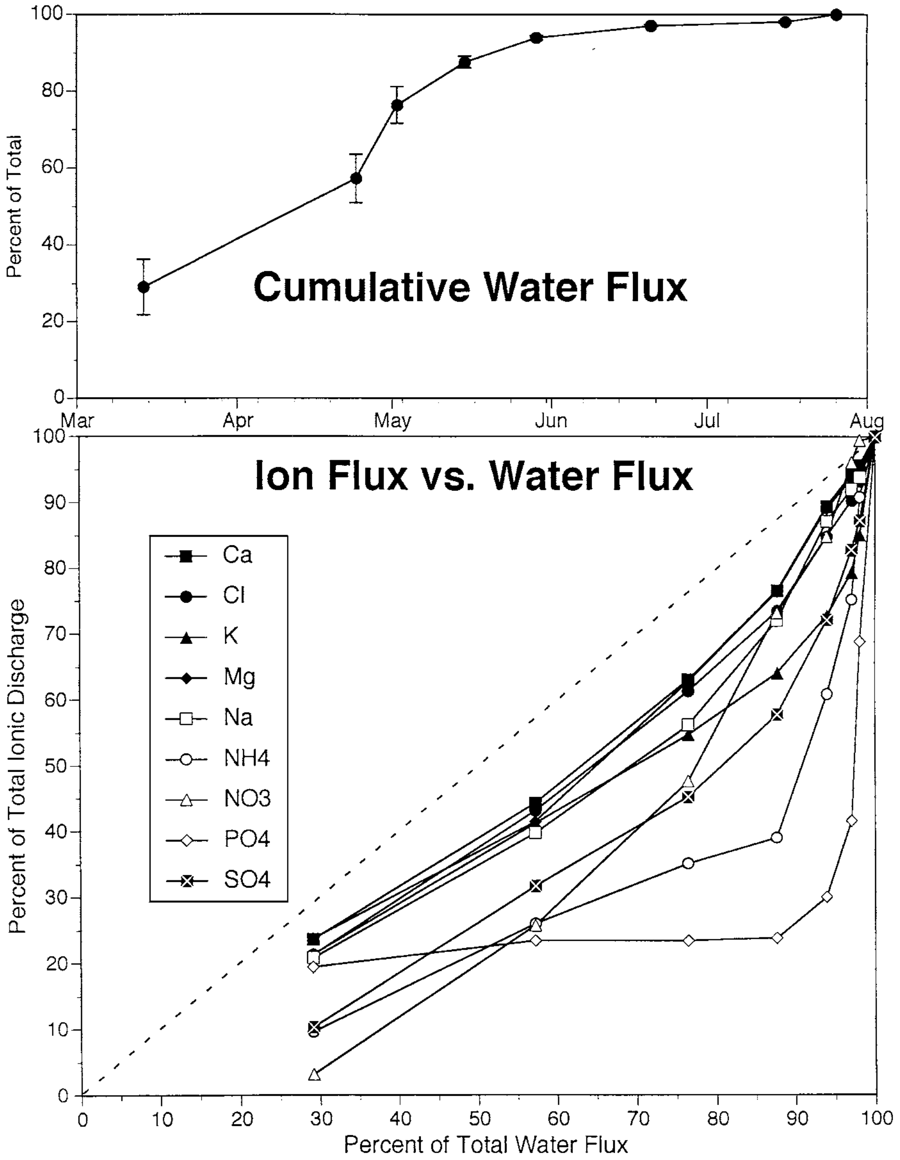

Figure 9. Cumulative water flux (top) and percent cumulative ion discharge plotted against percent of cumulative water flux in under-canopy snowmelt (bottom) during the 1995 snowmelt in Little Valley.

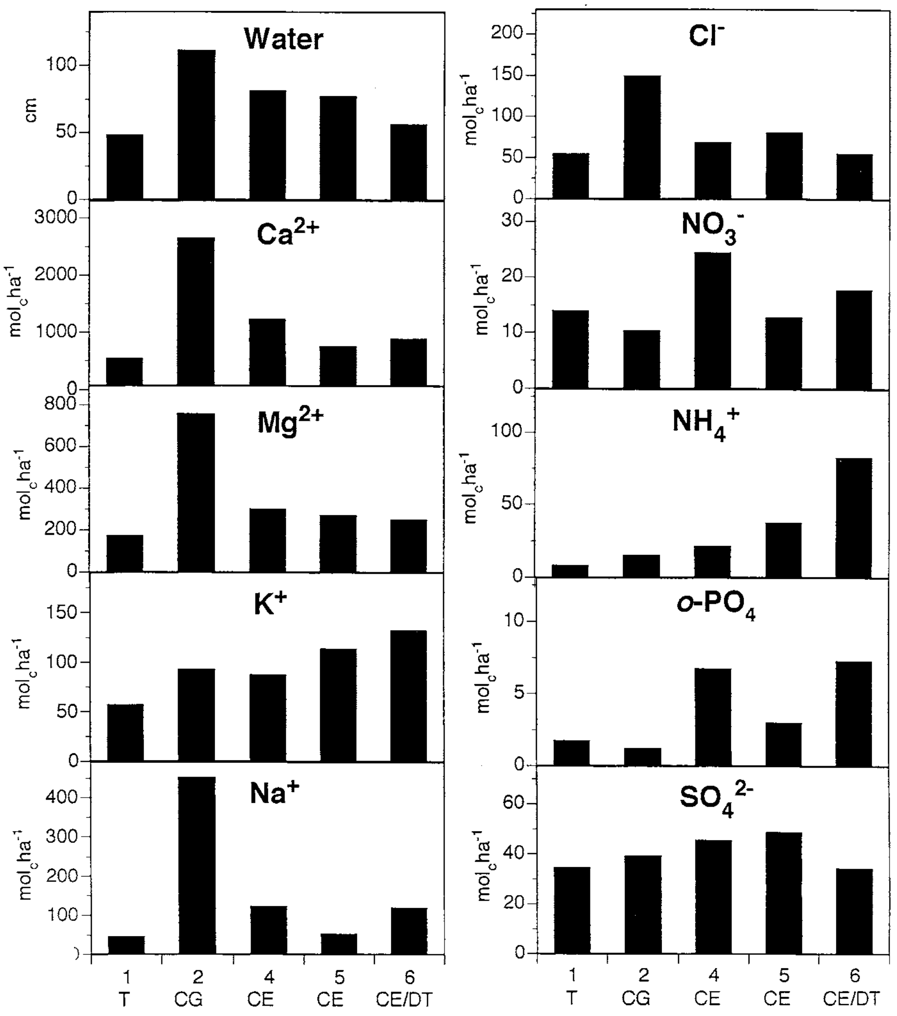

Figure 10. Water and ion fluxes in under-canopy snowmelt in various collectors in Little Valley during the 1995 snowmelt (T = under tree; CG = canopy gap; CE = canopy edge; DT = dead tree).

soil solution for the individual collectors in the 1994–1995 season are shown in Figure 12 (Collector #3 was not operational during this season because of animal damage). Water flux was considerably greater in one collector in a small canopy gap (#2) than in any of the other collectors, but the overall variation in water flux among collectors was not clearly related to canopy position. The fluxes of K^+, NH_4^+, NO_3^-, and o-PO_4 in snowmelt also varied substantially among collectors, but these variations were not related to those

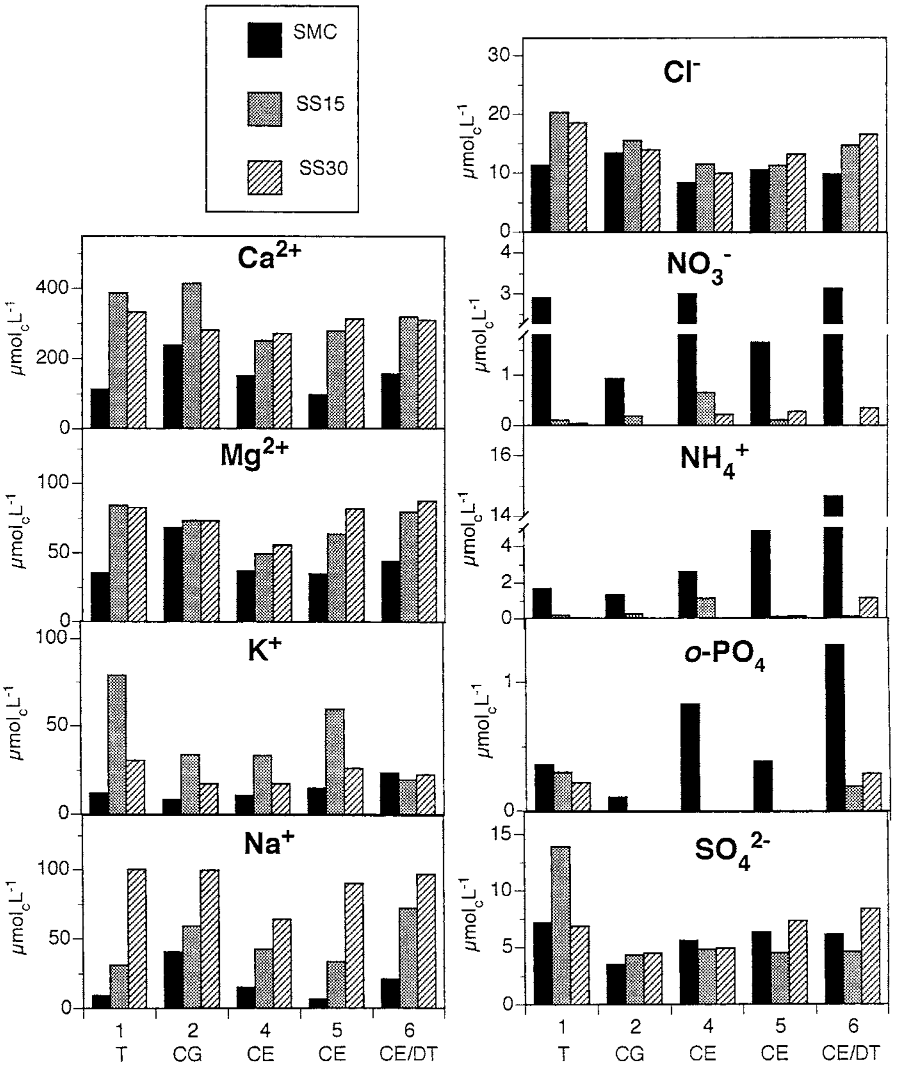

Figure 11. Ion concentrations in snowmelt under snowmelt (SMC), soil solution at 15 cm (SS15), and soil solution at 30 cm (SS30) in various collectors in Little Valley during the 1995 snowmelt (T = under tree; CG = canopy gap; CE = canopy edge; DT = dead tree).

in water flux or to the presence or absence of a tree canopy over the individual collectors (Figure 10). The fluxes of these ions were largely influenced by spatial variations in concentration, but concentration was not clearly related to canopy position (Figure 11).

Soil solution concentrations did not follow the same patterns as snowmelt concentrations (Figure 11). As noted previously, soil solution NO_3^-, NH_4^+, and

Table 4. Ratio of the percent of total annual ion flux to percent of total annual water flux at approximately halfway through snowmelt for the five monitoring years

Year	*1995*	*1996*	*1997*	*1998*	*1999*
% of H_2O flux	57%	52%	48%	43%	55%
Ratio of percent of total ion flux to percent of total water flux					
Ca^{2+}	0.78	1.03	0.64	0.59	0.87
K^{2+}	0.72	1.07	0.89	0.82	1.37
Mg^{2+}	0.73	1.04	0.96	0.79	1.08
Na^{2+}	0.70	1.15	0.76	0.40	0.93
Cl^{2+}	0.75	1.11	0.66	1.16	1.10
H^+	1.14	1.21	0.74	0.92	1.19
NH_4^+	0.46	0.90	1.88	0.85	0.41
NO_3^-	0.45	1.18	0.65	1.36	0.63
$H_2PO_4^-$	0.41	0.84	N.D.	N.D.	N.D.
SO_4^{2-}	0.55	0.64	0.74	1.04	0.87

o-PO_4 concentrations were considerably lower than in snowmelt because of biological and chemical interactions within the soil. Soil solution K^+ concentrations at the 15 cm depth were substantially greater than in SMC, but soil solutions at the 30 cm depth were reduced again. This pattern for K^+ is typical of more humid forest ecosystems (Cole & Rapp 1981; Johnson & Lindberg 1992; Fahey & Knight 1986), and reflects strong K cycling by the vegetation.

In contrast to K^+, NH_4^+, NO_3^-, and *o*-PO_4, the spatial patterns of Ca^{2+}, Mg^{2+}, Na^+, and Cl^- fluxes in snowmelt fairly closely resembled those of water flux (Figure 10). This was due to the influence of water flux itself and the patterns in concentration: the volume-weighted-average concentrations of Ca^{2+}, Mg^{2+}, Na^+, and Cl^- were greater in those collectors with greater water flux (especially collector #2) than in those with lower water flux (Figure 11). These patterns in snowmelt concentration did not carry into the soil solution, however: the concentrations of Ca^{2+}, Mg^{2+}, Na^+, and Cl^- were unrelated to those in snowmelt (Figure 11). The spatial pattern for Cl^- was what one would expect for a conservative ion: greater increases in concentration between snowmelt and soil solution near trees (because of greater water loss due to evapotranspiration) than in open areas. The spatial pattern of snowmelt SO_4^{2-} concentration was the only case in which there was apparent dilution: concentrations were lower where there was greater water flux, and the spatial variation in SO_4^{2-} flux was fairly uniform.

Table 5. Correlation coefficients (r^2), sign of slope, and significance of regressions of volume-weighted ion concentrations against snowmelt water fluxes over horizontal space (among snowmelt and soil solution collector replicates). Only parameters for correlations with p = 0.10 are shown

Season	Ion	Slope	r^2	P
Snowmelt				
1994–1995	NO_3^-	–	0.66	0.10
1994–1995	SO_4^{2-}	–	0.87	0.07
1998–1999	Cl^-	–	0.57	0.08
1998–1999	NH_4^+	+	0.82	0.01
Soil Solution, 15 cm depth				
1994–1995	$H_2PO_4^-$	–	0.70	0.08
1996–1997	Ca^{2+}	+	0.99	0.05
1996–1997	SO_4^{2-}	–	0.99	0.02
1994–1995	Mg^{2+}	–	0.98	0.01
1995–1996	K^+	–	0.67	0.09
Soil Solution, 30 cm depth				
1995–1996	Na^+	–	0.59	0.07
1998–1999	K^+	–	0.60	0.07

Snowmelt data from the 1994–1995 and 1995–1996 seasons suggested that Ca^{2+}, Mg^{2+}, Na^+, and Cl^- fluxes in snowmelt followed water flux fairly closely. Data from other seasons did not necessarily support this trend, however: increased snowmelt water flux caused increased ion flux in snowmelt only for some ions during some years (Table 4). There was little evidence of dilution effects either: significant, negative correlations between snowmelt water flux and volume-weighted average concentrations were found for only a few ions in some years (Table 5). Thus, it appeared that ion concentrations in both snowmelt and soil solution were controlled by factors other than water flux when analyzed on a spatial level.

Summary and conclusions

The analysis of inter-annual trends in this data set was complicated by the fact that all five years had above normal snowfall; nonetheless, the data show that inter-annual differences in ion input via snow can vary considerably and quite independently from total snowfall amount. Thus, even the simplest and most straightforward hypothesis – Hypothesis 1, that decreased snowfall would cause decreased ion inputs via snow – cannot be supported when comparing fluxes on an inter-annual basis. On a spatial basis, increased snowmelt resulted in increased inputs of only some ions (primarily base cations and Cl^- during some seasons). Thus, it is therefore not safe to assume that changes in snowfall amount will cause concomitant changes in ion inputs via snowfall in this system.

Soil solution NO_3^- and NH_4^+ concentrations and fluxes were uniformly low, and the variations in concentration that occurred bore no relationship to snowmelt water flux or the input of these ions from the snowpack. Apparently, biological uptake controlled NO_3^- and NH_4^+ quite closely at all times. Thus, Hypothesis 2 (lower snowfall will cause increased soil solution NH_4^+ and NO_3^- concentrations and increased leaching because of more freezing and thawing of litter and because of the earlier release of N from snowpack) was rejected on all counts.

Hypothesis 3 (decreasing snowfall will cause no change in soil solution base cation concentrations but will cause decreased base cation leaching because of buffering by cation exchange and weathering) was partially supported. While it was clear that weathering caused a net loss of base cations from these soils and that the water flux alone did not greatly influence base cation concentrations, it was equally clear that soil solution cation concentrations were affected by cation concentrations in snowmelt.

Hypothesis 4 (decreasing snowfall will cause no change in soil solution SO_4^{2-} or o-PO_4 concentrations but will cause decreased SO_4^{2-} or o-PO_4 leaching because of buffering by anion adsorption) was not supported. Soil solution o-PO_4 concentrations were uniformly low and unaffected by either water flux or by variations in inputs of o-O_4 from snowmelt. Soil solution SO_4^{2-} concentrations, while not directly related to water flux, closely followed the patterns in snowmelt water, suggesting minimal buffering by solid-phase soil SO_4^{2-} adsorption.

Hypothesis 5 (decreasing snowfall will cause increased soil solution concentrations of Cl^- because of concentration) was not supported. While it appeared that Cl^- was a conservative ion in this system, snowmelt Cl^- concentrations did not decrease with increasing water flux, either on a temporal or spatial basis.

Perhaps the most interesting result of this investigation was the timing of ion release during snowmelt. According to the literature (Fahey & Knight 1986; Bowman 1992; Marsh & Pomeroy 1999; Berg 1992; Williams & Melack 1991; Peters & Leavesley 1995; Williams et al. 1995), most ions exit the snowpack in advance of the bulk of the water. This pattern clearly did not hold for the Little Valley site. Possible reasons for this include (1) sublimation and (2) dry deposition of dust and organic detritus to the snowpack during the later periods of snowmelt. Schmidt et al. (1998) estimate that sublimation could account for the loss of about 20% of peak water equivalent from snowpack in forest systems of the Colorado Rocky Mountains. Sublimation may well accelerate during the later phases of snowmelt as daytime temperatures rise, causing increased concentration of ions remaining in the snowpack. The presence of both mineral and organic matter in the snow in Little Valley was quite evident during the later stages of snowmelt. These materials may be leached of nutrients as temperatures increase, resulting in higher ion concentrations.

Acknowledgements

This research was supported by the Nevada Agricultural Experiment Station, University of Nevada, Reno and in part by the Department of Energy. Technical help by Valerie Yturiaga and Donn Geisinger is greatly appreciated.

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