

Precipitation Chemistry in and Ionic Loading to an Alpine Basin, Sierra Nevada

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Wet deposition of solutes to an alpine catchment in the southern Sierra Nevada was measured from October 1984 through March 1988. Rainfall had a volume-weighted pH of 4.9, and snowfall had a volume-weighted pH of 5.3. Acetic and formic acids were important components of all wet deposition, contributing 25–30% of the measured anions in snowfall and, through analysis of charge balance deficits, the same percentage in rainfall. The NO_3^- to SO_4^{2-} equivalent ratio for all wet deposition was 1.16. Ammonium concentration was tenfold greater than H^+ in rainfall; ammonium nitrate and ammonium sulfate appear to be the principal nitrate and sulfate containing aerosols in wet deposition. Snowmelt runoff (1985 and 1986) or snowpack runoff plus rainfall during the period of snowpack runoff (1987) supplied 90% of the annual solute flux from wet deposition to the catchment. The amount of snow water equivalence (mm m^{-2}) and H^+ , SO_4^{2-} , and Cl^- (eq m^{-2}) in cumulative snowfall measured on snowboards was similar to the accumulated deposition of these parameters measured in snowpits at midwinter and during maximum snow accumulation periods, while about 20% of the NO_3^- in snowfall was not stored in the winter snowpack. Dry deposition was therefore not an important contributor of H^+ , NO_3^- , and SO_4^{2-} to the winter snowpack. The source of the ions in snowfall was air masses that originated over the Pacific Ocean, while low Cl^- and Na^+ relative to NO_3^- and NH_4^+ in rainfall indicate that local urban and agricultural areas were the major source of the ions in rainfall.

INTRODUCTION

In much of western North America and mountainous regions of Europe and Asia, deep snowpacks form through the late autumn, winter, and early spring. The montane snowpack accumulates wet and dry atmospheric deposition, which may be held in storage until release during a melt period. The rugged and variable topography characteristic of alpine areas can result in large spatial differences in the chemistry [Tranter *et al.*, 1987] and snow water equivalence [Elder *et al.*, this issue] of snow. Quantifying the solute storage in the snowpack of an alpine basin is therefore difficult but important to investigations of the effect of snowpack runoff on the hydrochemistry and aquatic biota of these basins. Furthermore, water input from precipitation to alpine basins is known to vary 50% or more on an annual basis [California Department of Water Resources, 1930–1989]. Therefore multiyear sampling is necessary to successfully characterize the average input of solutes to alpine basins from wet deposition.

In alpine environments there exists few data on year-round and multiyear precipitation chemistry. The quality and quantity of wet deposition can change significantly with precipitation type and with seasons at lower elevations. For example, in eastern North America the ratio of NO_3^- to SO_4^{2-} is much higher in snowfall than in rainfall [Chan *et al.*, 1987], which can have important consequences to the acidification of catchments [Galloway *et al.*, 1987]. Storm tracks have seasonal trends, which can shift the origin of ions in precipitation from regions with little anthropogenic influences to regions with high anthropogenic influences [Anlauf *et al.*, 1986].

In the western United States, atmospheric deposition at high elevations has received little attention, and several

important questions are outstanding. The relative importance of sea salt, continental, and anthropogenic aerosols is unknown. The relative importance in wet deposition of the strong acid anions (NO_3^- , SO_4^{2-} , and Cl^-) and organic acids, and the balancing cations H^+ and NH_4^+ , is also unknown. How these parameters vary on a seasonal basis, an annual basis, and by precipitation type has not been investigated at high elevation in the Sierra Nevada.

In this paper we quantify the precipitation chemistry over a 3-year period in an alpine catchment in the southern Sierra Nevada. Precipitation at the Emerald Lake watershed (ELW) ranged from one of the wettest years on record (1986) to one of the driest (1987). We compare the volume-weighted mean chemistry and ionic loading of snowfall to rainfall, with particular emphasis on the relationships of NO_3^- , SO_4^{2-} , and NH_4^+ . Source areas for ions in precipitation are evaluated. We assess the storage of solutes in the snowpack by comparing the solute loading from cumulative snowfalls to solute storage in snowpits at representative dates for midwinter, maximum snow accumulation, and spring melt periods. For purposes of chemical mass balance calculations and modeling we investigate spatial variation in the chemistry of snowfall and the snowpack to permit an accurate calculation of ionic loading, with estimates of standard error, to the catchment.

SITE DESCRIPTION

The ELW is located on the upper Marble Fork of the Kaweah River drainage in the southern Sierra Nevada of California (36°35'49"N, 118°40'30"W). The basin surface area is 120 ha, elevation ranges from 2800 m to 3416 m, and topography is steep and rugged, with a median slope of 31°. Exposure is generally toward the north, typical of cirques in the Sierra Nevada. West-facing slopes are more common than east-facing slopes [Dozier *et al.*, 1989].

The basin is located in a designated Wilderness Area, 8 km

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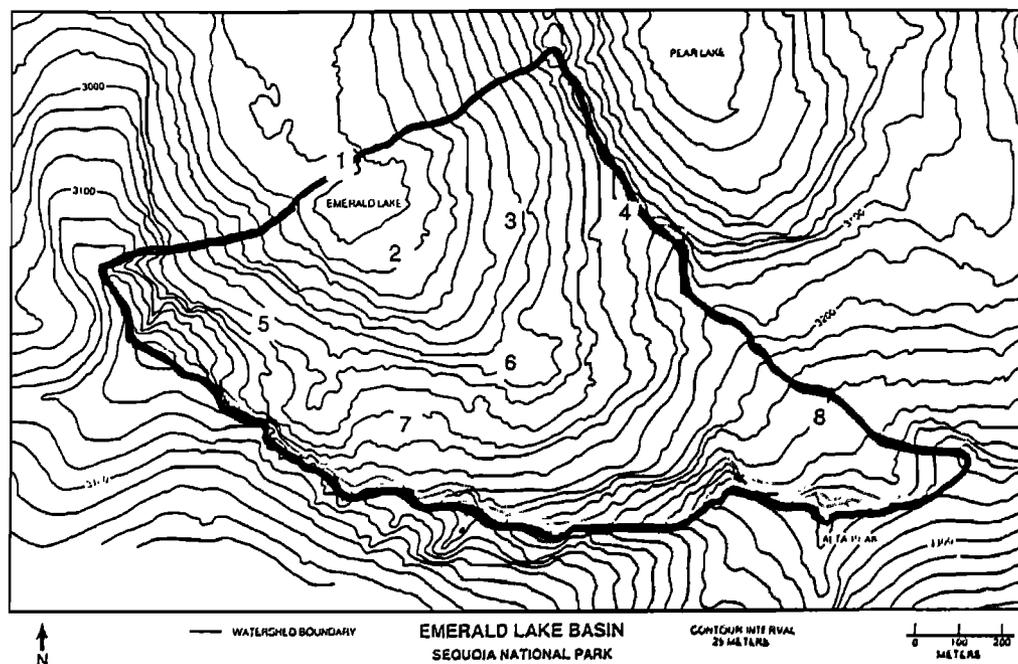


Fig. 1. Topographic map of the Emerald Lake watershed and wet deposition sampling sites: 1, tower; 2, inlet; 3, bench; 4, ridge; 5, ramp; 6, pond; 7, hole; 8, cirque. Sampling sites for snow events and snowpits in water years 1985 and 1986 were at 1, 2, 4, and 6. Snowpit locations during 1987 and 1988 were at 2, 3, 5, 6, 7, and 8.

from and 700 m above the nearest road. Access to the catchment is on foot or on skis. About 20 km to the east of the catchment, and 1000 m higher, is the crest of the Sierra Nevada. The catchment lies to the east and downwind of major urban and agricultural areas of California. The San Francisco Bay Area is about 200 km to the northwest of the basin, and the large agricultural area of the San Joaquin Valley begins only 35 km to the west. Little anthropogenic activity occurs in or adjacent to the Emerald Lake basin, but the atmosphere over the basin does have the potential for contact with air masses from highly populated areas. *Tonnessen* [this issue] provides a more detailed description of the location and physical attributes of the Emerald Lake basin.

METHODS

Precipitation Sampling

Sampling for wet deposition spanned three water years, 1985–1987, and included winter snowfall in 1988. Our water year began on October 1 and ran through the following September 30 and was designated by the second calendar year. Winter snowfall was defined as accumulating snowfall, generally deposited during the months of November through April; no rainfall occurred during this period. Winter snowfall was sampled using two techniques. In water years 1985 and 1986 snow was sampled on an event basis at 1–4 sites (Figure 1); for water years 1986, 1987, and 1988 snow was sampled at three to six snowpits (Figure 1) during the period of maximum snow accumulation, which occurred circa April 1 during all years.

Integrated samples of the entire snowpack were obtained by digging pits to the ground and collecting duplicate, contiguous, vertical cores in increments of 40 cm. The snow samples were collected using polyvinyl chloride (PVC) tubes

(5 cm diameter, 50 cm long), which had been soaked in 10% HCl and then rinsed at least five times with deionized water. The snow cores were transferred into polyethylene bags. Snowfall events were collected on 1-m² snowboards. Collection of snow on snowboards followed the same protocol as snowpits. Duplicate profiles were sampled at each snowboard, there were two snowboards at each site, and 1–4 sites were sampled, depending on weather and avalanche conditions.

The snow water equivalence (SWE) of each sample was determined individually, in 1985 and 1986 from the weight of the sample bag and volume of the core and in 1987 and 1988 by use of a 1-L density cutter, as detailed by *Elder et al.* [this issue]. The ionic concentrations of each snowfall event were determined by calculating the volume-weighted mean concentrations (VWM) for each vertical profile, then a weighted average was calculated for each board, then for each site, and finally, a VWM concentration for the snow event was calculated by combining weighted means from all sites. A similar procedure was used to calculate the VWM concentrations of solutes in the snowpack from snowpits.

Rain was defined as precipitation that was 100% liquid water, or liquid water plus hail, at the collector. Rain generally fell in the months of May through October. Autumn snow was defined as wet snow, or a mixture of snow and rain, that was deposited in the months of September and October (which are in different water years) and where significant snowmelt occurred after deposition. Designation of precipitation type was made by field personnel during the storm. Solutes in rain and autumn snow were collected with a wet-only Aerochem Metrics model 301 sampler, located near the inlet to Emerald Lake (site 2 in Figure 1).

The SWE used to calculate areal solute loading from snowfall for water year 1985 was from cumulative measurements from snowboards at the inlet site [*Dozier et al.*, 1989].

While this information was available in water year 1986, the SWE used to calculate areal solute loading for water years 1986 through 1988 was from snow surveys conducted during the period of maximum snow accumulation and corrected for snowmelt and sublimation losses [Kattelmann and Elder, this issue]. We believe this is an accurate measurement of the SWE in the basin, since depth of the snowpack was measured at 86 (1986) to 354 (1988) points, each of which was the average of five depth measurements, and density was measured at multiple snowpits [Elder *et al.*, this issue]. Areal estimates of rain and autumn snow at the ELW used a combination of Belfort rain gauges located at low (2800 m), medium (3000 m) and high (3200 m) elevations, along with eight pairs of nonrecording gauges distributed throughout the watershed [Kattelmann and Elder, this issue].

Ionic loading to the basin was calculated by combining the VWM chemistry of precipitation with the precipitation amount over the basin. Volume-weighted mean concentrations of solutes in the snowpack were calculated from cumulative event totals of winter snowfall in 1985 and 1986. Autumn snowfall in water year 1986 was common, therefore the accumulated solutes from autumn snowfall were added to winter snowfall in 1986, to correctly calculate the ionic concentration of the snowpack at maximum accumulation. For water years 1987 and 1988 we used the VWM concentrations from six snowpits selected to represent the major elevational, slope, and radiation classes of the basin (Figure 1). Comparison of precipitation chemistry from cumulative event samples to snowpack storage of solutes, conducted at the inlet site in 1986, indicated that the two techniques produce results within 10% of each other, as long as snow temperatures remain below 0°C. For this reason our protocol for sampling the precipitation chemistry of winter snowfall was changed from event sampling in 1986 to snowpack sampling at the period of maximum accumulation in 1987 and 1988.

Sample Collection, Storage, and Analysis

Careful cleaning, collection, storage, processing, and analysis were required to insure reliable chemical measurements of the very dilute snow that occurs in the Sierra Nevada. Only plasticware (usually PVC, polyethylene, or polycarbonate) containers were used. Prior to use the containers were soaked in 10% HCL and rinsed at least five times with deionized water (conductance 0.2–0.5 $\mu\text{S cm}^{-1}$). If liquid samples were to be obtained, the containers were rinsed with the sample also. Bags used to collect snow samples were acid-washed as above in 1985 and 1986; in 1987 and 1988 bags were rinsed five times with deionized water, soaked overnight in deionized water, and then rinsed five more times with deionized water. The simpler procedure was followed in 1987 and 1988 after a laboratory comparison showed no contamination of blanks from either procedure.

All snow samples were kept frozen at -20°C until ready for analysis. In the laboratory, individual samples were placed in a covered polyethylene bucket and melted at room temperature in 1985 and 1986 ($\approx 20^{\circ}\text{C}$) and at 4°C in 1987 and 1988. As soon as the sample was melted, air-equilibrated pH and conductivity were measured on unfiltered samples. Subsamples were filtered through prerinsed, 47-mm filters with approximately 1- μm pore size (Gelman A/E glass fiber in 1985, 1986, and the first part of 1987; Nuclepore polycar-

bonate filters in 1987 and in 1988). One set of subsamples was immediately analyzed for ammonium and phosphate. A second set was stored in the dark at 4°C for subsequent cation and anion determinations. A third set in 1987 and 1988 was preserved with chloroform and stored in the dark at 4°C for organic acid analysis.

The pH measurements were made with combination electrodes suitable for use in dilute waters (Sargent Welch S-30072-15 or Ross 8104) and a Fisher Acumet 805 pH meter. For each series of measurements the electrode was calibrated with pH 7.00 and pH 4.00 reference buffers and washed twice for 3 min with stirred deionized water. The pH calibration was then verified with low ionic strength solutions of HCl (10^{-5} and 10^{-4} N); calibration was repeated if the measured pH values of these solutions differed from the expected values by more than 0.1 units. The electrode was rinsed with an aliquot of sample, and the temperature-compensated pH determination made on a fresh, quiescent sample after 5 min. Conductance was measured with a Yellow Springs Instruments Model 32 meter and glass electrode with a 0.1 cell constant. Simultaneous temperature measurements were made, and conductivity was standardized at 20°C using a coefficient of 2% per $^{\circ}\text{C}$. The conductivity cell was calibrated with dilute solutions of KCl.

Ammonium and phosphate were determined spectrophotometrically by the indophenol-blue and molybdenum-blue methods [Strickland and Parsons, 1972]. Calcium, magnesium, sodium, and potassium were analyzed with a Varian AA6 atomic absorption spectrophotometer. An air-acetylene flame was used; addition of lanthanum chloride suppressed chemical and ionization interferences during calcium and magnesium determinations. Especially dilute samples were also analyzed with a graphite furnace and manual 20 μL injections. Chloride, nitrate, sulfate, acetic acid (CH_3COO^-), and formic acid (HCOO^-) were measured by ion chromatography (Dionex Model 2010i), employing chemical ion suppression and conductivity detection.

An overall precision, expressed as percent relative standard deviation (RSD, the percent ratio of the standard deviation to the mean), was obtained for the entire study period as the mean RSDs for cations ($n = 10$) and anions ($n = 23$). The individual RSDs were calculated from samples to which known additions were made in duplicate. Duplicate samples were separated by 10–15 samples in each run. Analytical precisions for Ca^{2+} , Mg^{2+} , Na^+ , and K^+ were 3.1, 1.0, 3.3, and 6.2 RSD, respectively. Analytical precisions for NO_3^- , SO_4^{2-} , and Cl^- were 1.2, 2.7, and 13.4 RSD, respectively. The detection limit of all solutes (defined as two times the standard deviation of standards measured near the detection limit) was less than 0.5 $\mu\text{eq L}^{-1}$, except for Ca^{2+} which was 1.0 $\mu\text{eq L}^{-1}$. Analytical accuracy was assessed using National Bureau of Standards certified controls. Our charge balance control demonstrated there was no bias in our analytical performance [Berg *et al.*, 1989].

Evaluation of ion leaching from filters was conducted by comparing 85 duplicate snow samples in 1987, filtered from Gelman and Nuclepore filters, as well as comparison with known standards. There was no filter effect on ionic concentrations, except for Na^+ . Gelman A/E glass fiber filters that are prerinsed add, on average, 2.0 $\mu\text{eq L}^{-1}$ of Na^+ to samples, while Nuclepore filters do not affect ionic concentrations of Na^+ in samples. Ninety out of 392 samples in 1987 were filtered with Gelman A/E glass fiber filters before

TABLE 1. Charge Balance Summary for Inorganic Ions in Wet Deposition

Type	Year	<i>n</i>	Σ+	Σ-	Σ Ions	Σ+/Σ-	% IOD
Rain	1985	4	122	88	210	1.38	16
Rain	1986	6	62.0	46.2	108	1.34	15
Rain	1987	13	127	100	227	1.27	12
Autumn snow	1985	6	37.5	27.3	64.8	1.37	16
Autumn snow	1986	5	41.7	29.0	70.7	1.44	18
Autumn snow	1987	1	54.7	38.7	93.4	1.41	17
Winter snow	1985	29	11.9	9.3	21.2	1.28	12
Winter snow	1986	85	9.1	6.5	15.6	1.40	17
Winter snow	1987	328	12.4	8.6	21.0	1.44	18
Winter snow	1988	392	9.0	4.7	13.7	1.91	31

Here *n* is the number of individual samples analyzed, Σ+ is the sum of the positive inorganic ions, Σ- is the sum of the negative inorganic ions, Σ Ions is the sum of major inorganic ions, Σ+/Σ- is the ratio of cations to anions, and %IOD is (Σ+ - Σ-)/(Σ+ + Σ-) times 100.

Nucleopore filters were employed. An average value of 2.0 $\mu\text{eq L}^{-1}$ was subtracted from the measured Na^+ in these 90 samples, as well as all snow samples from 1985 and 1986, to correct for Na^+ contamination by the glass fiber filters. If the corrected Na^+ value was 0 or less, that sample was assigned a Na^+ concentration of 0.1 $\mu\text{eq L}^{-1}$.

Charge balance totals for the major inorganic ions in wet deposition for water years 1985 through 1987, and winter snowfall in 1988, were calculated to evaluate the quality of wet deposition data (Table 1). Average cation to anion ratios ranged from 1.27 to 1.91. There was no difference in the average cation to anion ratio by precipitation type, with the exception of the high ratio (1.91) in winter snowfall in 1988. Ion percent differences (IOD) ranged from 12 to 31%; IOD is the difference of cations minus anions divided by the sum of cations plus anions, times 100%. For winter snowfall these IOD percentages are well within the chemical reanalysis criteria of $\pm 60\%$ set by the NADP quality assurance guidelines for charge totals less than 50 $\mu\text{eq L}^{-1}$ [Peden, 1983]. Of the 834 individual snow samples, only 4 exceeded the IOD reanalysis criteria set by the NADP.

The consistent bias of positive charge in snowpack samples needs clarification. Our quality control indicates no bias in our analytical performance. Acid neutralizing capacity (ANC) was not consistently measured, because at the pH of the samples, carbonate equilibrium reactions indicate that HCO_3^- concentrations should be less than 1 $\mu\text{eq L}^{-1}$. Occasional analysis for ANC using the Gran titration method always resulted in concentrations less than 1 $\mu\text{eq L}^{-1}$. Dissolved organic carbon is known to occur in western snow at very low levels [Laird *et al.*, 1986]. Our measurements of dissolved organic N and P in snow support the likelihood of dissolved organic carbon, and hence organic acids, in snow (Melack, unpublished data, 1991). Measurements of acetate and formate were therefore started in 1987. Measurement of these organic acids in 1988 improved the charge balance of the seasonal snowpack from a cation to anion ratio of 1.40 in 1986 to 1.22 in 1988.

Samples of rainfall and autumn snowfall were refrigerated at about 5°C and mailed within 24 hours to the analytical laboratory at the California Air Resources Board. Conductance and pH were measured immediately in the field as well as in the laboratory. Analytical techniques were the same as for winter snow. The laboratory participated in semiannual EPA performance surveys to determine the accuracies of ion analyses. Accuracy of Ca^{2+} was consistently biased on the

high side. No other ions showed bias in accuracy. Analytical precisions for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and NH_4^+ were 29.2, 6.8, 29.1, 12.7, and 9.2 RSD, respectively. Analytical precisions for NO_3^- , SO_4^{2-} , Cl^- , pH and conductance were 6.0, 3.6, 9.5, 1.6, and 1.4 RSD, respectively. Additional details on analytical techniques, accuracy, and precision are reported by Blanchard *et al.* [1989].

More details on analytical techniques and quality control and quality assurance are provided by Dozier *et al.* [1989] and Sickman and Melack [1989].

RESULTS

Annual Wet Deposition

The VWM concentration of each of the major ions in the annual wet deposition to the catchment was less than or equal to 5.4 $\mu\text{eq L}^{-1}$ for water years 1985 through 1987 (Table 2). Ammonium and H^+ each accounted for about 18% of the total ionic content of precipitation, followed closely by NO_3^- (17%), SO_4^{2-} (14%) and Cl^- (12%). The remaining 21% of ionic flux was divided among Ca^{2+} , Na^+ , K^+ , and Mg^{2+} , in that order.

The average annual wet deposition to the catchment, for water years 1985 through 1987, was 472 eq ha^{-1} (Table 2). There was a twofold difference in annual loading from wet deposition during water years 1985 through 1987. Solute loading in water years 1986 and 1987 was similar, even though 1986 was one of the wettest water years on record and 1987 one of the driest.

Seasonal variability in solute loading from wet deposition was pronounced. Solute flux from winter snowfall was about 300 eq ha^{-1} , from autumn snowfall about 100 eq ha^{-1} , and from rain about 35 eq ha^{-1} in years of normal (1985) and above normal (1986) precipitation. On a percentage basis, winter snowfall for both years deposited about 91% of the annual water to the basin and about 68% percent of the ion flux to the ELW (Table 3); autumn snow provided about 8% of the water flux and 20% of the ion flux to the basin. Annual snowfall (autumn and winter snowfall) for these two water years supplied about 99% of the water and 90% of the solute flux to the catchment.

The below normal water year (1987) had different fluxes of water and solutes, by precipitation type. Water flux from rainfall in 1987 was 159 mm, about five times the 32 mm deposited in 1986 and about ten times the 16 mm deposited in

TABLE 2. VWM Concentrations and Average Loading of Ions in Annual Wet Deposition, Water Years 1985 Through 1987

	Volumn Weight Mean, $\mu\text{eq L}^{-1}$				Loading, eq ha^{-1}			
	1985	1986	1987	Mean*	1985	1986	1987	Average†
SWE, mm	1157	2625	959	1580
pH	5.24	5.31	5.22	5.27
Conductance, $\mu\text{S cm}^{-1}$	4.4	3.8	6.2	4.5
H^+	5.8	4.9	6.0	5.3	67	128	58	84
NH_4^+	2.6	3.3	14.4	5.4	30	87	138	85
Ca^{2+}	2.9	1.3	5.6	2.6	34	35	54	41
Mg^{2+}	0.8	0.4	1.9	0.8	9	10	18	12
Na^+	2.4	1.6	3.5	2.2	28	41	34	34
K^+	1.0	0.9	1.0	0.9	11	23	10	15
NO_3^-	3.5	3.1	11.9	5.0	41	81	114	79
SO_4^{2-}	3.7	2.5	9.8	4.3	43	65	94	67
Cl^-	4.5	3.2	2.8	3.5	52	85	27	55
Σ Ions	27.2	21.1	56.9	30.0	315	555	547	472

SWE is snow water equivalence.

*Volume-weight mean ionic concentration.

†Arithmetic average ionic loading.

1985. Rainfall in 1987 accounted for 17% of the water flux to the basin and 66% of the annual solute flux, while autumn snow only provided only 2% of the water and 4% of the solute flux, and winter snow supplied 81% of the water and 30% of the solutes. However, 85% of the solute flux in rainfall in 1987 occurred during the time period of snowpack runoff.

Winter Snowfall

VWM chemistry of snow. The VWM concentrations of major ions in winter snowfall for water years 1985 through 1988 were very low (Table 4). Hydrogen had the highest concentration of the major ions ($4.6 \mu\text{eq L}^{-1}$); all other ions had concentrations less than $3 \mu\text{eq L}^{-1}$. Analysis for the organic acids, acetate and formate, began in water year 1987. These organic acids composed 9 and 21% of measured anions in 1987 and 1988. Methodological problems associated with analysis of organic acids in 1987, primarily degradation over time during storage, probably resulted in low values for 1987.

The average ratio of NO_3^- to SO_4^{2-} in winter snow varied from 0.77 to 1.75, on an equivalent basis (Table 5). The NO_3^- to SO_4^{2-} ratio was lowest in years of normal and above

normal snowfall and greatest in years of below normal snowfall. The NH_4^+ to Σ^- ratio in winter snowfall ranged from 0.1 to 0.4 (Table 5). The balancing of strong acid anions by NH_4^+ was least in years of normal and above normal snowfall and most in years of below normal snowfall. Balancing of strong acid anions in winter snowfall by H^+ was greater than that of NH_4^+ in all years.

Linear regression analysis shows that NH_4^+ was significantly correlated with the sum of NO_3^- and SO_4^{2-} for all winter snowfalls in water years 1985 and 1986 ($\text{NH}_4^+ = -1.24 + 0.69(\text{NO}_3^- + \text{SO}_4^{2-})$; $p < 0.001$; $n = 20$) (Figure 2). The r^2 of 0.82 indicates that the sum of NO_3^- and SO_4^{2-} accounts for most of the variation in the concentration of NH_4^+ in winter snowfall. Other factors are also important in determining the concentrations of NO_3^- and SO_4^{2-} in winter snowfall, as indicated by the y intercept being less than zero.

Solute storage. Solute storage in the winter snowpack was investigated in water year 1986 by comparing the chemistry of cumulative snowfalls measured on snowboards with the chemistry of the snowpack at the same site during midwinter (January 9), just prior to spring runoff (March 5), and after spring runoff had started (May 5). Hydrogen, SO_4^{2-} , and Cl^- had similar VWM concentrations and load-

TABLE 3. Percent Flux of Ions and Water, by Precipitation Type, Water Years 1985-1987

	Rain			Autumn Snow			Winter Snow		
	1985	1986	1987	1985	1986	1987	1985	1986	1987
SWE	1	1	17	8	8	2	91	91	81
H^+	4	3	36	12	12	2	84	85	62
NH_4^+	24	9	72	46	53	6	30	38	21
Ca^{2+}	16	17	73	17	43	1	67	41	27
Mg^{2+}	8	10	49	13	22	1	79	68	50
Na^+	10	4	83	19	15	1	71	81	17
K^+	8	3	64	10	13	1	82	84	35
NO_3^-	15	9	67	27	38	4	58	53	29
SO_4^{2-}	11	9	74	17	33	2	72	58	24
Cl^-	5	2	53	14	11	3	81	87	44
Σ Ions	11	6	66	19	27	4	70	67	30

SWE is snow water equivalence.

TABLE 4. VWM Ionic Concentrations ($\mu\text{eq L}^{-1}$), pH, and Conductance ($\mu\text{S cm}^{-1}$) in Winter Snowfall, Water Years 1985–1988

	1985	1986	1987	1988	Mean*
pH	5.29	5.34	5.34	5.42	5.34
Conductance	4.0	3.3	3.5	2.5	3.3
H ⁺	5.3	4.6	4.6	3.8	4.6
NH ₄ ⁺	0.9	1.4	3.8	1.9	1.7
Ca ²⁺	2.2	0.6	1.8	1.5	1.3
Mg ²⁺	0.7	0.3	1.1	0.5	0.6
Na ⁺	1.9	1.4	0.7	1.0	1.3
K ⁺	0.9	0.8	0.4	0.3	0.7
NO ₃ ⁻	2.3	1.8	4.2	2.1	2.3
SO ₄ ²⁻	3.0	1.6	2.9	1.2	2.0
Cl ⁻	4.0	3.1	1.5	1.4	2.8
CH ₃ COO ⁻	0.5	2.1	1.3
HCOO ⁻	0.3	0.6	0.4
Σ Ions	21.2	15.6	21.8	16.4	19.0

*Mean is the volume-weighted mean for all four years.

ing (equivalents m^{-2}) in cumulative snowfalls and in the snowpack, prior to snowpack runoff. Snow water equivalence also had similar amounts in cumulative loading and in snowpits. Nitrate had a small but persistent decrease in snowpits compared to cumulative events. For example, on March 5 at the inlet, SWE and loading of H⁺, SO₄²⁻, and Cl⁻ in the snowpit were all within 10% of cumulative event totals (Figure 3). Nitrate loading in the snowpack, on the same date and on January 9, 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 or H⁺. Basic cations and NH₄⁺ concentrations were variable in cumulative event and snowpack concentrations. This variability may reflect natural differences between cumulative snow event and snowpack loading or may be an artifact of concentrations being near detection limits.

Spatial variability of snow chemistry. Spatial variability

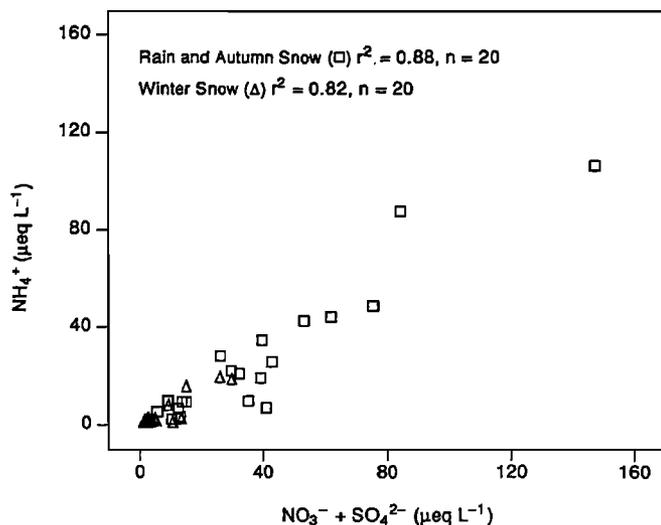


Fig. 2. Comparison of NH₄⁺ concentration ($\mu\text{eq L}^{-1}$) to the sum of NO₃⁻ and SO₄²⁻ concentrations ($\mu\text{eq L}^{-1}$), in winter snowfall (triangles) and rain and autumn snowfall (squares), for all precipitation events in water years 1985 and 1986. Ammonium was significantly correlated with the sum of NO₃⁻ and SO₄²⁻ for all precipitation types.

TABLE 5. Equivalent Ratios of NO₃⁻/SO₄²⁻, H⁺/Σ⁻, and NH₄⁺/Σ⁻ in Wet Deposition, by Precipitation Type

Type	Year	NO ₃ ⁻ /SO ₄ ²⁻	H ⁺ /Σ ⁻	NH ₄ ⁺ /Σ ⁻
Rain	85	1.32	0.19	0.49
	86	1.21	0.06	0.68
	87	1.11	0.13	0.63
Autumn snow	85	1.51	0.31	0.55
	86	1.47	0.26	0.74
	87	2.93	0.16	1.14
Winter snow	85	0.77	0.57	0.10
	86	1.12	0.71	0.21
	87	1.45	0.53	0.45
	88	1.75	0.81	0.40

Σ⁻ is the sum of NO₃⁻, SO₄²⁻, and Cl⁻.

in the VWM concentration of strong acid anions in snowfall was assessed using a one-way analysis of variance (ANOVA). For the three snowfalls in water year 1986 that were sampled at sufficient sites to use the ANOVA, within-site spatial variability was greater than between-site variability. To illustrate, four replicate snow cores were sampled at

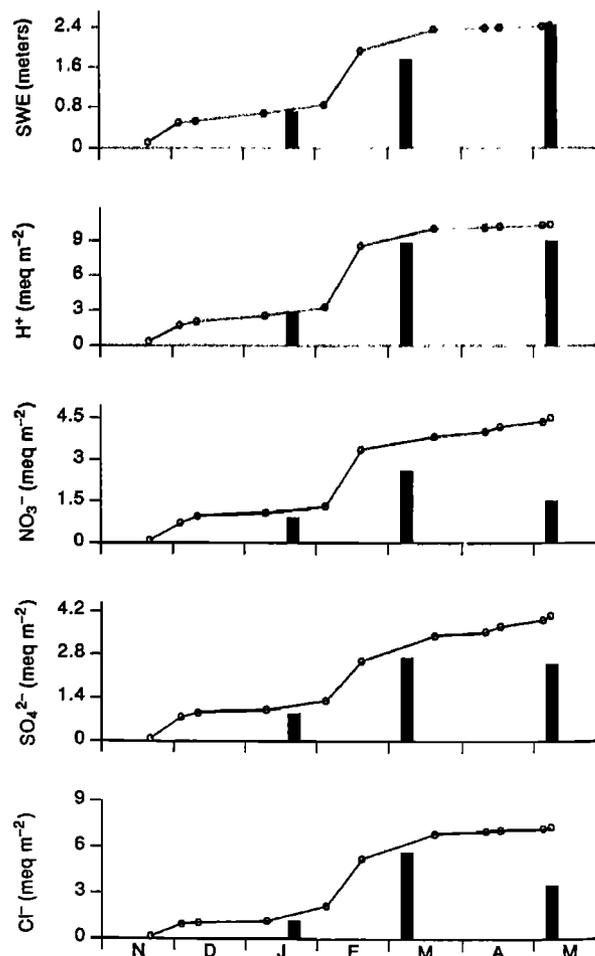


Fig. 3. Comparison of cumulative snowfall loading (curves) to snowpack loading (bar graphs) in 1986 at the inlet for SWE, H⁺, and the strong acid anions. Snow water equivalence, H⁺, SO₄²⁻, and Cl⁻ had good agreement between cumulative snowfall loading and snowpit loading, prior to the initiation of snowmelt runoff in April. Nitrate loading in the snowpack was about 20% lower than in snowfall.

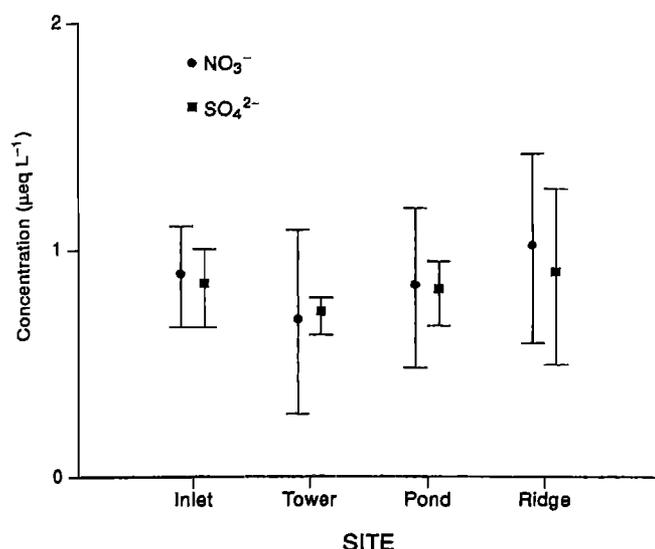


Fig. 4. Spatial variability in the concentrations of NO_3^- (circles) and SO_4^{2-} (squares) at sites 1, 2, 4, and 6 during a 171-mm SWE snowfall on January 9, 1986. The length of the standard deviation is represented by the vertical lines; sample size was four at each site.

four sites within the catchment during a snowfall (171-mm SWE) on January 9 (Figure 4). The one-way ANOVA for the VWM concentrations of NO_3^- ($F_{3,12} = 0.57$, $p = 0.65$) and SO_4^{2-} ($F_{3,12} = 0.42$, $p = 0.74$) yielded no significant differences among the tower, inlet, pond, and ridge sites. The concentrations of strong acid anions in these three snowfalls did not vary significantly from one part of the basin to another.

Spatial variation in the VWM chemistry of the snowpack from six sites was evaluated in water years 1987 and 1988 (Table 6). The maximum RSD for conductance, H^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , NO_3^- , and SO_4^{2-} was less than or equal to 30% for both water years; the mean RSD for these six ions was about 20%. The slightly larger RSD for Cl^- may in part be a result of the relatively high analytical error in measuring Cl^- . The standard error of the mean for these ions was within 5–10% of the mean. Sodium and K^+ concentrations were near their detection limits, which may explain their

TABLE 7. Ionic Loading (eq ha^{-1}) of the Basin's Snowpack at Maximum Snow Accumulation, Water Years 1985–1988

	1985	1986	1987	1988
H^+	53	95	31	24
NH_4^+	9	49	25	12
Ca^{2+}	23	18	11	9
Mg^{2+}	7	7	7	3
Na^+	19	31	4	6
K^+	9	17	3	2
NO_3^-	23	50	28	13
SO_4^{2-}	31	41	19	8
Cl^-	41	63	10	9
CH_3COO^-	3	13
HCOO^-	2	4
Σ Ions	215	371	143	103

relatively high RSD. Similarly, methodological problems in measuring the organic acids in water year 1987 may be responsible for their large variances in that year.

The sum of the major inorganic ions stored in the basin's snowpack at maximum accumulation ranged from 86 eq ha^{-1} in 1988 to 371 eq ha^{-1} in 1986 (Table 7). Solute loading of individual ions in the snowpack at maximum snow accumulation for the four water years ranged from 2 eq ha^{-1} (K^+ in 1988) to 95 eq ha^{-1} (H^+ in 1986). The RSD for SWE of 62% (Table 8) is twofold to tenfold higher than the RSD for the VWM concentrations of ions in sufficient concentration to provide good analytical precision. Even though the amount of snow at any one point in the basin is highly variable, *Elder et al.* [this issue] were able to provide a good estimate of the mean SWE in the basin by using a large sample size. Using standard error as a measure of the uncertainty in the estimate of the mean SWE in the basin, the standard error was within 4% of the mean SWE in water years 1987 and 1988.

The standard deviation and standard error for ionic loading to the basin at maximum snow accumulation were calculated for water years 1987 and 1988 by propagating the standard deviation and error from measurements of the VWM concentrations of solutes in the snowpack (from Table 6) and the SWE of the snowpack (from Table 8) using the procedure described by *Bevington* [1969]:

TABLE 6. Spatial Variation in the VWM Ionic Concentrations ($\mu\text{eq L}^{-1}$) and Conductance ($\mu\text{S cm}^{-1}$) of the Snowpack at Maximum Snow Accumulation ($n = 6$), Water Years 1987 and 1988

	1987					1988				
	\bar{X}	SD	SE	RSD	RSE	\bar{X}	SD	SE	RSD	RSE
Conductance	3.5	0.4	0.2	11	4	2.5	0.3	0.1	12	5
H^+	4.6	1.0	0.4	20	8	3.8	0.2	0.1	6	2
NH_4^+	3.8	1.2	0.5	30	12	1.9	0.5	0.2	26	10
Ca^{2+}	1.8	0.4	0.2	21	9	1.5	0.3	0.1	20	8
Mg^{2+}	1.1	0.1	<0.1	7	3	0.5	0.1	<0.1	20	8
Na^+	0.7	0.4	0.1	51	21	1.0	0.4	0.2	40	16
K^+	0.4	0.1	0.1	34	14	0.3	0.2	0.1	67	27
NO_3^-	4.2	0.7	0.3	17	7	2.1	0.4	0.2	19	8
SO_4^{2-}	2.9	0.4	0.2	13	5	1.2	0.3	0.1	25	10
Cl^-	1.5	0.4	0.2	25	10	1.4	0.5	0.2	36	15
CH_3COO^-	0.5	0.7	0.3	133	54	2.1	0.4	0.2	19	8
HCOO^-	0.3	0.4	0.2	147	60	0.6	0.2	0.1	33	13

\bar{X} is the volume-weighted mean concentration, SD is the arithmetic standard deviation, SE is the standard error, RSD is the relative standard deviation ($\text{SD}/\bar{X} \times 100$), and RSE is the relative standard error ($\text{SE}/\bar{X} \times 100$).

TABLE 8. Snow Water Equivalence (SWE) Measurements (in centimeters) at Maximum Snow Accumulation, Water Years 1987 and 1988

Year	<i>n</i>	$\overline{\text{SWE}}$	SD	SE	RSD, %	RSE, %
1987	256	59.8	37.2	2.3	62	3.9
1988	354	63.0	39.5	2.1	63	3.3

Here *n* is the number of snow depth measurements. $\overline{\text{SWE}}$ is the mean SWE over the basin. SD is the standard deviation of SWE over the basin. SE is the standard error of the mean SWE, RSD is the relative standard deviation ($\text{SD}/\overline{\text{SWE}} \times 100$), and RSE is the relative standard error ($\text{SE}/\overline{\text{SWE}} \times 100$).

$$SX = [(\overline{C_i}^2 \times SX_{\text{SWE}}^2) + (\overline{\text{SWE}}^2 \times SX_{C_i}^2)]^{1/2}$$

where *SX* is the standard deviation or standard error of ionic loading to the basin at maximum accumulation, $\overline{C_i}$ is the VWM concentration of an ion in the basin, SX_{C_i} is the standard deviation or error of that ion, $\overline{\text{SWE}}$ is the mean SWE of the basin, and SX_{SWE} is the standard deviation or error of the measurement of SWE (Table 9). If there is a correlation in measurement error between the two parameters, then the covariance between parameters needs to be considered. Since the measurements of SWE and solute chemistry were independent, the covariance term can be ignored when propagating measurements of standard deviation and error. Calculations of measurement standard deviation and error with and without the covariance terms showed little difference, indicating that there was no significant covariance between the two measurements.

Variance in ionic loading was high relative to the standard error in ionic loading. The standard deviation of ionic loading for each ion was in the range of 60 to 70% of the mean. In comparison, the standard error was less than 11% of the mean for all the ions in Table 9. Ionic loading was highly variable from point to point in the catchment. However, the large sample size used to measure SWE resulted in the precision of our estimate of mean loading being within 10% of the mean.

Chemistry of Rain and Autumn Snowfall

The pH of rainfall was about 4.9 (Table 10), compared to a pH of about 5.3 for winter snowfall. The conductance of rainfall was about 20 $\mu\text{S cm}^{-1}$, compared to about 3.5 $\mu\text{S cm}^{-1}$ for winter snowfall. In general, the VWM concentrations of the major ions in rainfall were about 10 times greater

than in winter snowfall. Autumn snowfall was generally intermediate in concentration between rainfall and winter snowfall. Ammonium, NO_3^- , and SO_4^{2-} accounted for about 65% of the total ionic charge in rainfall and autumn snowfall.

Solute concentrations in rainfall had an average cation to anion ratio of about 1.30 (Table 1). However, with an ionic strength of about 200 $\mu\text{eq L}^{-1}$, the ion percent difference (IOD) values of 15 and 16% for solutes in seasonal rainfall equal or exceed the reanalysis criteria set by the NADP quality assurance guidelines [Peden, 1983]. The IOD values thus indicate the presence of unmeasured ions. Autumn snowfall had the same positive bias in charge balance as rainfall. The positive bias in the charge balance of rainfall and autumn snowfall and our measurements of organic acids in snowfall both indicate that CH_3COO^- and HCOO^- probably comprise about 25–30% of the anions in rain and autumn snow.

Seasonal VWM NO_3^- concentrations were higher than seasonal VWM SO_4^{2-} concentrations of rainfall and autumn snowfall in all three water years (Table 5). Nitrate to sulfate ratios in rainfall ranged from 1.11 to 1.32, and in autumn snowfall ranged from 1.51 to 2.93. These ratios are in the middle range of the NO_3^- to SO_4^{2-} ratios found in winter snowfall, with the exception of the 2.93 value in the fall of 1987. Ammonium to strong acid anion (Σ^-) ratios ranged from 0.49 to 0.63 in rainfall and from 0.55 to 1.14 in autumn snowfall (Table 5). The NH_4^+ to H^+ ratio in rainfall and autumn snowfall was always greater than one. Ammonium loading in rainfall in water year 1986 was about tenfold greater than H^+ loading in rainfall of that year.

As with winter snowfall, a simple linear regression analysis indicates that NH_4^+ in rainfall and autumn snowfall in water years 1985 and 1986 was significantly correlated with the sum of NO_3^- and SO_4^{2-} ($\text{NH}_4^+ = -4.34 + 0.78(\text{NO}_3^- + \text{SO}_4^{2-})$; $p < 0.001$; $n = 20$) (Figure 2). The r^2 of 0.88 indicates that the sum of NO_3^- and SO_4^{2-} concentrations accounts for most of the variation in the concentration of NH_4^+ in rainfall and autumn snowfall. As with winter snowfall, the *y* intercept was negative.

DISCUSSION

Chemistry of Winter Snow

Acidity. Winter snowfall at the ELW was slightly acidic (Table 4). The annual hydrogen ion concentration of 4.6 $\mu\text{eq L}^{-1}$ in winter snow from water years 1985 through 1988 at the ELW is comparable to the background (summer) acidity

TABLE 9. Spatial Variation in Ionic Loading (eq ha^{-1}) of the Basin's Snowpack at Maximum Snow Accumulation ($n = 6$), Water Years 1987 and 1988

	1987					1988				
	\overline{X}	SD	SE	RSD	RSE	\overline{X}	SD	SE	RSD	RSE
H^+	31 ± 5	20	3	65	7	24 ± 2	15	1	63	7
NH_4^+	25 ± 6	18	3	70	10	12 ± 3	8	1	68	8
Ca^{2+}	11 ± 2	8	1	68	7	9 ± 2	6	1	66	7
NO_3^-	28 ± 4	18	2	64	6	13 ± 2	7	1	66	6
SO_4^{2-}	19 ± 2	12	1	64	5	8 ± 2	5	1	68	8
Cl^-	10 ± 2	7	1	67	8	9 ± 3	6	1	72	11

\overline{X} is the volume-weighted mean concentration, plus or minus the width of the 95% confidence interval, SD is the standard deviation, SE is the standard error, RSD is the relative standard deviation ($\text{SD}/\overline{X} \times 100$), and RSE is the relative standard error ($\text{SE}/\overline{X} \times 100$).

TABLE 10. VWM Ionic Concentrations ($\mu\text{eq L}^{-1}$), pH, and Conductance ($\mu\text{S cm}^{-1}$) in Rainfall and Autumn Snowfall, Water Years 1985–1987

	Rain				Autumn Snow			
	1985	1986	1987	Mean*	1985	1986	1987	Mean*
pH	4.93	4.87	4.88	4.88	5.07	5.11	5.21	5.10
Conductance	19.1	13.0	19.3	18.3	6.8	8.0	9.1	7.7
H ⁺	16.7	10.7	13.1	13.0	8.3	7.4	6.2	8.0
NH ₄ ⁺	42.8	23.4	63.0	55.3	15.1	21.8	44.4	20.8
Ca ²⁺	34.1	17.9	24.4	24.0	6.2	7.0	1.5	6.7
Mg ²⁺	4.7	3.1	5.3	4.8	1.3	1.1	0.8	1.2
Na ⁺	18.1	5.0	17.2	15.4	5.5	3.0	1.3	3.7
K ⁺	5.6	2.0	3.7	3.8	1.2	1.4	0.5	1.5
NO ₃ ⁻	40.4	22.2	48.2	42.8	11.8	14.7	25.5	14.4
SO ₄ ²⁻	30.6	18.3	43.4	38.5	7.8	10.0	8.7	9.2
Cl ⁻	17.1	5.6	8.9	9.1	7.6	4.3	4.5	5.2
Σ Ions	210	108	227	206	64.8	70.7	93.4	70.6

*Volume-weighted mean for the three water years.

of the Arctic, and less than the acidity of winter snowfall in the Canadian Arctic [Barrie *et al.*, 1985]. The pH of winter snowfall at the ELW was 0.2 pH units lower than values reported by other investigations on the quality of snowfall in the Sierra Nevada [Feth *et al.*, 1964; Brown and Skau, 1975; Melack *et al.*, 1982; Laird *et al.*, 1986]. A transect of snowpack chemistry in the Cascade Mountains–Sierra Nevada from the United States–Canadian border to a point northeast of Bakersfield, California, generated a median pH of 5.6 [Laird *et al.*, 1986].

Solute storage. Storage of solutes in snowpacks that remain below 0°C have been reported to be similar to those in cumulative snowfall [e.g., Cadle *et al.*, 1984] and to show significant losses from the snowpack relative to cumulative snowfall [e.g., Jeffries and Snyder, 1981]. The agreement of H⁺, SO₄²⁻, and Cl⁻ loadings in the snowpack and in cumulative snowfall at the ELW (Figure 3) is similar to that reported by Cadle *et al.* [1984] for a northern Michigan snowpack. Cadle *et al.* [1984] report a NO₃⁻ loss of 10% from the snowpack relative to cumulative snowfall but attribute the loss in part to sampling and analytical problems. The 20% loss of NO₃⁻ from the snowpack at the ELW agrees with the findings of Jeffries and Snyder [1981], who report a similar loss of all major ions (except Cl⁻) from the snowpack in central Ontario. They attribute this loss to migration through the snowpack to underlying soils, which occurred during periods of no significant melting. Barry and Price [1987] and Jones and Laberge [1988] report that NO₃⁻ can be lost from a snowpack under cold conditions (<0°C) while SO₄²⁻ is not lost in the same snowpack.

Dry deposition can be a major pathway of solute flux from the atmosphere to catchments. In California, dry deposition has been shown to be an important source of solute flux [Ashbaugh *et al.*, 1989]. The rate of dry deposition is surface dependent and increases with increasing turbulence and surface roughness [Whelpdale and Shaw, 1974]. The stable temperature gradients over snow surfaces and low surface roughness of snow generally result in snow having low depositional velocities, ranging from about 0.05 to 1.6 cm s⁻¹ for SO₄²⁻ [Whelpdale and Shaw, 1974; Dovland and Eliassen, 1976; Barrie and Walmsley, 1978; Granat and Johansson, 1983; Cadle *et al.*, 1985; Bales *et al.*, 1987].

The equivalence between cumulative snowfall and snowpack loading indicates that dry deposition was not an impor-

tant 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⁺, SO₄²⁻, NO₃⁻, and Cl⁻, in water year 1986 (Figure 3). However particulates were excluded from the chemical analyses by filtering; therefore the contribution of particulates to dry deposition cannot be ascertained. The possibility that ionic losses from the snowpack were matched by dry deposition cannot be discounted but is unlikely. The snowfall pattern at the ELW is one of large magnitude but infrequent storms, resulting in a snowpack surface that quickly evolves to older, sintered snow grains. Bales *et al.* [1989] have shown in laboratory studies that SO₄²⁻ depositional velocities (0.02 cm s⁻¹) are lowest for colder, dry snow that has undergone significant metamorphism. Our field data corroborate the laboratory work of Bales *et al.* that dry deposition of SO₄²⁻ to well-sintered snow is low. Furthermore, our field data suggest that dry deposition of HNO₃ and HCl gases to the snowpack in this area of the Sierra Nevada are not important contributors to solute flux. It was not possible to evaluate the importance of the dry deposition of basic cations and NH₄⁺ to the winter snowpack.

Nitrate, Sulfate, and Ammonium in Wet Deposition

Nitrate in wet deposition to alpine areas of California is as important, or more important, than SO₄²⁻ as a potential acidifying agent. The NO₃⁻ to SO₄²⁻ ratio was 1.16 on an equivalent basis for all wet deposition to the ELW for water years 1985–1987 (Table 5). The mean NO₃⁻ to SO₄²⁻ ratio for wet deposition during the 3 years agrees with the findings of Stohlgren and Parsons [1987] at Giant Forest in Sequoia National Park, McColl *et al.* [1982] in northern California, and Liljestrang and Morgan [1980] in southern California, all of whom report a NO₃⁻ to SO₄²⁻ ratio greater than one. This NO₃⁻ to SO₄²⁻ ratio is much different than that of annual precipitation in the eastern United States, where SO₄²⁻ concentrations are generally 2–3 times greater than NO₃⁻ concentrations [Munger and Eisenreich, 1982].

There is little difference in the ratio of NO₃⁻ to SO₄²⁻ associated with precipitation type at the ELW, in contrast to eastern North America, where there is a consistent pattern of a high NO₃⁻ to SO₄²⁻ ratio in snow and a low NO₃⁻ to SO₄²⁻ ratio in rain at the same locations [Galvin and Cline,

1978; Frantisak *et al.*, 1980; Barrie *et al.*, 1983 Topol, 1986; Chan *et al.*, 1987]. However, the NO_3^- to SO_4^{2-} ratio in wet deposition at the ELW is similar to that of snowfall in eastern North America. The preferential scavenging by snow of NO_3^- over SO_4^{2-} is well established [Huebert *et al.*, 1983; Chang, 1984; Chan and Chung, 1986] and has often been invoked to explain the higher NO_3^- to SO_4^{2-} ratios of snowfall in eastern North America. In California, NO_x emissions can be 3 times higher than SO_2 emissions [California Air Resources Board, 1979]. The relative constancy of the NO_3^- to SO_4^{2-} ratio in rain and snow at the ELW may partly be due to the relatively low SO_2 emissions and high NO_x emissions in California.

Ammonium nitrate (NH_4NO_3) appears to be the principal NO_3^- -containing aerosol in wet deposition to the ELW. Photochemically initiated reactions result in the oxidation of NO_x to HNO_3 . Nitric acid can then react with NH_3 to form NH_4NO_3 aerosols. Wolff [1984] reports that in areas such as southern California, where NO_x emissions exceed SO_2 emissions and where there are strong sources of NH_3 , the $\text{NO}_3^-/\text{HNO}_3$ equilibrium strongly favors the production of NH_4NO_3 . Examination of the relationship between NH_4^+ and NO_3^- in aerosols in the Central Valley of California by the California Air Resources Board shows a very strong relationship between NH_4^+ and NO_3^- , with a correlation analysis producing an r^2 of 0.95 [California Air Resources Board, 1988]. This statistical relationship between NH_4^+ and NO_3^- agrees with our findings and suggests that NH_4NO_3 is the principal NO_3^- -containing aerosol in wet deposition to the ELW.

Further evidence that NH_4NO_3 is the principal NO_3^- -containing aerosol, and that ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) may be an important SO_4^{2-} -containing molecule was that there was no increase in protons associated with the increase in NO_3^- and SO_4^{2-} concentrations of annual winter snowfall in 1987 and 1988 compared to 1986. However, NH_4^+ concentrations in annual snowfall increased 270% from 1986 to 1987. The correspondence between increases in NO_3^- and SO_4^{2-} concentrations with the increase in NH_4^+ concentrations suggests that NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ are the principal aerosols containing NO_3^- and SO_4^{2-} , respectively.

Source of Ions in Wet Deposition

Cations and anions in precipitation originate from a variety of sources, including oceanic spray, terrestrial dust, gaseous pollutants, and volcanic emissions [Likens *et al.*, 1977]. Solute load in precipitation is to a large extent determined by the origin and pathway of the air masses from which the precipitation falls [Galloway *et al.*, 1984]. Air masses that form over oceans contain diagnostic aerosols that originate from sea salts [Henriksen, 1980]. There are no known sources of terrestrial Cl^- near the ELW. If we make the reasonable assumption that most Cl^- in precipitation originates from sea salt aerosols, then Cl^- can be used to indicate the origin of some ions contained in wet deposition flux to the ELW. Ammonium and NO_3^- aerosols have a terrestrial source and can be used to infer air masses that originate over land or that originate over marine areas and then mix with terrestrial air masses.

Precipitation from frontal systems that originate over the Pacific Ocean is not contaminated by strong acids. For example, Kennedy *et al.* [1979] report that precipitation in

the sparsely populated coastal region of the Mattole River basin of northern California had an average pH of 5.3 and average concentrations of $1.6 \mu\text{eq L}^{-1}$ of NO_3^- and $2.7 \mu\text{eq L}^{-1}$ of SO_4^{2-} . These ionic concentrations are comparable to the ionic concentrations of winter snowfall in the ELW during years of normal and above normal precipitation. Consequently, the ions in winter snowfall appear to originate predominately from marine sources. Moreover, relatively low concentrations of NH_4^+ in winter snowfall relative to rainfall indicate that the oceanic frontal systems undergo only limited mixing with terrestrial air masses before depositing snowfall in the ELW.

Low Cl^- and high NH_4^+ concentrations in rain suggest that localized convective systems are the main source of ions in rainfall. Afternoon upslope air flows, induced by heating of air along the mountain slopes, transport air masses from the San Joaquin Valley to the upper reaches of Sequoia National Park on a daily basis in the summer months [Smith *et al.*, 1981]. Aerosol and gas phase species from the San Joaquin Valley are likely to supply a large percentage of the ions in rainfall. The agreement between NH_4^+ and NO_3^- ratios in rainfall to the ELW and in aerosols over the Central Valley of California is further evidence that the origin of ions in rainfall has a large terrigenous component.

SUMMARY AND CONCLUSIONS

Wet deposition was monitored from October 1984 through March 1988 at the Emerald Lake watershed in the southern Sierra Nevada. Precipitation amounts ranged from one of the wettest years (1986) on record to one of the driest years (1987). Hydrogen and NH_4^+ each accounted for about 18% of the total ionic charge of solutes in precipitation, followed closely by NO_3^- (17%), SO_4^{2-} (14%), and Cl^- (12%). The remaining portion of ionic flux is divided among Ca^{2+} , Na^+ , K^+ , and Mg^{2+} , in that order. Organic acids comprised about 25% of the total anionic content of wet deposition. Solute concentrations in rainfall were about tenfold higher than in snowfall, with the exception of H^+ , which was about 2.5-fold more concentrated in rain than in snow.

Snowfall was the major source of ions to the catchment from wet deposition in years of normal or above normal precipitation, due to the high percentage of precipitation that was deposited as snow. Almost all of the solute flux from snowfall was stored in the seasonal snowpack, to be released during spring runoff. Dry deposition was not an important contributor of H^+ , NO_3^- , SO_4^{2-} , or Cl^- loading to the winter snowpack. During the year of large solute flux from rainfall (1987), 85% of the solute flux from rain was deposited during the time period of snowpack runoff. Therefore about 90% of the annual solute flux from wet deposition entered the aquatic component of the catchment during the time period of snowpack runoff. Most of the chemical loading to aquatic ecosystems in alpine areas of the Sierra Nevada thus occurs during the period of snowpack runoff.

The NO_3^- to SO_4^{2-} equivalent ratio for all wet deposition was 1.16. Ammonium nitrate and ammonium sulfate appear to be the principal nitrate- and sulfate-containing aerosols in wet deposition. Ammonium balanced as much as eleven-fold more strong acid anions in rainfall than did H^+ . Source-receptor relationships in precipitation quality were important to the wet deposition of high-altitude catchments in the Sierra Nevada. Our research shows that NH_4^+ was signif-

cantly correlated with the sum of NO_3^- and SO_4^{2-} , for all precipitation types, in wet deposition to the ELW. Principle source areas for NO_3^- , SO_4^{2-} , and NH_4^+ may therefore be the same in winter snowfall, autumn snowfall, and rainfall. Changes in the air quality of the San Joaquin Valley may directly effect the quality of precipitation in catchments in the Sierra Nevada.

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