Atmospheric Environment Vol. 27A, No. 15, pp. 2337–2349, 1993.
Printed in Great Britain.

0004-6981/93 $6.00 + 0.00
Pergamon Press Ltd

THE INFLUENCE OF MOUNTAIN METEOROLOGY ON PRECIPITATION CHEMISTRY AT LOW AND HIGH ELEVATIONS OF THE COLORADO FRONT RANGE, U.S.A.

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(*First received* 18 *July* 1990 *and in final form* 13 *May* 1993)

Abstract—We explored the seasonal characteristics in wet deposition chemistry for two sites located at different elevations along the east slope of the Colorado Front Range in Rocky Mountain National Park. Seasonally separated precipitation was stratified into highly concentrated (high salt), dilute (low salt), or acid-dominated precipitation groups. These groups and unstratified precipitation data were related to mean easterly or westerly zonal winds to determine direction of local transport. Strong acid anion associations were also determined for the stratified and unstratified precipitation data sets. We found that strong acid anions, acidity, ammonium, and high salt concentrations originate to the east of Rocky Mountain National Park, and are transported via up-valley funneling winds or convective instability from differential heating of the mountains and the plains to the east. These influence the composition of precipitation at Beaver Meadows, the low elevation site, throughout the year, while their effect on precipitation at Loch Vale, the high elevation site, is felt most strongly during the summer. During the winter, Loch Vale precipitation is very dilute, and occurs in conjunction with westerly winds resulting from the southerly location of the jet stream.

Key word index: Colorado, deposition chemistry, precipitation, sulfate, nitrate, ammonium, Rocky Mountains, wind.

1. INTRODUCTION

It has been demonstrated in the eastern United States of America that the increased precipitation associated with mountains has contributed directly to increased deposition of strong acid anions on high elevation ecosystems (Lovett and Kinsman, 1990). Although western U.S. mountains do not receive nearly as much acidic deposition as their eastern counterparts (Young *et al.*, 1988), this same argument has been extrapolated to the western U.S.A. Many have concluded from this that some high elevation western U.S.A. aquatic ecosystems are at great risk from wet-deposited SO_4^{2-} and NO_3^- (Landers *et al.*, 1987; Baron, 1992; Turk and Spahr, 1991; Lewis *et al.*, 1984).

Precipitation increases with elevation in mountainous terrain due to two distinct processes, convective instability and large-scale orographic lifting. Convective instability is brought about by differential heating of low vs high elevation air masses. This results in uplift through the funneling effects of valleys on airstreams, and also enhances thunderstorm activity in the mountains (Bossert *et al.*, 1989; Toth and Johnson, 1985; Banta and Schaaf, 1987). Large-scale orographic lifting occurs when synoptic scale flow is forced to rise as it encounters mountain barriers. As the rising air cools and condenses, precipitation is enhanced (Barry and Chorley, 1978). Along the eastern slopes of the Front Range of Colorado these processes are seasonally and directionally different (Barry, 1973). Precipitation associated with convective instability occurs most often during the summer months, bringing air masses in from the southeast and southwest, while precipitation of cyclonic origin dominates winter precipitation processes and originates from the northwest (Hansen *et al.*, 1978; Barry, 1973).

Surface winds can differ dramatically from geostrophic winds (Barry and Chorley, 1976), making it difficult to understand the nature of atmospheric transport in complex terrain (Bossert *et al.*, 1989). In mountainous terrain, however, extensive work has shown that regional-scale air flows are dominated by diurnal cycles (Toth and Johnson, 1985; Bossert *et al.*, 1989; Defant, 1951). Winds are topographically constrained to flow up-valley in the daytime, forced by solar heating on the plains. They reverse and flow down-valley at night, as a result of nocturnal radiative cooling that occurs rapidly on mountaintops. This diurnal pattern draws agricultural and urban air up to high elevations (Parrish *et al.*, 1990; Langford and

Fehsenfeld, 1992). Thunderstorm development is related to the diurnal inflow and outflow from mountains. As the uplifted air condenses to form cloud droplets, it releases latent heat, creating updrafts that form the nuclei of thunderstorms (Barry and Chorley, 1976). These updrafts accelerate as long as the given air mass retains a lower density than that of the surrounding air. At this point, an abrupt reversal in air flow occurs, and strong downdrafts modify the patterns of air flow (Bossert *et al.*, 1989; Barry and Chorley, 1976; Banta and Schaaf, 1987).

We explored the seasonal characteristics in wet deposition chemistry for two sites located at different elevations along the east slope of the Colorado Front Range in the Rocky Mountain National Park. Our interest was in determining whether or not the same air masses were responsible for chemical composition of precipitation at both sites. This has a practical application, since many mountainous areas are sensitive to acidic deposition (Eilers *et al.*, 1986; Landers *et al.*, 1987), yet do not have year-round deposition measurement stations due to winter access problems. This makes it difficult to predict the effects of current or increased loading of strong acid anions. A recent paper by Warren *et al.* (1991) suggests that strong correlations of weekly SO_4^{2-} from six high and low elevation pairs of precipitation sampling sites in the southern Rockies has two possible causes. Either similar air masses affect precipitation composition at both sets of sites, or the weekly sampling interval allows sufficient averaging of individual storms to mask different air mass sources.

If the precipitation chemistry and wind-related chemical composition indicate both sites are influenced by the same air masses, it could be due to one or both of two factors: (a) a regionally uniform background mixture of solutes that is deposited proportional to the amount of wet deposition (Oppenheimer *et al.*, 1985; Epstein *et al.*, 1986); or (b) both sites influenced by the same local sources of emissions and soil materials that are deposited proportional to the amount of wet deposition (Lewis *et al.*, 1984; Warren *et al.*, 1992). If the sites are compositionally and meteorologically different, it could be due to complex meteorological or atmospheric chemical behavior that brings air parcels of differing chemical composition to low and high elevations (Parrish *et al.*, 1990; Lewis *et al.*, 1984). Complex meteorology is an argument against predicting high elevation deposition from lower elevation, more easily accessible, monitoring sites.

2. METHODS

2.1. *Wet deposition chemistry*

Wet deposition has been collected since June 1981 at Beaver Meadows and since September 1983 at Loch Vale. Both sites are located on the eastern slope of the Front Range in Rocky Mountain National Park, Colorado (Fig. 1). The Loch Vale site is located just below treeline (3160 m) in Loch Vale Watershed, a narrow, glaciated mountain valley. Beaver Meadows (2490 m) is less than 15 km NE of Loch Vale, and is located on the edge of a mountain meadow. Beaver Meadows receives an average of 40 cm ($s=7.1$) precipitation yr^{-1}. Average annual precipitation recorded from Loch Vale is 100 cm ($s=12.9$) (Fig. 2). Beaver Meadows records slightly greater precipitation during the summer than during the winter. In contrast, greater than 60% of Loch Vale precipitation occurs during the winter. Both sites are part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), and sample collection and analytical procedures are documented in Peden (1986).

Data were obtained from the National Atmospheric Deposition Program (NADP/NTN, 1991). Data were included only from weeks where sample volumes were greater than 10 ml and sample collection protocols were followed. Concentrations are presented as volume-weighted means (VWM) in microequivalents per liter ($\mu eq\,\ell^{-1}$). The VWM was calculated as

$$\mathrm{VWM} = \sum(C_i P_i)/\sum P_i$$

where C_i is the concentration of the ith sample, and P_i is the precipitation volume of that sample. Deposition is presented as $g\,m^{-2}$ and is calculated from the product of the VWM and the total measured precipitation for the seasonally separated data.

Both laboratory and field H^+ are presented in all tables. However, a study by Bigelow *et al.* (1989) revealed a systematic bias between National Atmospheric Deposition Program field and laboratory H^+. They separate the bias according to a combination of causes, including a fixed component of about $-7\,\mu eq\,\ell^{-1}$ due to sample bucket and lid contamination and a summertime seasonal neutralization that nationally accounts for 0 to $+2\,\mu eq\,\ell^{-1}$. There is an additional geographical component of $-5\,\mu eq\,\ell^{-1}$ when median field H^+ is subtracted from laboratory H^+ for northern Colorado. Bigelow *et al.* (1989) attribute the seasonal and geographic bias to a number of causes, including less windy conditions during summer months, increased summer microbial consumption of NH_4^+ and organic acids within the bucket, and neutralization of H^+ by soil-derived Ca^{2+}, Mg^{2+}, and NH_4^+. Because these factors confound interpretation of laboratory H^+, we have chosen to discuss only field H^+.

Analyses were conducted based on water years, 1 October–30 September. Winter samples include all dates 1 October–30 April, and summer samples include the remainder of the year, 1 May–30 September.

Samples were stratified into those with low salt and low H^+ concentrations (*low salt/low acid*), samples with low salt concentrations whose cation composition was dominated by H^+ (*acid-dominated*), and those with *high salt* content (Verry and Harris, 1988). Low salt/low acid samples were defined as

$$(Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+) < 50\,\mu eq\,\ell^{-1}$$

and

$$H^+ \leq (Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+).$$

High salt samples were delineated as

$$(Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+) > 50\,\mu eq\,\ell^{-1}$$

(Verry and Harris 1988).

Acid-dominated samples were identified as those where

$$H^+ > (Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+)(\mu eq\,\ell^{-1}).$$

Most acid-dominated samples also were low salt in that their base cations summed to less than $50\,\mu eq\,\ell^{-1}$. There were four winter and two summer Beaver Meadows samples that were high salt and also acid-dominated; one summer high salt sample from Loch Vale was acid-dominated.

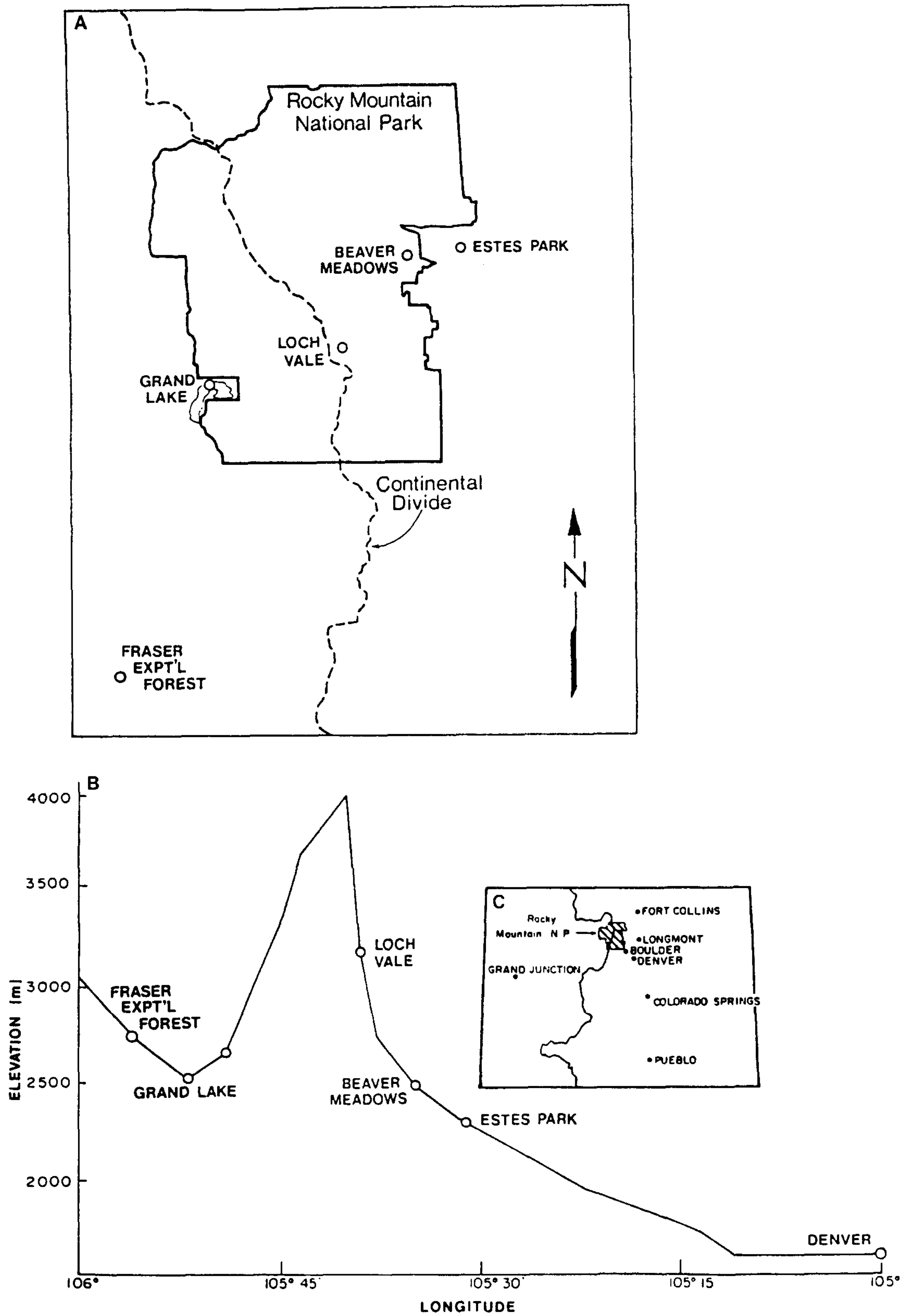

Fig. 1. Location of Loch Vale and Beaver Meadows NADP/NTN sampling sites in (a) Rocky Mountain National Park; (b) along an elevational transect across the Continental Divide in Colorado; and (c) within the State of Colorado.

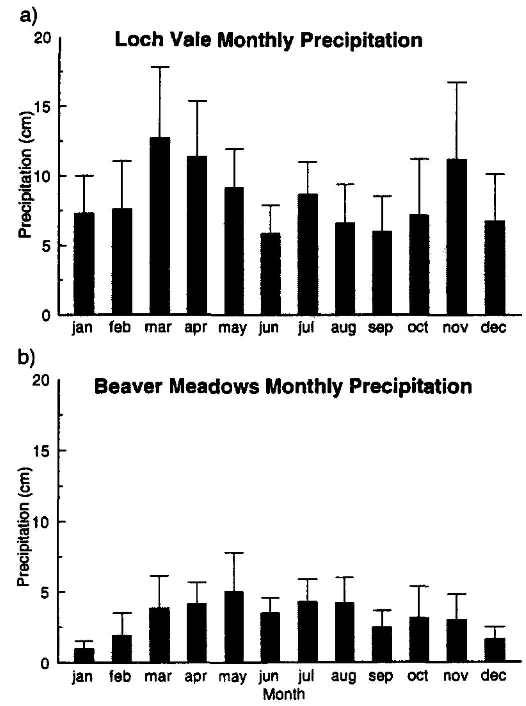

Fig. 2. Mean monthly precipitation (cm) and one standard deviation for (a) Loch Vale (1984–1991) and (b) Beaver Meadows (1980–1991) NADP/NTN sampling sites in Rocky Mountain National Park.

Spearman's rank correlations were calculated between NO_3^- and SO_4^{2-} and other major ions and precipitation for seasonally separated precipitation. Rho values indicate the tendency for pairs of values to be associated; values approaching +1 or −1 indicate strong positive or negative association, respectively (Bhattacharyya and Johnson, 1977).

2.2. *Wind*

Wind speed and direction were measured in Loch Vale Watershed (LVWS) with a Remote Area Weather Station located adjacent to the wet deposition collector. Two-minute averages of wind speed and direction were taken on the hour. Wind data were not collected at the Beaver Meadows NADP site. They were obtained from the nearby NOAA PROFS (Program for Regional Observing and Forecasting Services) meteorological station located 1.5 km from Beaver Meadows at Rocky Mountain National Park Headquarters. Five-minute averages were taken on the hour. Orthogonal westerly and southerly wind components were computed for hourly observations for both Loch Vale and Beaver Meadows. The precipitation-weighted mean westerly zonal wind component for the week was then calculated as

$$u=\sum(u_i p_i)/\sum(p_i)$$

where u_i and p_i are the hourly zonal wind component and precipitation, respectively. A total of 252 and 60 weeks of NADP/NTN data from Loch Vale and Beaver Meadows, respectively, were matched with mean zonal winds. We made no attempt to match precipitation and wind records by date for the two sites.

3. RESULTS

3.1. *Wet deposition*

3.1.1. *Concentrations.* Precipitation at both sites was extremely dilute. Calcium, NH_4^+, and H^+ were the most abundant cations at both Loch Vale and Beaver Meadows; SO_4^{2-} and NO_3^- were the most abundant anions (Table 1). Concentrations of all solutes except Na^+ were greater during the summer at both sites, with H^+, Ca^{2+}, NH_4^+, SO_4^{2-}, and NO_3^- exhibiting the greatest absolute increases of summer over winter. Beaver Meadows had exceptionally high concentrations of most solutes in 1981 compared with all other

Table 1. Annual and seasonal volume-weighted mean precipitation concentrations ($\mu eq\,\ell^{-1}$) for two NADP/NTN sites in Rocky Mountain National Park. Data are missing (—) for Loch Vale in 1986 and Beaver Meadows in 1987

Site	Year	Field H^+	Lab. H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-	Ppt (cm)
Loch Vale	1984	12.4	7.3	8.1	3.1	0.5	3.1	6.8	10.9	14.5	2.6	111.1
	1985	14.3	9.0	12.1	3.6	1.0	3.5	6.2	13.0	17.4	3.4	109.8
	1986	—	—	—	—	—	—	—	—	—	—	106.3
	1987	12.3	6.9	5.0	1.3	0.4	3.0	5.6	9.7	10.0	1.9	96.4
	1988	11.9	7.8	5.7	1.2	0.3	2.4	2.7	8.7	11.0	1.7	78.0
	1989	13.2	4.6	8.9	1.9	0.4	3.9	6.9	10.8	12.4	2.2	90.5
	1990	10.4	6.3	10.0	2.2	0.4	2.4	8.3	12.9	11.5	2.5	112.5
	Oct–Apr	9.6	5.0	7.0	2.0	0.3	3.6	4.4	9.1	10.5	2.1	58.7
	May–Sep	16.7	9.0	12.2	2.7	0.7	2.7	9.1	14.1	17.6	2.9	37.2
Beaver Meadows	1981	29.7	10.3	18.9	6.7	1.2	5.1	18.6	23.5	32.4	4.3	33.4
	1982	15.3	10.8	10.6	2.9	1.2	2.4	7.5	15.0	19.0	2.6	36.8
	1983	12.7	8.6	11.8	3.1	1.0	5.0	8.9	15.0	18.0	3.1	45.3
	1984	12.9	7.9	13.4	4.4	2.0	4.9	13.5	17.6	20.0	3.4	43.1
	1985	17.5	10.2	10.5	3.2	1.0	2.6	9.7	15.2	19.0	3.5	41.7
	1986	13.5	8.5	8.2	1.7	2.8	2.6	12.8	15.0	16.1	3.5	44.0
	1987	—	—	—	—	—	—	—	—	—	—	—
	1988	16.3	6.5	12.4	2.3	0.7	4.3	5.8	15.1	15.6	2.6	25.4
	1989	11.2	5.5	13.1	2.3	0.7	3.8	14.5	18.0	16.6	3.2	33.2
	1990	9.2	5.8	16.0	2.3	0.5	2.2	14.4	15.8	13.7	2.3	46.6
	Oct–Apr	11.1	6.0	9.6	2.5	0.8	3.7	7.5	12.5	12.1	2.6	16.2
	May–Sep	19.0	10.0	14.7	3.5	1.9	3.3	15.8	20.4	24.2	4.1	20.9

years. This contributed to greater interannual variability at Beaver Meadows than at Loch Vale. The cation to anion ratio was fairly close to 1.0 for both sites when lab H^+ was used to calculate charge balance; it ranged 0.94–1.10 for Loch Vale, and 0.96–1.3 for Beaver Meadows.

3.1.2. *Deposition.* Primarily due to the increased amount.of precipitation, deposition of all solutes was 1–4-times greater at higher elevation Loch Vale than at Beaver Meadows (Table 2). This relation held true for both winter and summer deposition. In general, Loch Vale and Beaver Meadows deposition values agreed well with those reported by Lewis *et al.* (1984) from a one-year bulk deposition survey across Colorado. An exception is Cl^-; NADP values from the two Rocky Mountain National Park sites were 4–5-times lower than those reported by Lewis *et al.* (1984).

3.2. *Associations of strong acid anions with other solutes*

3.2.1. *Loch Vale.* Nitrate was associated with all other solutes in unstratified summer precipitation from Loch Vale ($n = 87$, Table 3). The strongest associations of NO_3^- were with SO_4^{2-} and NH_4^+. Sulfate was also associated with most solutes, and very strongly associated with Ca^{2+}, Mg^{2+}, and NO_3^-. It was not associated with H^+. Low salt/low acid stratification ($n = 46$) revealed similar NO_3^- and SO_4^{2-} associations, although the connection with base cations was slightly weaker. Low salt/low acid stratification revealed a relation of SO_4^{2-} with H^+. Only 16 summer samples were classified high salt, and their composition was different than unstratified or low salt samples. The anions were most strongly associated with each other and H^+, NO_3^- was additionally associated with NH_4^+. Acid-dominated precipitation ($n = 25$) revealed strong H^+: SO_4^{2-} and H^+: NO_3^- associations, and both anions were associated also with Ca^{2+}, Mg^{2+}, and each other. Nitrate was again associated with NH_4^+. Solutes in summer precipitation showed negative association with precipitation amount.

Winter NO_3^- from the total, unstratified data set showed an association with Ca^{2+}, Mg^{2+} NH_4^+ and SO_4^{2-} ($n = 105$, Table 3). Sulfate from the winter, unstratified, data set was most strongly associated with base cations Mg^{2+}, Ca^{2+}, and K^+, and less strongly associated with NO_3^- and Cl^-. Half of the winter precipitation samples stratified into the low salt/low acid category and this stratification did not elucidate any solute relationships ($n = 58$). Winter acid dominant precipitation was still very dilute, and there were no strong associations. The median H^+ in these samples ($n = 44$) was 14 $\mu eq\,\ell^{-1}$, and the maximum H^+ was 31 $\mu eq\,\ell^{-1}$. Only three Loch Vale winter samples stratified into the high salt category. High salt SO_4^{2-} and NO_3^- were association with all base cations except NH_4^+. There was no associated with precipitation, and a negative association with H^+.

Table 2. Seasonal solute deposition (g m^{-2}) for Loch Vale and Beaver Meadows NADP/NTN sites in Rocky Mountain National Park. Values are means and standard deviation (in parentheses) of 6 and 9 summers (1/5–30/9) and for 8 and 11 winters (1/10–30/4) for Loch Vale and Beaver Meadows, respectively

	Ca^{2+}	Mg^{2+}	K^+	Na^+	NH_4^+	NO_3^-	Cl^-	SO_4^{2-}	H^+ (*10^{-3})
Loch Vale									
Summer	0.11 (0.05)	0.016 (0.005)	0.013 (0.007)	0.028 (0.010)	0.07 (0.02)	0.38 (0.06)	0.05 (0.01)	0.38 (0.07)	3.69 (1.63)
Winter	0.08 (0.04)	0.014 (0.010)	0.008 (0.005)	0.048 (0.015)	0.05 (0.02)	0.34 (0.11)	0.05 (0.02)	0.30 (0.12)	3.09 (1.38)
Beaver Meadows									
Summer	0.06 (0.02)	0.010 (0.004)	0.016 (0.012)	0.018 (0.006)	0.06 (0.02)	0.28 (0.07)	0.03 (0.01)	0.26 (0.09)	2.26 (0.71)
Winter	0.03 (0.02)	0.005 (0.003)	0.005 (0.006)	0.013 (0.006)	0.02 (0.01)	0.11 (0.04)	0.01 (0.01)	0.09 (0.02)	0.93 (0.29)

Table 3. Spearman rank correlation coefficients (rho values) of seasonally separated wet deposition from the Loch Vale NADP/NTN site. Only data from weeks where sample volumes were greater than 10 ml and sample collection protocols were followed 1983–1991 were used. Summer data are defined as 1/5–30/9 of each water year, and winter data include samples from 1/10–30/4 of each water year. Low salt/low acid samples are those where $\sum(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + NH_4^{+}) < 50\ \mu eq\ \ell^{-1}$. High salt data are those samples where $\sum(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + NH_4^{+}) \geq 50\ \mu eq\ \ell^{-1}$. Acid-dominant samples are those where $H^{+} > \sum(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + NH_4^{+})$. Sample sizes for summer, low salt/low acid summer, high salt summer, and acid-dominant summer samples are 87, 46, 17, and 25, respectively. Sample sizes for winter, low salt/low acid winter, high salt winter and acid-dominant samples are 105, 58, 3 and 44, respectively

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	LABH	FLDH	SO_4^{2-}	NO_3^{-}	Cl^{-}	mm ppt
All summer											
NO_3^{-}	0.619	0.618	0.530	0.537	0.644	0.355	0.525	0.782	—	0.627	−0.573
SO_4^{2-}	0.812	0.807	0.660	0.720	0.564	0.270	0.483	—	0.782	0.723	−0.522
Low salt/low acid summer											
NO_3^{-}	0.372	0.395	0.389	0.472	0.549	0.489	0.684	0.768	—	0.538	−0.486
SO_4^{2-}	0.652	0.594	0.433	0.617	0.467	−0.188	0.351	—	0.768	0.669	−0.420
High salt summer											
NO_3^{-}	0.083	0.174	−0.047	0.375	0.606	0.625	0.559	0.811	—	0.480	−0.438
SO_4^{2-}	0.125	0.245	0.071	0.404	0.493	0.650	0.605	—	0.811	0.560	−0.588
Acid-dominated summer											
NO_3^{-}	0.642	0.699	0.318	0.193	0.584	0.588	0.718	0.736	—	0.359	−0.621
SO_4^{2-}	0.745	0.828	0.292	0.522	0.489	0.728	0.842	—	0.736	0.410	−0.285
All winter											
NO_3^{-}	0.564	0.532	0.261	0.482	0.593	0.148	0.231	0.584	—	0.436	−0.286
SO_4^{2-}	0.685	0.695	0.376	0.595	0.404	0.004	0.174	—	0.584	0.506	−0.182
Low salt/low acid winter											
NO_3^{-}	0.578	0.572	0.156	0.522	0.592	0.367	0.533	0.623	—	0.482	−0.289
SO_4^{2-}	0.656	0.719	0.281	0.574	0.319	0.219	0.480	—	0.623	0.474	−0.074
High salt winter											
NO_3^{-}	1.000	1.000	0.500	1.000	−1.000	−0.500	−0.500	1.000	—	1.000	−1.000
SO_4^{2-}	1.000	1.000	0.500	1.000	−1.000	−0.500	−0.500	—	1.000	1.000	−1.000
Acid-dominated winter											
NO_3^{-}	0.231	0.101	0.166	0.077	0.422	0.585	0.400	0.294	—	0.289	−0.237
SO_4^{2-}	0.309	0.263	0.338	0.155	0.220	0.427	0.315	—	0.294	0.360	−0.226

Table 4. Spearman rank correlation coefficients (rho values) of seasonally separated wet deposition from Beaver Meadows NADP/NTN site. Only data from weeks where sample volumes were greater than 10 ml and sample collection protocols were followed 1980–1991 were used. Summer data are defined as 1/5–30/9 of each water year, and winter data include samples from 1/10–30/4 of each water year. Low salt/low acid samples are those where $\sum(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}+NH_4^{+})<50\ \mu eq\,\ell^{-1}$. High salt data are those samples where $\sum(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}+NH_4^{+})\geq 50\ \mu eq\,\ell^{-1}$. Acid-dominant samples are those where $H^{+}>\sum(Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}+NH_4^{+})$. Sample sizes for summer, low salt/low acid summer, high salt summer, and acid-dominant summer are 130, 62, 45, and 25, respectively. Sample sizes for winter, low salt/low acid winter, high salt winter, and acid-dominant winter samples are 145, 92, 21, and 36, respectively

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	LABH	FLDH	SO_4^{2-}	NO_3^{-}	Cl^{-}	mm ppt
All summer											
NO_3^{-}	0.698	0.704	0.607	0.641	0.632	0.444	0.429	0.850	—	0.622	−0.551
SO_4^{2-}	0.789	0.777	0.653	0.674	0.604	0.384	0.450	—	0.850	0.668	−0.534
Low salt/low acid summer											
NO_3^{-}	0.506	0.531	0.408	0.498	0.470	0.711	0.609	0.752	—	0.391	−0.391
SO_4^{2-}	0.686	0.637	0.466	0.521	0.434	0.634	0.615	—	0.752	0.469	−0.330
High salt summer											
NO_3^{-}	0.531	0.466	0.328	0.466	0.442	0.486	0.379	0.775	—	0.450	−0.532
SO_4^{2-}	0.580	0.718	0.538	0.466	0.287	0.480	0.526	—	0.775	0.565	−0.561
Acid-dominated summer											
NO_3^{-}	0.780	0.714	0.688	0.616	0.502	0.642	0.871	0.781	—	0.555	−0.596
SO_4^{2-}	0.901	0.703	0.622	0.472	0.474	0.604	0.793	—	0.781	0.649	−0.528
All winter											
NO_3^{-}	0.505	0.392	0.396	0.351	0.573	0.160	0.297	0.524	—	0.452	−0.218
SO_4^{2-}	0.749	0.757	0.650	0.683	0.446	−0.050	0.220	—	0.524	0.668	−0.384
Low salt/low acid winter											
NO_3^{-}	0.403	0.260	0.292	0.238	0.487	0.317	0.517	0.407	—	0.297	−0.123
SO_4^{2-}	0.656	0.720	0.533	0.593	0.267	−0.247	0.120	—	0.407	0.563	−0.291
High salt winter											
NO_3^{-}	−0.598	−0.439	−0.475	−0.339	0.576	0.687	0.464	0.046	—	−0.013	0.164
SO_4^{2-}	0.080	−0.025	0.186	0.084	0.198	0.181	0.273	—	0.046	0.087	−0.283
Acid-dominated winter											
NO_3^{-}	0.264	0.189	0.235	0.165	0.553	0.341	0.379	0.231	—	0.404	−0.161
SO_4^{2-}	0.717	0.661	0.524	0.705	0.497	0.102	0.715	—	0.231	0.616	−0.258

3.2.2. *Beaver Meadows.* Sulfate and NO_3^- were negatively associated with precipitation and were most strongly associated with each other in all strata in Beaver Meadows summer precipitation (Table 4). In the unstratified summer data set the anions were associated with all other solutes except H^+ ($n=130$). In the low salt/low acid stratum both SO_4^{2-} and NO_3^- were associated with H^+. Sulfate was additionally associated with Mg^{2+}, K^+, and Ca^{2+} ($n=62$). There were strong associations of SO_4^{2-} with most other solutes, and of NO_3^- with all other solutes in the 25 acid-dominated summer samples from Beaver Meadows. Within the 43 summer high salt stratified samples, NO_3^- was only strongly associated with SO_4^{2-} and Ca^{2+}, while SO_4^{2-} showed an association with Ca^{2+}, Mg^{2+}, Na^+, H^+, NO_3^-, and Cl^-.

The strong acid anions showed a slight negative association to precipitation in all winter samples. Unlike the summer samples, SO_4^{2-} and NO_3^- were not strongly associated with each other. Instead, their strongest affiliations varied according to stratification category. In the unstratified data set NO_3^- was associated strongly with NH_4^+, and slightly associated with SO_4^{2-} and Ca^{2+} ($n=145$). Most winter precipitation was low salt/low acid, and NO_3^- was slightly associated with H^+ ($n=92$). Winter SO_4^{2-} was associated with most other solutes except H^+ and NH_4^+ in the unstratified data set. These associations were repeated less strongly in the low salt/low acid stratum. Acid-dominated precipitation was dilute, with a median field H^+ of 17 $\mu eq\,\ell^{-1}$. Acidity was related to SO_4^{2-}, but not to NO_3^-. Sulfate in acid-dominated samples was also associated with base cations, while NO_3^- was mainly associated with NH_4^+. High salt winter precipitation was very different in composition than any other precipitation ($n=21$). Nitrate was negatively associated with all base cations except NH_4^+. Sulfate was not associated with any other solute in high salt winter samples.

3.3. *Association of strong acid anions with zonal winds*

The percent distribution of precipitation by zonal wind speed (Fig. 3) reveals that easterly events are very rare at Loch Vale, so that total deposition is greatest during precipitation associated with westerly winds. Westerly events are comparatively rare at the Beaver Meadows site, revealing that total deposition is greatest during precipitation associated with easterly winds.

Plots of unstratified VWM NO_3^- and SO_4^{2-} concentrations vs mean zonal wind component revealed some seasonal differences. Negative values of zonal winds (u) in these plots (indicating easterly winds during precipitation) were associated with much higher concentrations of NO_3^- at Loch Vale in summer period (Fig. 4a). Low salt/low acid stratified precipitation revealed nearly identical patterns to

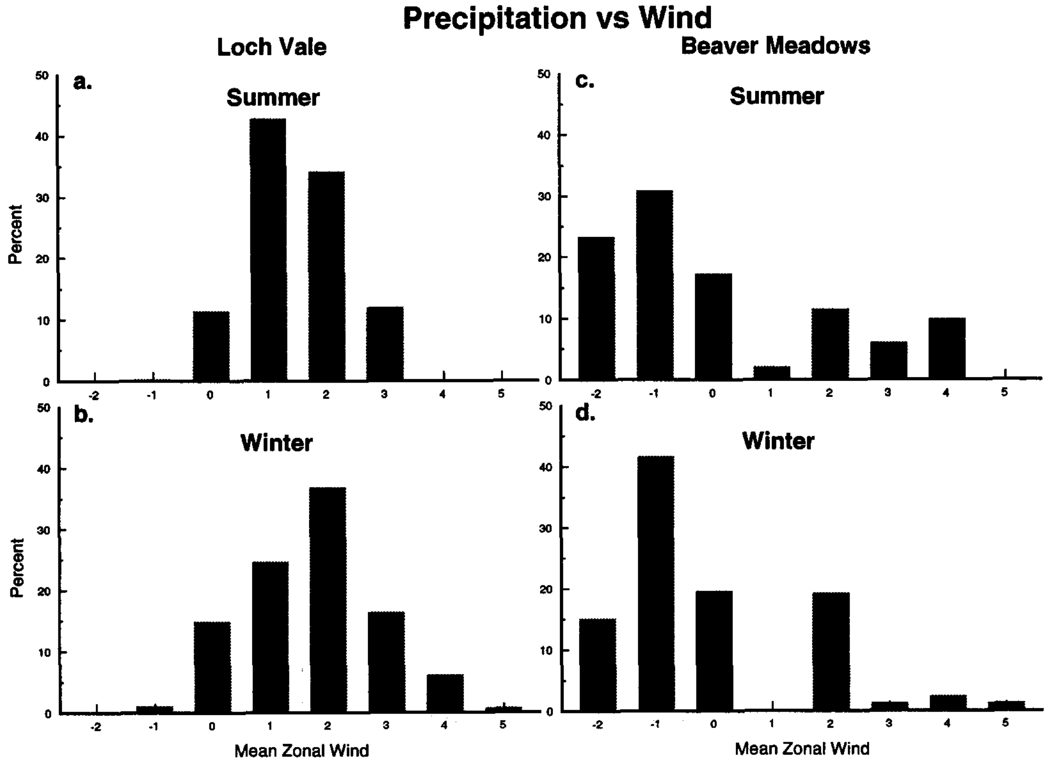

Fig. 3. Percent of total seasonal precipitation vs mean zonal wind at Loch Vale during (a) summer, and (b) winter; and at Beaver Meadows during (c) summer and (d) winter.

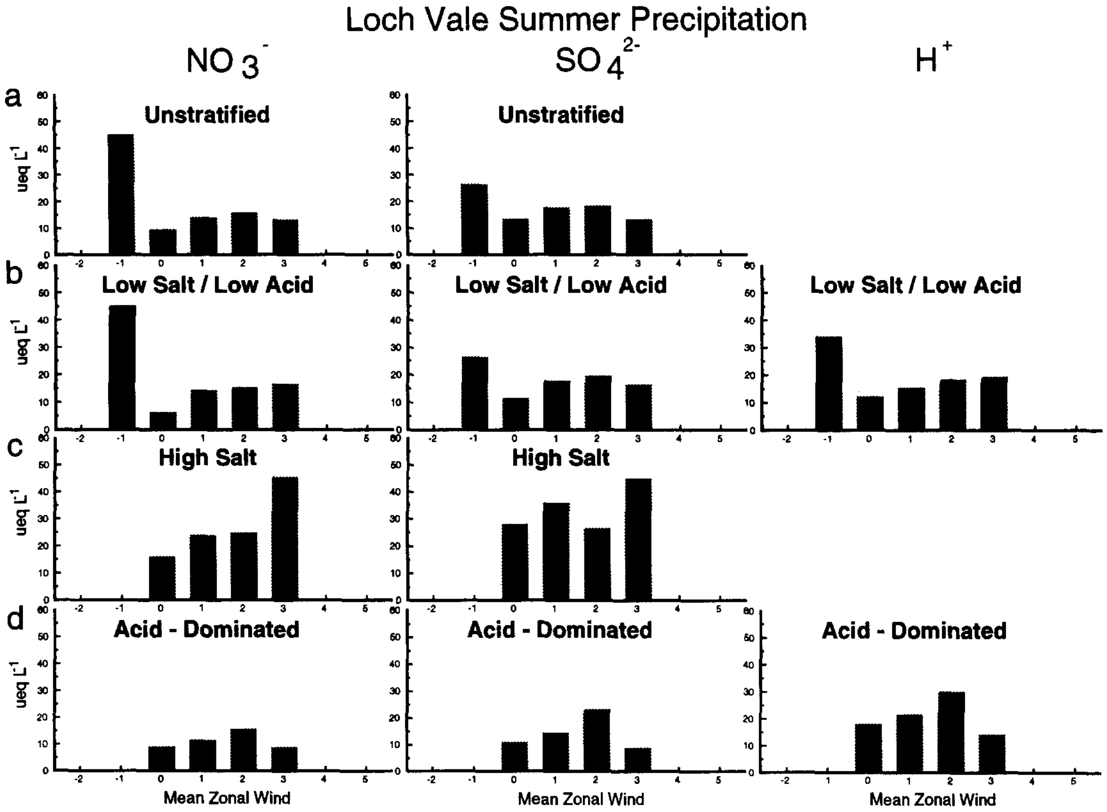

Fig. 4. Concentrations (μeqℓ^{-1}) of NO_3^-, SO_4^{2-}, and H^+ vs mean zonal wind for Loch Vale summer precipitation stratification categories: (a) low salt/low acid; (b) acid-dominated; (c) high salt; and (d) unstratified.

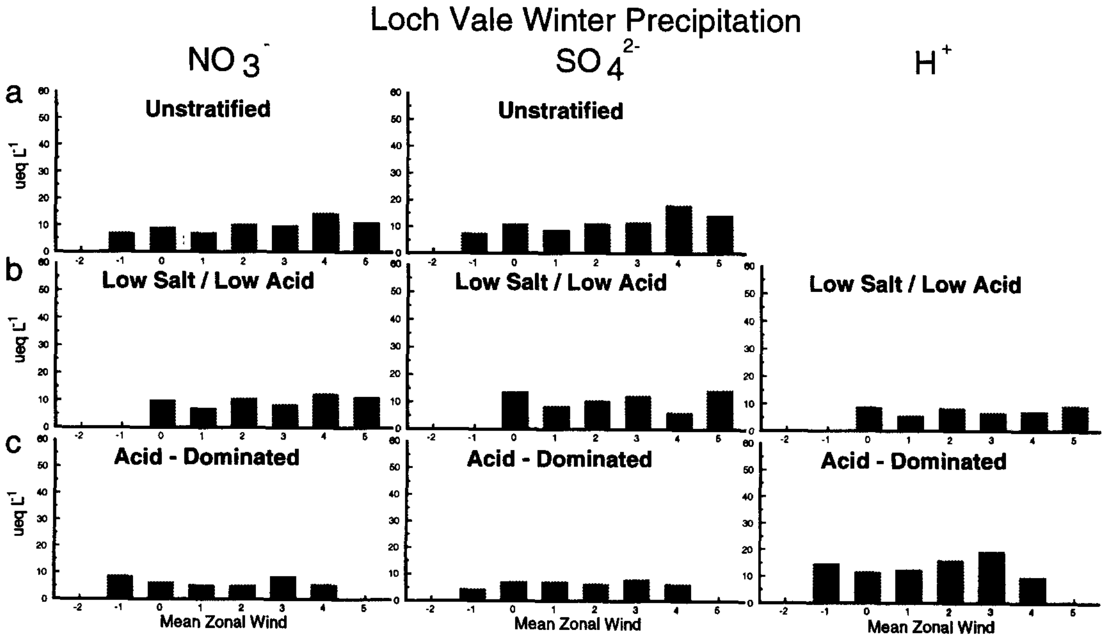

Fig. 5. Concentrations (μeqℓ^{-1}) of NO_3^-, SO_4^{2-}, and H^+ vs mean zonal wind for Loch Vale winter precipitation stratification categories: (a) low salt/low acid; (b) acid-dominated; and (c) unstratified.

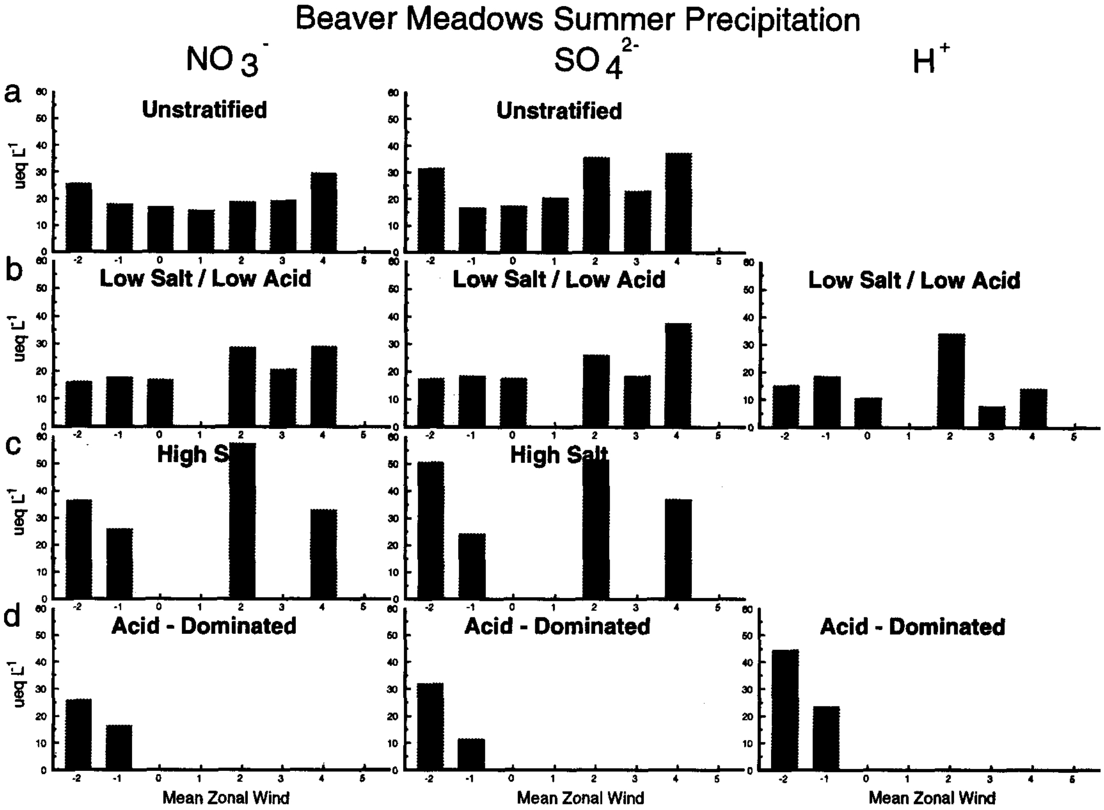

Fig. 6. Concentrations (μeq ℓ^{-1}) of NO_3^-, SO_4^{2-}, and H^+ vs mean zonal wind for Beaver Meadows summer precipitation stratification categories: (a) low salt/low acid; (b) acid-dominated; (c) high salt; and (d) unstratified.

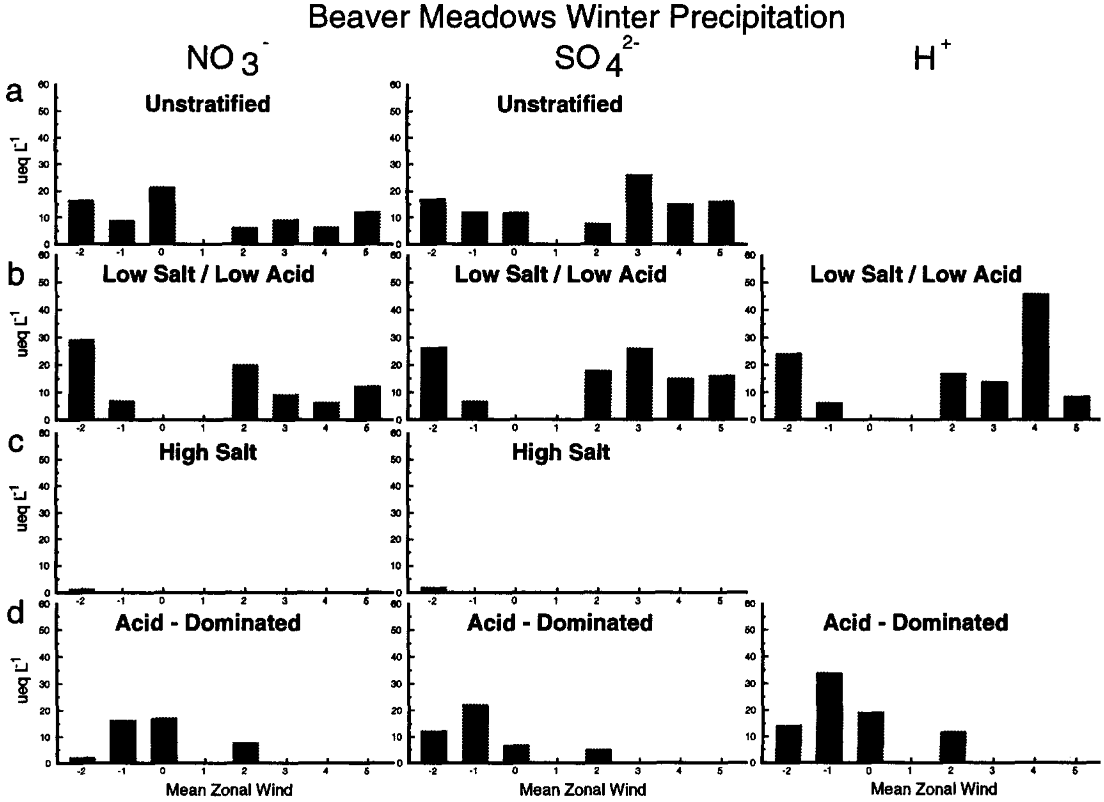

Fig. 7. Concentrations (μeq ℓ^{-1}) of NO_3^-, SO_4^{2-}, and H^+ vs mean zonal wind for Beaver Meadows winter precipitation stratification categories: (a) low salt/low acid; (b) acid-dominated; (c) high salt; and (d) unstratified.

unstratified precipitation (Fig. 4b). In contrast, the 16 high salt precipitation events showed the highest concentrations of both SO_4^{2-} and NO_3^- associated with moderately strong westerly winds (Fig. 4c). Acid-dominated precipitation was associated with moderate westerly zonal winds, and clearly *not* associated with easterly zonal winds (Fig. 4d). In the winter, concentrations of all solutes were very low. Slightly higher NO_3^- and SO_4^{2-} concentrations from the full data set were associated with moderately strong westerly winds (Fig. 5a). Low salt/low acid stratification caused the westerly wind association to be less well-defined (Fig. 5b). There was no directional distinction for acid-dominated precipitation (Fig. 5c). Unfortunately, wind data were not available for the few winter high salt weeks at Loch Vale.

At Beaver Meadows, the highest summer NO_3^- precipitation was associated with strong easterly and strong westerly winds for the unstratified data set (Fig. 6a). The pattern for SO_4^{2-} was similar, and SO_4^{2-} was additionally associated with moderate westerly winds. Moderate to strong westerly winds brought higher NO_3^- in low salt/low acid stratified summer precipitation (Fig. 6b). Sulfate in low salt/low acid summer precipitation behaved similarly to SO_4^{2-} in the unstratified data set. The anions in high salt summer precipitation were associated with strong easterlies, and moderate to strong westerlies (Fig. 6c). Acid-dominated precipitation came exclusively from the east via strong to moderate easterly zonal winds (Fig. 6d). During the winter, NO_3^- concentrations were greater with easterly winds, while higher SO_4^{2-} concentrations were associated with moderate to strong westerly winds (Fig. 7a). Low salt/low acid stratified precipitation patterns were similar, and also clearer (Fig. 7b). Strong easterly winds were associated with the one high salt stratified winter precipitation sample for which there was wind data at Beaver Meadows (Fig. 7c). Acid-dominated precipitation was mostly associated with strong to moderate easterly zonal winds, with some also associated with moderate westerlies (Fig. 7d).

4. DISCUSSION

In the full, unstratified summer data set from both Beaver Meadows and Loch Vale, most solutes were significantly correlated with each other. Verry and Harris (1988) attribute this to the presence of SO_4^{2-} and NO_3^- from soil dust, marine aerosols, or other sources, and this obscures the relationship of H^+ to these ions. They suggest stratification into high and low salt events to clarify the relationship. However, in the dilute precipitation of Rocky Mountain National Park, low salt stratification did little to clarify anthropogenic vs other sources of strong acid anions. Low salt stratification revealed stronger associations of SO_4^{2-} and NO_3^- with field H^+ in the summer at Beaver Meadows when compared with all summer and high salt stratified deposition, but strong associations were still apparent between the anions and Ca^{2+} and Mg^{2+}. For Loch Vale, where most summer precipitation was dilute, separation of low salt samples did not greatly increase the relation of SO_4^{2-} or NO_3^- with acidity. Summer high salt stratified samples, however, included strong H^+: SO_4^{2-}, NH_4^+: NO_3^- and H^+: NO_3^- associations, suggesting that mixing of pollutant emissions and natural salts is common. This is not unreasonable, considering the juxtaposition of the semi-arid, agricultural, eastern plains of Colorado with the Denver urban corridor.

4.1. *Summer wind: solute associations*

Summer low salt/low acid precipitation, which was most summer precipitation at Loch Vale, was brought by easterly or moderate westerly winds. Acid-dominated summer precipitation at Loch Vale was associated with moderate westerly winds, and high salt events were the result of moderate to strong westerlies. These precipitation types all have the same subtropical source of moisture, but our observations suggest their composition is influenced by local winds. Up-valley air flows occur daily during the summer, and this most common type of surface wind is associated with low salt/low acid precipitation. Because these winds are gentle, there is time in transit for acidic aerosols to be neutralized, and they do not entrain the terrigenous particles that cause high salt events at Loch Vale. Convective rainfall (thunder storms) in summer can be accompanied by strong downdrafts (Hansen *et al.*, 1973). These are measured as down-valley (westerly) events at the Loch Vale weather station, even though these storms are triggered by upslope lifting along the entire mountain front. The strong updrafts that precede thunderstorms serve to carry soil dust and polluted air quickly to the mountains. The acidic or high salt content of convectively introduced precipitation is a consequence of whether the storms pass over urban or agricultural areas to the east. Terrain geometry at Loch Vale constrains the airflow into down-valley or up-valley directions (Baron *et al.*, 1992).

Only half of the summer precipitation at Beaver Meadows was low salt/low acid, and was brought by easterly and moderate to strong westerly winds. High salt precipitation also exhibited a bimodal pattern of easterly or westerly zonal winds. This suggests both up-valley inflows and thunder storm genesis activity are responsible for low salt/low acid and high salt events. Acid dominated precipitation exclusively came from the east, as a result of strong up-valley winds. The open terrain at the Beaver Meadows/headquarters location permits surface airflow to come from any compass direction. This makes it difficult to extract a clear association of solutes with zonal winds.

Parrish *et al.* (1990) observed that mountain–valley winds carry polluted air parcels into the mountains on a daily basis. They are then mixed into the higher level westerly flow that persists throughout the day. Thus when it rains at Beaver Meadows, strong acid anions may be rained out regardless of surface wind direction during precipitation. This is possibly less evident at the higher elevation location because, at 3100 m, Loch Vale is closer to the prevailing higher level westerly flow; pollutants that are not quickly rained out at this elevation are transported away to the east, or to the free troposphere (Parrish *et al.*, 1990).

4.2. *Winter wind: solute associations*

The moisture source for wintertime precipitation comes primarily from the North Pacific, and moisture is transported rapidly via the jet stream (Hansen *et al.*, 1978; Parrish *et al.*, 1990; Bollinger *et al.*, 1984). The development of winter inversion layers along Front Range urban areas can prevent polluted air parcels close to the Earth's surface from becoming incorporated into upper air masses, although uncommon upslope wind events been observed to transport air parcels with extremely high NO_x concentrations to mountain ecosystems (Heubert *et al.*, 1982). Most winter precipitation at Loch Vale and Beaver Meadows was low salt, reflecting air parcels transported rapidly from the Pacific Ocean (Parrish *et al.*, 1990). Acid-dominated precipitation had a slightly greater easterly zonal wind component at Loch Vale than low salt/low acid precipitation. H^+: NO_3^- and NH_4^+: NO_3^- associations were very important constituents of most Loch Vale precipitation, although winter high salt events were dominated by soil cations. Uncommonly strong upslope winds from the Front Range urban and agricultural areas occasionally brought highly polluted precipitation to Beaver Meadows; these high salt events were dominated by NH_4^+: NO_3^- and H^+: NO_3^- associations. This is in keeping with the association of NO_3^- with easterly zonal winds.

A study of high elevation snowpack revealed greater concentrations of sulfate and nitrate in northern Colorado than in southern Colorado (Turk *et al.*, 1992). The greatest concentrations were found downwind (east) of the Yampa River Valley. Sulfate in the downwind samples was isotopically distinct from other Colorado snowpack samples, suggesting a different source of sulfate for the area downwind from the Yampa River valley compared to the other snowpack sample sites in Colorado. The slightly higher NO_3^- and SO_4^{2-} concentrations associated with westerly winter winds at Loch Vale may be due to this western source.

Interestingly, SO_4^{2-} was not an important constituent of high salt winter precipitation at Beaver Meadows. Sulfate in unstratified and low salt winter precipitation was correlated with base cations at Beaver Meadows and Loch Vale. This suggests that winter SO_4^{2-} originates either as calcium or magnesium salts, or industrially originated SO_4^{2-} reacts with $CaCO_3$ or $MgCO_3$ in the atmosphere (Young *et al.*, 1988; LeFohn and Krupa, 1988; Hooper and Peters, 1989). A comparison of sulfur isotope and ion ratios between soils and precipitation in the southwest United States of America did not indicate that soil dust was the major source of SO_4^{2-} in precipitation (Schlesinger and Peterjohn, 1988). Hooper and Peters (1989) found only 15 of 87 NADP sites west of the Mississippi River had Ca^{2+} and SO_4^{2-} correlations, but half of these stations also revealed sea salt influences instead of soil dust.

The three winter high salt samples from Loch Vale revealed a chemical signature that suggests eolian dust rather than urban or feedlot pollution. Unfortunately, none of the high salt samples had valid wind data, so their association with mean zonal wind is unknown. High particulate snow events occur periodically throughout the western United States of America, and eolian-derived materials have been suggested as important inputs to tundra soils (Olsson and Denning, 1990; Litaor, 1987).

Wind and precipitation patterns at Beaver Meadows were similar to those of Loch Vale during the winter, with the exception that moderate westerly winds accompanied a few high salt events. Thus the orographic, synoptic-scale precipitation so important to Loch Vale is not as important to deposition at Beaver Meadows. Ammonium and NO_3^- were much less important solutes in Beaver Meadows precipitation, except during high salt events. Both H^+: NO_3^- and H^+: SO_4^{2-} were common to summer acid dominated precipitation, while only H^+: SO_4^{2-} was dominant in winter acid dominated precipitation.

Overall, the combination of zonal wind and solute association information leads us to conclude that strong acid anions, acidity, ammonium, and high salt concentrations originate to the east of both sites in the Rocky Mountain National Park, and are transported via upslope winds or convective instability from differential heating. These influence the composition of precipitation at Beaver Meadows throughout the year, while their effect on Loch Vale precipitation is felt most strongly during the summer. During the winter, Loch Vale precipitation is very dilute, and occurs in conjunction with westerly zonal winds resulting from orographic or cyclonic precipitation. There is some slight evidence of a western source of strong acid anions. More research is needed to characterize this possibility.

For practical applications, summer deposition could probably be extrapolated to high elevations from lower elevation sampling sites, but winter solute deposition might be overestimated based only on increased precipitation at the higher site. By modifying extrapolations based on an understanding of mountain meteorology, high elevation deposition can be estimated more realistically.

Acknowledgements—We thank Brian Newkirk and Tammy Bearly for help with the data analysis. John Weaver and John Kleist provided access to the PROFS data. We are grateful to David Bigelow, Rob Edwards, and two anonymous reviewers for constructive comments on this and earlier drafts of this manuscript. This study was supported by the National Park Service.

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