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Major-ion chemistry of the Rocky Mountain snowpack, USA

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Abstract

During 1993–97, samples of the full depth of the Rocky Mountain snowpack were collected at 52 sites from northern New Mexico to Montana and analyzed for major-ion concentrations. Concentrations of acidity, sulfate, nitrate, and calcium increased from north to south along the mountain range. In the northern part of the study area, acidity was most correlated (negatively) with calcium. Acidity was strongly correlated (positively) with nitrate and sulfate in the southern part and for the entire network. Acidity in the south exceeded the maximum acidity measured in snowpack of the Sierra Nevada and Cascade Mountains. Principal component analysis indicates three solute associations we characterize as: (1) acid (acidity, sulfate, and nitrate), (2) soil (calcium, magnesium, and potassium), and (3) salt (sodium, chloride, and ammonium). Concentrations of acid solutes in the snowpack are similar to concentrations in nearby wetfall collectors, whereas, concentrations of soil solutes are much higher in the snowpack than in wetfall. Thus, dryfall of acid solutes during the snow season is negligible, as is gypsum from soils. Snowpack sampling offers a cost-effective complement to sampling of wetfall in areas where wetfall is difficult to sample and where the snowpack accumulates throughout the winter. Published by Elsevier Science Ltd.

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1. Introduction

Knowledge of the chemical composition of atmospheric deposition is critical in understanding regional and local air pollution and its effects on hydrologic systems. Atmospheric deposition is monitored nationally by the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). Although automated wetfall samplers used by the NADP/NTN work well in most areas, these samplers are less efficient in sampling environments dominated by dry and

blowing snowfall. Problems include: (1) difficulty in triggering sensors, (2) overflowing of collection buckets by large snow events, (3) under-collection of blowing snow, and (4) need for reliable electrical power (solar power in remote areas can be insufficient during periods of prolonged cloudiness). In remote areas having large seasonal snowpacks, access for routine collection of samples and servicing of samplers is difficult. In wilderness areas, law restricts the placing of permanent instrumentation and access by mechanized means. As a result of these issues, few stations in the NADP/NTN network exist at high elevations, and these few sites may collect only about 10–30% of snowfall (Turk et al., 1993). If this small percentage of total snowfall is different chemically from the total snowfall, then estimates of total snowfall chemistry are biased. Because

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snowfall concentration data are multiplied by snow amount to obtain total loading amount, data at higher elevations are critical to obtain accurate estimates of total loading.

At sites of high elevation or latitude, the seasonal snowpack is a ubiquitous receptor of atmospheric deposition. Further, the snowpack provides most of the water and some solutes such as sulfate to high-elevation lakes and streams (Turk and Spahr, 1991). Amplification of acidity during early snowmelt may cause biological damage to amphibians in the Rocky Mountains (Turk and Campbell, 1997; Williams et al., 1996). As long as the site does not experience prolonged periods above freezing, the snowpack preserves an integrated measure of atmospheric deposition. The prevalence of such sites in major mountain ranges offers unique opportunity for synoptic surveys across broad regions. Synoptic sampling of seasonal snowpack in the Sierra Nevada/Cascade Mountains (Fig. 1 inset) was done in 1983 (Laird et al., 1986), but only localized sampling of this type has been conducted since. To determine whether synoptic sampling of the seasonal snowpack was feasible throughout the US Rocky Mountains, sampling was conducted in 1993–97 at sites shown in Fig. 1.

2. Sample collection and analysis

Snowpack samples were collected in early March to mid-April of 1993–97 just prior to the start of snowmelt to capture most of the winter deposition in a single sample (Ingersoll, 1999). Workers wearing powderless latex gloves and using precleaned plastic shovels and scoops collected depth-integrated samples from the vertical face of a snowpit. Snowpack temperature was measured at 10-cm increments to verify that the snowpack was below freezing. The top 5 cm and bottom 10 cm of snow were excluded to prevent contamination by soil or other debris. Snow columns were cut from the wall of snowpits and placed in precleaned 8-l Teflon bags. Snow samples were kept frozen at -10°C until the samples were processed and analyzed.

Snow samples were melted at room temperature in the Teflon collection bags and were processed within 12 h. An unfiltered sample was used for alkalinity and pH determination. Other major-ion concentrations were determined on filtered (0.45- μm polyethersulphone filters) aliquots. Major cation concentrations were determined on aliquots acidified with double-distilled, concentrated nitric acid by inductively coupled plasma for calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^{+}), and atomic absorption for potassium (K^{+}) only. Chloride (Cl^{-}) and sulfate (SO_4^{2-}) concentrations were determined by ion chromatography. Nitrate (NO_3^{-}) and ammonium (NH_4^{+}) were determined by air-segmented,

continuous-flow colorimetry. Dissolved organic carbon (DOC) was determined by UV-promoted persulfate oxidation and infrared detection. Detection limits were less than or equal to $1\ \mu\text{eq/l}$ for major cations and anions and $0.2\ \text{mg/l}$ for DOC. Field and process blanks ($n = 23$) from this study and in subsequent years processed by the same methods were at or below the analytical detection limits. Specific conductance was measured in microsiemens per centimeter at 25°C with a platinum electrode; pH was determined in standard units with a combination glass electrode designed for dilute waters. Alkalinity was determined by Gran titration.

Quality control involved systematically analyzing deionized-water blanks, an internal reference sample, and USGS standard reference water samples. Approximately 40% of sample batch run time for the analytical instrumentation was dedicated to analyzing blanks, duplicates, internal reference samples, and USGS standards. Replicate snow samples were collected to determine the precision of data from individual sites, and the results are presented in Section 3.5.

3. Results and discussion

3.1. Solute associations

The major-ion concentrations may be compared among solutes and among subregions (discussed in the next section) by examination of Fig. 2. Among cations, the concentration order on an equivalent basis is: $\text{H}^{+} \sim \text{Ca}^{2+} > \text{NH}_4^{+} > \text{Na}^{+} \sim \text{Mg}^{2+} > \text{K}^{+}$. Among anions, the concentration order is: $\text{NO}_3^{-} \sim \text{SO}_4^{2-} > \text{Cl}^{-}$. To maintain charge balance, changes in H^{+} (free acidity) mostly are controlled by the relative variations of Ca^{2+} , NH_4^{+} , NO_3^{-} , and SO_4^{2-} . Because the pH typically was about 5, HCO_3^{-} can be ignored.

Additional constituents were determined for a subset of samples. Depending on the constituent, 30–70% of all samples were analyzed and mean concentrations were: acetate ($1.2\ \mu\text{eq/l}$), formate ($0.6\ \mu\text{eq/l}$), total dissolved nitrogen as N ($17\ \mu\text{M/l}$), and total dissolved phosphorus as P ($0.4\ \mu\text{M/l}$).

Solute associations were identified by a principal-components analysis (PCA) of all yearly samples at the 52 sites. The data were not transformed. Components having eigenvalues of 1 or higher were retained. Loading values of 0.6 or larger were considered in selecting constituents for each factor, except for Na^{+} (0.5). PCA indicates three solute associations we characterize as: (1) acid (H^{+} , SO_4^{2-} , NO_3^{-}), which explains 23% of variance; (2) soil (Ca^{2+} , Mg^{2+} , K^{+}), which explains 42% of variance; and (3) salt (Na^{+} , Cl^{-} , NH_4^{+}), which explains 12% of variance. These three components are similar to those identified in wetfall throughout the

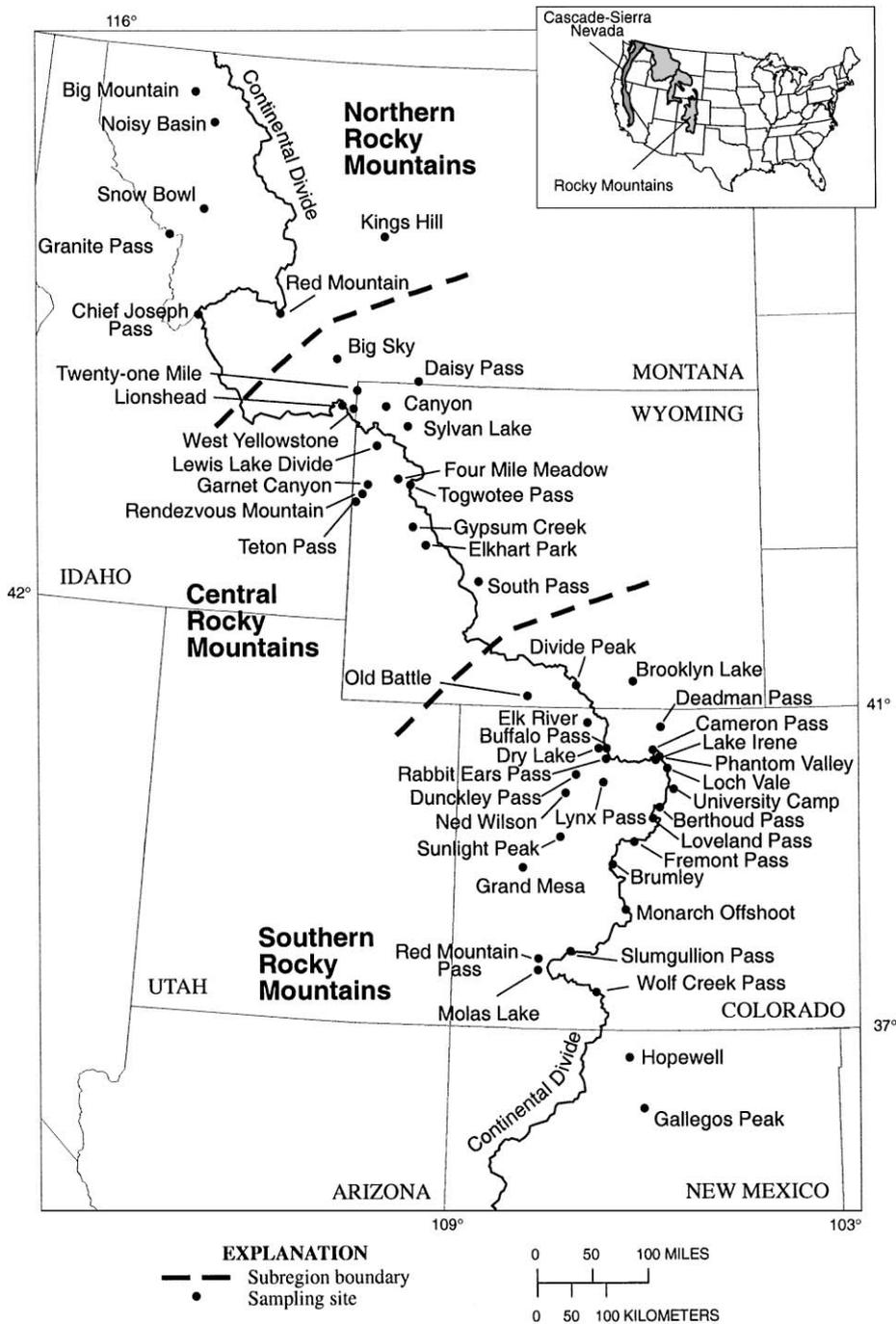
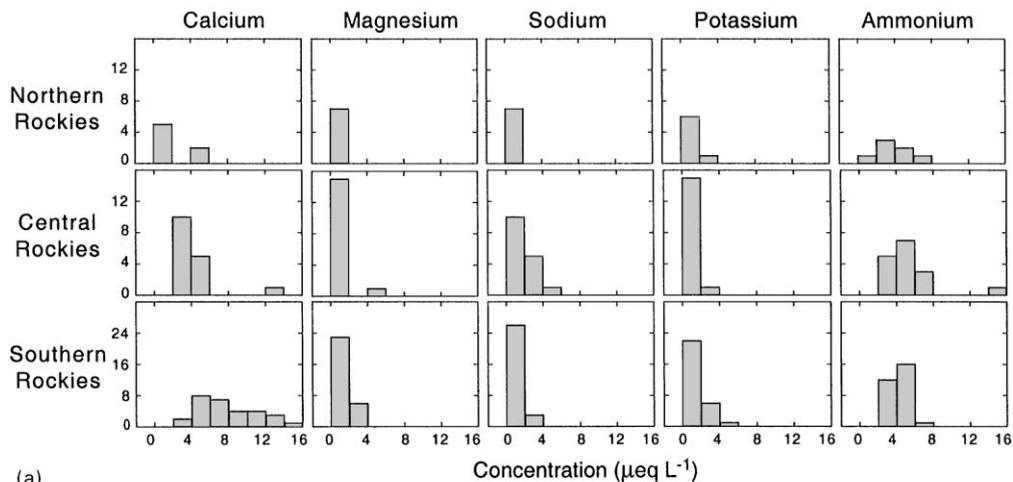


Fig. 1. Location map of sites in the US Rocky Mountain snowpack network sampled from 1993 to 1997.

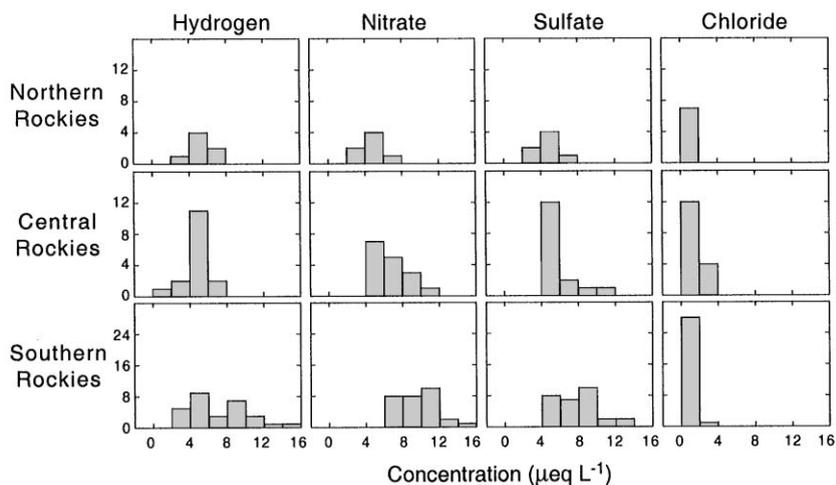
United States (Hooper and Peters, 1989). The soil component likely varies as a function of land use and of seasonal changes in plant cover, soil moisture, and windspeed. The acid component likely varies as a function of proximity to, and magnitude of, sources of fossil-fuel combustion. The salt component likely varies

with proximity to saline soils and to roadways where salt is used for ice removal. Animal waste and fertilizer probably contribute NH_4^+ that neutralizes acid anions.

Solute associations also were examined by linear regression among samples in each subregion to determine how these associations change geographically.



(a)



(b)

Fig. 2. Histograms of cation (a) and hydrogen ion and anion (b) concentrations in the Rocky Mountain snowpack, separated by subregion. Because of differences in number of samples among regions, vertical axis scale is not constant.

Table 1

Pearson correlation coefficients of H⁺ with selected ions in the Northern Rocky Mountain subregion (NRMS), the Central Rocky Mountain subregion (CRMS), the Southern Rocky Mountain subregion (SRMS), and for all sites in the snowpack network

Constituent	NRMS (n = 7)	CRMS (n = 16)	SRMS (n = 29)	All Sites (n = 52)
Ca ²⁺	-0.461	-0.411	-0.686 ^a	-0.177
NH ₄ ⁺	0.088	-0.054	0.460 ^b	0.046
SO ₄ ²⁻	0.144	0.272	0.640 ^a	0.609 ^a
NO ₃ ⁻	0.093	0.238	0.730 ^a	0.642 ^a
Cl ⁻	0.050	-0.310	-0.327	-0.204

^aCorrelations significant at p = 0.001 level.

^bCorrelations significant at p = 0.01 level. All other correlations not significant at p = 0.05.

Solutes necessarily correlate with other solutes in their identified PCA component; however, changes among subregions may show how changing sources affect the chemistry of snow. The acid component, represented by H⁺ had the strongest correlation (negative) across subregions with the soil component, represented by Ca²⁺ (Table 1). However, in the southern Rocky Mountain subregion (SRMS) and for the entire network, H⁺ correlated very strongly with NO₃⁻ and SO₄²⁻.

3.2. Subregional associations

The geographic scope of the region sampled, a distance of about 1500 km, and differences in proximity to major source areas of atmospheric pollutants likely

would result in large-scale geographic patterns of solute concentrations. Additionally, differences in topography of the mountainous terrain sampled may direct air masses along preferred trajectories that further strengthen geographic patterns of solute concentrations. These source- and topography-related patterns may occur at the local and regional scale. We divide the Rocky Mountains within the United States into three subregions (Fig. 1) based on differences in source areas of moisture and pollutants as well as in topography. It should be noted that although the sites lie in a generally north–south orientation, variables other than latitude are important. Sites may be either east or west of topographic features including the Continental Divide. Such topographic differences have been shown to have a small but statistically significant effect on concentrations of NO_3^- and SO_4^{2-} during the snow accumulation season, but a greater effect during warmer weather (Heuer et al., 2000). Also, the prevailing winds generally from west to east may be altered by drainage flow and the passage of atmospheric pressure cells so that even sources downwind with respect to the prevailing wind can be important at a site. To fully understand the influences at a given site or area, a more detailed meteorological examination of an enhanced local array of sites may be necessary.

The chemistry of atmospheric deposition at a given location represents the sum of all natural and anthropogenic sources locally and regionally. These sources may differ greatly in their contribution to the constituents reported here. As a result of these differences among sources, not all constituents change similarly between sites within a subregion or from one subregion to another. Comparison at the broadest scale among subregions in Fig. 2 indicates that both the soil and acid components increase in mean concentration from the northern Rocky Mountain subregion (NRMS) to the SRMS. However, the mean H^+ concentration is noticeably higher in the SRMS because at some sites the increase in NO_3^- and SO_4^{2-} from local sources exceeds the neutralizing effect of lower increases in Ca^{2+} concentrations. This effect is presented in detail in Mast et al. (2001).

3.3. Geographic patterns and extreme values

The lowest concentrations of Ca^{2+} and Mg^{2+} tend to occur in Montana and northern Wyoming, and the largest concentrations tend to be in southern Colorado and northern New Mexico. Anomalously large concentrations occur at Teton Pass in west-central Wyoming. Low concentrations of Na^+ occur throughout the network; however, largest concentrations are at Teton Pass and South Pass in Wyoming and along the urbanized Front Range of Colorado. Concentrations

of K^+ seem to be distributed similar to Na^+ . Low concentrations of NH_4^+ occur throughout the network; however, the largest concentration occurs at Lionshead in southern Montana, coincident with anomalously large concentrations of SO_4^{2-} , NO_3^- , and Cl^- .

The lowest concentrations of SO_4^{2-} and NO_3^- tend to occur in Montana and northern Wyoming (Fig. 3), and the largest concentrations tend to be in northern Colorado and probably are due to local powerplant emissions (Mast et al., 2001). Anomalously large concentrations occur at Lionshead in southern Montana and at South Pass in Wyoming. Low concentrations of Cl^- occur throughout the network; however, largest concentrations tend to be at Teton Pass in west-central Wyoming, and at Lionshead in southern Montana, and along the Front Range of Colorado. The former two sites are downwind of topographic low points and the agricultural area of the Snake River Plain, and the latter area is a major center of population and associated roadways where salt is used to remove ice.

The sites were ranked by H^+ concentration, and the 10 sites having the lowest (2.0–3.7 $\mu\text{eq/l}$) and highest (8.8–14.6 $\mu\text{eq/l}$) concentration (each group representing about 20% of sites) were selected. The concentrations of Ca^{2+} and of SO_4^{2-} plus NO_3^- for these sites are shown in Fig. 4. The lowest concentrations of H^+ do not occur in the NRMS, where concentrations of SO_4^{2-} and NO_3^- are lowest. Although the 10 highest concentrations of H^+ all occur in the SRMS, 5 of the 10 lowest concentrations also occur in the SRMS; the other 5 lowest occur in the CRMS.

Causes of these extreme concentrations of H^+ were examined by classifying concentrations of SO_4^{2-} , NO_3^- , and Ca^{2+} as high (20% or more higher than mean of the network), average (less than 20% higher or less than mean of the network), and low (20% or more less than mean of the network). Of the 10 sites having lowest concentrations of H^+ , 6 have high concentrations of Ca^{2+} (>7.0 $\mu\text{eq/l}$) but 4 have low concentrations (<4.6 $\mu\text{eq/l}$). However, 6 sites have low concentrations of SO_4^{2-} (<5.0 $\mu\text{eq/l}$), and 4 sites have average concentrations (5.3–6.8 $\mu\text{eq/l}$). Similarly, 5 sites have either low (<6.2 $\mu\text{eq/L}$) or average concentrations (7.5–8.4 $\mu\text{eq/l}$) of NO_3^- . Thus, low concentrations of H^+ are never associated with high concentrations of SO_4^{2-} or NO_3^- , even in combination with high concentrations of Ca^{2+} . High concentrations of Ca^{2+} appear to be associated with low concentrations of H^+ , except in cases where concentrations of NO_3^- and SO_4^{2-} also are fairly low.

Of the 10 sites having highest concentrations of H^+ , 8 sites have high concentrations of SO_4^{2-} (>7.6 $\mu\text{eq/l}$), and 9 sites have high concentrations of NO_3^- (>9.2 $\mu\text{eq/l}$). Of these 10 sites, 2 also have high concentrations of Ca^{2+} , and 3 have low concentrations of Ca^{2+} . Thus, high concentrations of H^+ are virtually

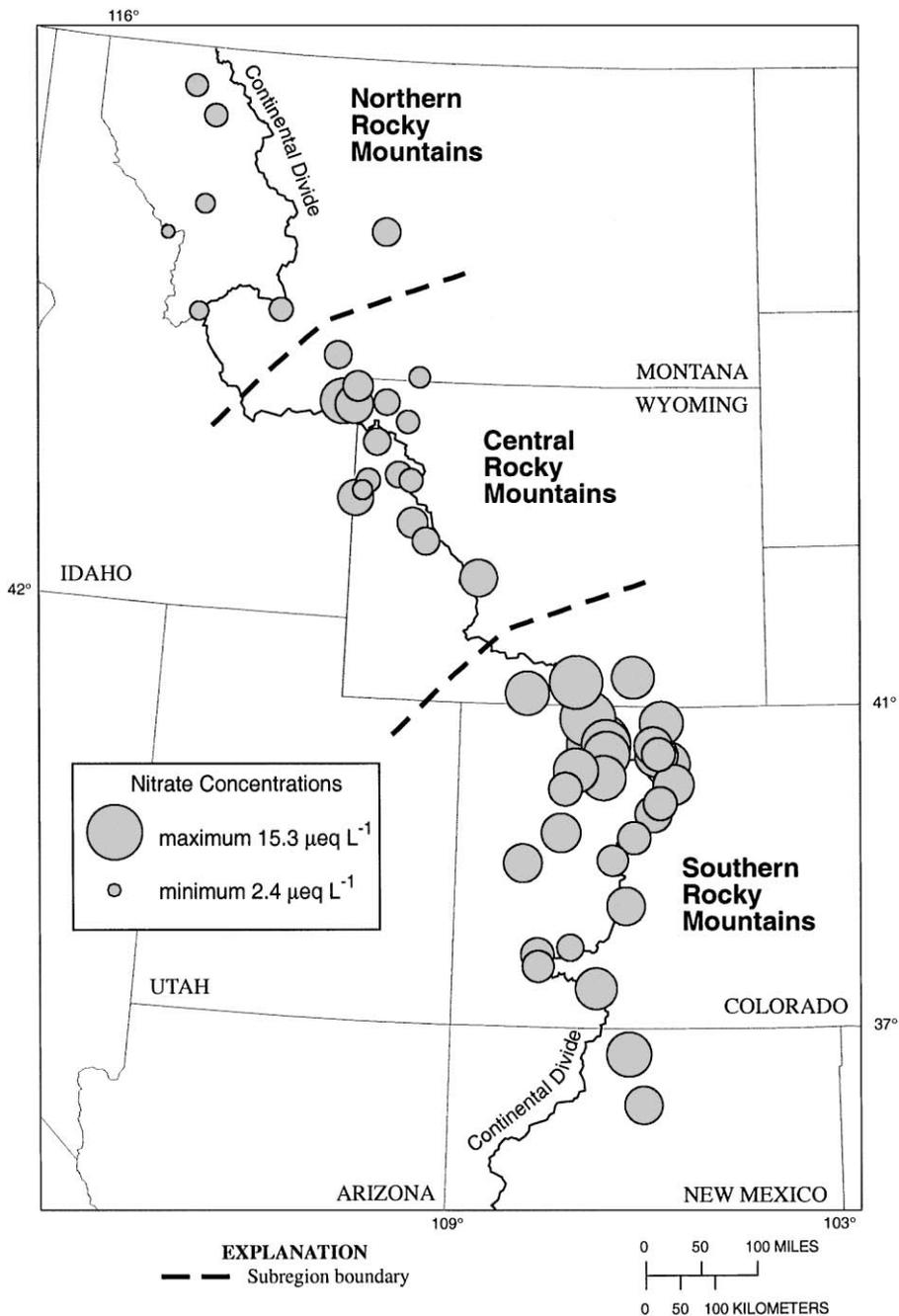


Fig. 3. Average nitrate concentrations at sites in the Rocky Mountain snowpack network from 1993 to 1997.

always associated with high concentrations of SO_4^{2-} and NO_3^- . To summarize, the soil and acid components are of roughly equal importance at sites with the lowest concentrations of H^+ . However, at sites having the highest concentrations of H^+ , the acid component clearly is more important.

3.4. Comparison with Sierra Nevada and Cascade Mountains

The only comparable snowpack survey was conducted over a similar range of latitude at 70 sites in the Sierra Nevada and Cascade Mountains (SN/CM) in 1983

(Laird et al., 1986). Although the temporal difference in surveys makes comparison difficult, some major differences are apparent (Table 2). Concentrations of Cl^- are much higher in the SN/CM (mean = 6.3 $\mu\text{eq/l}$) than in any of the Rocky Mountain subregions (max = 3.1 $\mu\text{eq/l}$). Closer proximity to the Pacific Ocean likely accounts for this difference. In contrast, SO_4^{2-} concentrations are much lower in the SN/CM (mean = 3.0 $\mu\text{eq/l}$) than in any of the Rocky Mountain subregions (mean = 6.3 $\mu\text{eq/l}$) except the NRMS, where maximum

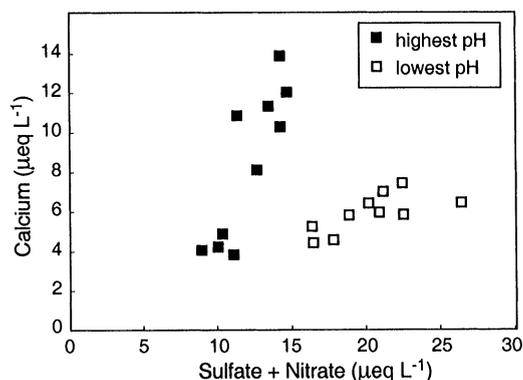


Fig. 4. Calcium as a function of sulfate plus nitrate for sites having lowest and highest pH.

values equal those in the SN/CM. Mean concentrations of NO_3^- are much lower in the SN/CM (1.8 $\mu\text{eq/l}$), but maximum concentrations in the SN/CM (8.6 $\mu\text{eq/l}$) slightly exceed maximum concentrations in the NRMS (6.2 $\mu\text{eq/l}$). Differences in concentration of SO_4^{2-} and NO_3^- may be caused by the cumulative effect of emissions sources between the two areas and higher water content of the SN/CM snowpack. Mean concentrations of Ca^{+2} in the SN/CM (2.0 $\mu\text{eq/l}$) approximate mean concentrations in the NRMS (2.2 $\mu\text{eq/l}$), are about one-half those in the CRMS (3.6 $\mu\text{eq/l}$), and are much less than in the SRMS (7.9 $\mu\text{eq/l}$). Wind erosion of soil upwind (west) of the Rocky Mountains is discussed in detail later and probably accounts for differences in concentrations of Ca^{2+} . Mean concentrations of H^+ (3.0 $\mu\text{eq/l}$) were less than in any Rocky Mountain subregion (4.4–7.1 $\mu\text{eq/l}$), but maximum concentrations (8.0 $\mu\text{eq/l}$) about equaled maximum concentrations in the NRMS (7.3 $\mu\text{eq/l}$) and the CRMS (7.2 $\mu\text{eq/l}$). Mean (7.1 $\mu\text{eq/l}$) and maximum (14.6 $\mu\text{eq/l}$) concentrations of H^+ in the SRMS greatly exceeded those of the SN/CM. These differences are discussed in detail later.

3.5. Comparison with National Atmospheric Deposition Program

The NADP/NTN operates the National Trends Network that measures wetfall at 220 sites nationwide.

Table 2

Maximum, minimum, and mean values of selected ions in the Northern (NRMS), Central (CRMS), Southern (SRMS), and all Rocky Mountain snowpack sites and in the Sierra Nevada and Cascade Mountains. Data for Rocky Mountain sites are average of 5 yr (1993–97). Data for Sierra Nevada/Cascade sites are for 1983 (Laird et al., 1986)

		NRMS ($n = 7$)	CRMS ($n = 16$)	SRMS ($n = 29$)	All sites ($n = 52$)	Sierra–Cascade
H^+	Max	7.3	7.2	14.6	14.6	8.0
	Min	4.1	2.0	2.7	2.0	0.5
	Mean	5.5	4.4	7.1	6.0	3.0
Ca^{2+}	Max	4.4	10.3	13.9	13.9	8.0
	Min	0.9	1.7	3.5	0.9	0.25
	Mean	2.2	3.6	7.9	5.8	2.0
NH_4^+	Max	5.6	13.3	5.6	13.3	12.8
	Min	1.4	2.6	2.3	1.4	0.2
	Mean	3.4	4.6	3.9	4.0	5.7
SO_4^{2-}	Max	6.6	9.4	11.5	11.5	6.6
	Min	2.5	2.8	4.6	2.5	0.8
	Mean	4.1	4.9	7.7	6.3	3.0
NO_3^-	Max	6.2	10.3	15.1	15.1	8.6
	Min	2.3	3.3	6.1	2.3	0.1
	Mean	4.5	5.7	9.6	7.7	1.8
Cl^-	Max	1.1	3.1	2.2	3.1	29.0
	Min	0.7	0.7	0.7	0.7	0.3
	Mean	0.9	1.3	1.2	1.2	6.3

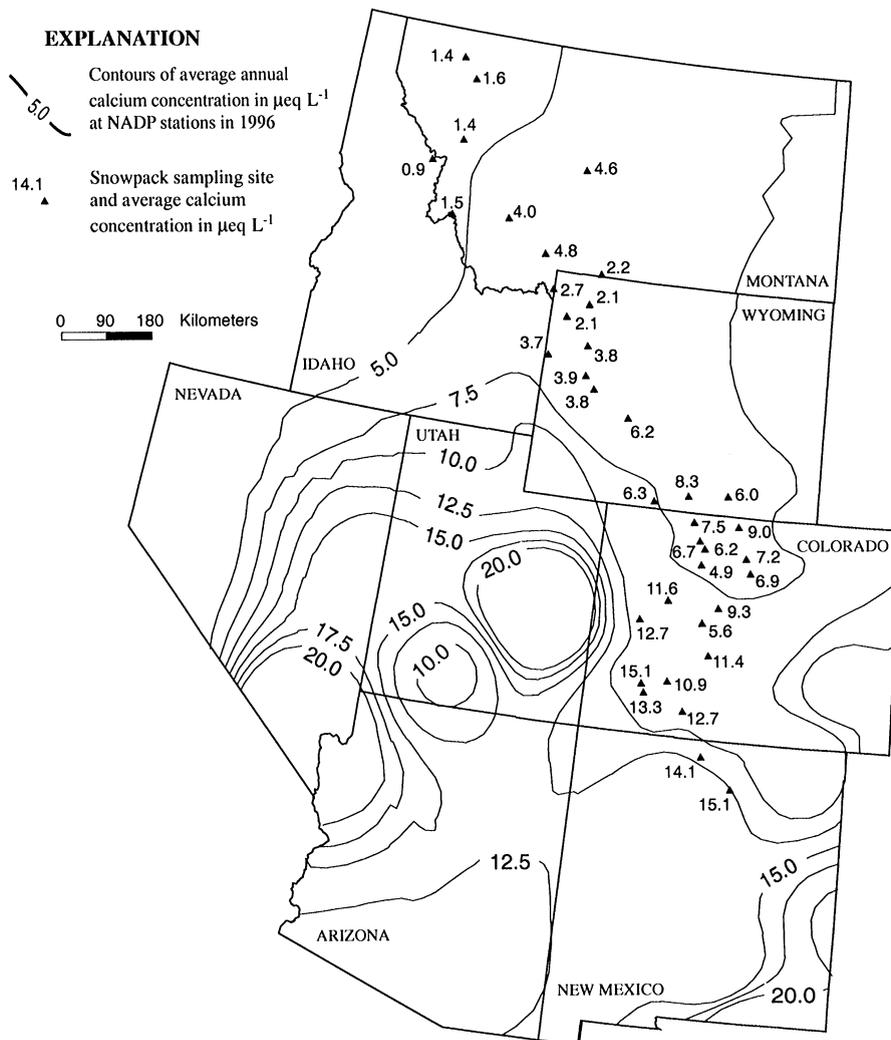


Fig. 5. Contours of volume-weighted mean calcium concentrations for 1996 at NADP/NTN stations in the western US, and average calcium concentrations at selected sites in the Rocky Mountain snowpack network from 1993 to 1997.

To determine whether the data reported in this study are equivalent to the NADP/NTN data, it is useful to look at comparisons of data at regional scale and at the site level. The NADP/NTN data also allow some conclusions to be drawn about possible source areas for some of the spatial patterns observed in this study. Regional-scale comparisons may best be made by comparing data in this study (1993–97) with contour maps prepared with NADP/NTN data for 1996 (NADP, 1997) because site density in the NADP/NTN network is very sparse in Montana and Wyoming. Space does not allow sufficient figures to compare all constituents, but Ca^{2+} is especially useful because it illustrates the complementary nature of the two data sets. Even though Ca^{2+} tends to be associated with relatively large dust particles that are preferentially removed by orographic effects, the spatial

trends and absolute concentrations are similar in both data sets (Fig. 5). Additionally, the NADP/NTN data indicate that source areas for increased concentration of Ca^{2+} in the SRMS are nearby, lower elevation areas centered in Utah.

Site-level comparisons may be made using data in Table 3, which presents analytical differences of 49 individual (not averaged) snowpack samples at 10 sites with nearby (generally less than 2 km) NADP/NTN sites (October–March data). If dryfall is significant during periods between storms, snowpack concentrations should be higher than NADP/NTN concentrations, which represent wetfall only. The data indicate that NADP/NTN concentrations of acid solutes in wetfall collected during the period of snowpack accumulation were very similar to concentrations in the snowpack.

Table 3

Mean and median differences in percent between NADP/NTN samples (October–March volume-weighted mean) and non-averaged snowpack samples from this study. Negative numbers indicate concentration in snowpack is higher than in NADP/NTN sample. Difference = $100 * (\text{NADP/NTN-snowpack}) / \text{NADP/NTN}$

	Mean difference in % ($n = 49$)	Median difference in % ($n = 49$)
H ⁺	7	12
Ca ²⁺	– 45	– 46
Mg ²⁺	– 74	– 55
Na ⁺	35	40
K ⁺	– 350	– 100
NH ₄ ⁺	– 16	– 6
SO ₄ ²⁻	– 2	– 1
NO ₃ ⁻	– 6	– 2
Cl ⁻	33	41

This agrees with results from a study of high-elevation lakes throughout the Rocky Mountains by Turk and Spahr (1991), who concluded dryfall of sulfate could not be large relative to wetfall. This comparison also suggests that sublimation of the snowpack is no more than a small percentage during the period before maximum accumulation; however, sublimation likely would be much greater as the snowpack warms and liquid water is present.

Differences are much greater for soil solutes, which indicates that dryfall of soil-derived dust is only slightly less than wetfall deposition of soil solutes. Differences are greatest for K⁺, which suggests that some source in addition to dryfall of soil solutes likely is important. K⁺ likely is added to the snowpack both as dryfall dust and in organic detritus from plant tissue, which commonly blow onto the snowpack. Regressions of K⁺ with dissolved organic carbon have Pearson's correlation coefficients from 0.36 to 0.88 for data from individual years ($n = 52$) and 0.74 for the data averaged over all 5 yr ($n = 52$). All regressions are significant at the $p = 0.01$ level.

Data from two replicate snowpits located about 5 m apart at Rabbit Ears Pass were collected each year. The agreement between each year's replicates, expressed as % relative standard deviation (RSD) and averaged over the 5 yr, varied among solute classes. The %RSD for solutes was: soil—Ca²⁺ (21), Mg²⁺ (30), and K⁺ (65); acid—H⁺ (13), SO₄²⁻ (4), and NO₃⁻ (8); and salt—Na⁺ (45), Cl⁻ (16), and NH₄⁺ (4). The acid solutes, probably transported as submicron particles, are much more consistent between replicate snowpits than are coarser particles of soil and salt. It is likely that these coarser particles, when deposited as dryfall onto crusted snow, are readily redistributed by winds between snowfall events. These differences among solute classes indicate that it is important to use data averaged over

several years and among geographically grouped sites to obtain the best estimate of solute concentration, especially for the soil and salt solutes. The benefits of such averages to estimating the central tendency of the data can be seen in Fig. 2.

The comparisons in the three previous paragraphs provide information on the nature of dryfall in the Rocky Mountains. Because the dryfall consists of soil components, for example Ca²⁺ but not SO₄²⁻, it follows that gypsum from soils cannot be a major contributor to dryfall deposition of SO₄²⁻. Because soil particles are readily removed from the atmosphere during wetfall and because these particles seem to contain negligible SO₄²⁻, gypsum from soils cannot be a major contributor to wetfall deposition of SO₄²⁻. This confirms findings that soil likely is not a source of atmospheric sulfate, based on stable sulfur isotopes (Schlesinger and Peterjohn, 1988; Mast et al., 2001).

NADP/NTN concentrations of Na⁺ and Cl⁻ are about a one-third higher than are snowpack concentrations, but there are no mechanisms by which these solutes could be removed from the snowpack without removing other solutes. Thus, there may be a source of bias in Na⁺ and Cl⁻ in one of the data sets.

The only other solute concentration that is higher in the NADP samples than in snowpack samples is H⁺. If the difference is real, it likely results from a slight neutralization of H⁺ in the snowpack samples by dryfall dust. This neutralization could occur between the time the samples are thawed and filtered for further processing.

NADP/NTN sites are useful for measuring chemistry of atmospheric deposition throughout the year and for providing a consistent collection method that allows comparison with sites not suitable for snowpack sampling. Snowpack sampling is useful in areas where the NADP/NTN sampling method does not operate well in winter and where wintertime access is difficult. Snowpack sampling can accurately represent the chemistry of one-half or more of the annual atmospheric deposition while requiring only a single sample annually and little capital investment in instrumentation and site improvement. Also, snowpack sampling is more easily adapted to differing requirements of exotic solutes and to needs for changing site density to represent areas of current interest.

4. Conclusions

A network of 52 sites operated for 5 yr throughout the US Rocky Mountains provides an opportunity to determine subregional differences in snowpack chemistry and how the balance among solute components (acid, soil, and salt) change to produce very large or low concentrations of acid. Both the highest and some of the

lowest concentrations of H^+ occur in the southern Rocky Mountains. The sites with the lowest concentration of H^+ may have high or low concentrations of the major soil component Ca^{2+} , but have only low or average concentrations of the major acid components NO_3^- and SO_4^{2-} . In contrast, the sites with the highest concentrations of H^+ almost always have high concentrations of NO_3^- and SO_4^{2-} and average or low concentrations of Ca^{2+} . The organic anions formate and acetate are present, but at much lower concentrations than NO_3^- and SO_4^{2-} .

Although studies of similar scale are scarce, comparison with a 1983 survey of snowpack in the Sierra Nevada and the Cascade Mountains indicates that the Rocky Mountain snowpack is much more acidic. The Rocky Mountain snowpack contains much higher concentrations of Ca^{2+} , NO_3^- , and SO_4^{2-} but much lower concentrations of Cl^- .

Concentrations of acid solutes in the snowpack are similar to concentrations in nearby NADP/NTN wetfall collectors. Thus, dryfall of acid solutes during the snow season is negligible. In contrast, dryfall of soil solutes seems to be only slightly less than wetfall deposition. K^+ may be contributed to snowpack from organic detritus such as pine needles.

Snowpack sampling offers a cost-effective complement to sampling of wetfall in areas where wetfall is difficult to sample and where snowpack accumulates throughout the winter. The two types of sampling are complementary and need to be used interchangeably as climatic conditions vary geographically.

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