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# Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: implications for winter dry deposition

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## Abstract

Depth-integrated snowpack chemistry was measured just prior to maximum snowpack depth during the winters of 1992–1999 at 12 sites co-located with National Atmospheric Deposition Program/National Trend Network (NADP/NTN) sites in the central and southern Rocky Mountains, USA. Winter volume-weighted mean wet-deposition concentrations were calculated for the NADP/NTN sites, and the data were compared to snowpack concentrations using the paired *t*-test and the Wilcoxon signed-rank test. No statistically significant differences were indicated in concentrations of  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$  ( $p > 0.1$ ). Small, but statistically significant differences ( $p \leq 0.03$ ) were indicated for all other solutes analyzed. Differences were largest for  $\text{Ca}^{2+}$  concentrations, which on average were  $2.3 \mu\text{eq l}^{-1}$  (43%) higher in the snowpack than in winter NADP/NTN samples. Eolian carbonate dust appeared to influence snowpack chemistry through both wet and dry deposition, and the effect increased from north to south. Dry deposition of eolian carbonates was estimated to have neutralized an average of  $6.9 \mu\text{eq l}^{-1}$  and a maximum of  $12 \mu\text{eq l}^{-1}$  of snowpack acidity at the southernmost sites. The good agreement between snowpack and winter NADP/NTN  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations indicates that for those solutes the two data sets can be combined to increase data density in high-elevation areas, where few NADP/NTN sites exist. This combination of data sets will allow for better estimates of atmospheric deposition of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  across the Rocky Mountain region. Published by Elsevier Science Ltd.

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## 1. Introduction

Alpine/subalpine ecosystems are an important natural resource in the Rocky Mountain region. Several large river systems, including the Colorado, Missouri, and Rio Grande Rivers, originate in the Rocky Mountains along the continental divide. Winter precipitation that is stored in seasonal snowpacks is transported downstream by these river systems and is used for agriculture, industry, and recreation by millions of people in the

Rockies and surrounding states. Changes in precipitation chemistry or amount could adversely affect high-elevation ecosystems by modifying their extent and ecological diversity and could impact downstream ecosystems as well. Thus, the health of high-elevation ecosystems is of vital concern for resource managers in the Rocky Mountains.

Aquatic resources in alpine/subalpine ecosystems are considered highly sensitive to atmospherically deposited pollutants (Williams et al., 1996; Baron et al., 2000; Campbell et al., 2000). This sensitivity stems from the abundance of talus and exposed bedrock and the lack of well-developed soils in the alpine/subalpine zone

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(Clow and Sueker, 2000). High-elevation lakes and streams are particularly vulnerable during snowmelt, when large amounts of water and solutes are released from melting snowpacks in a short amount of time. If pollutants exist in the snowpack, they tend to move directly into lakes and streams because of minimal interaction with geologic materials.

Reliable estimates of atmospheric deposition are critical inputs to models used for predicting ecosystem sensitivity to atmospherically deposited pollutants. However, measuring atmospheric deposition at high elevations is extremely difficult and has been done at only a few intensively studied sites. High-elevation areas in the Rocky Mountains typically are remote and difficult to access, especially during the winter, when most deposition occurs. Atmospheric deposition inputs are measured in the United States as part of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), in which wet-deposition chemistry and amount are measured weekly at 220 sites nationally. Thirty NADP/NTN sites are in the Rocky Mountains, but few are located at high elevations (>2400 m) because they are logistically difficult to maintain (Turk et al., 2001). Of the NADP/NTN sites currently operating in the Rocky Mountains, 15 are at elevations >2400 m, and eight are at elevations >3000 m.

Because of the paucity of NADP/NTN sites at high elevations, few atmospheric deposition data are available for those areas. To address this problem, a snowpack sampling network was initiated in the early 1990s by the US Geological Survey (USGS), in cooperation with other Federal, State, and local agencies. The goal of the network is to complement the NADP/NTN and fill the gap in information on atmospheric deposition at high elevations. Snowpack sampling is logistically easier than maintaining an NADP/NTN site because sampling occurs only once per year, just prior to the time of maximum snowpack depth. Because 60–80% of annual precipitation at high elevations falls as snow, snowpack sampling can provide a cost-effective means of measuring the chemistry of a large fraction of annual deposition (Turk et al., 2001).

It is important to establish the comparability of data collected through snowpack sampling and through the NADP/NTN. Snowpack samples provide a measure of bulk atmospheric deposition in the winter, incorporating both wet and dry deposition, but NADP/NTN samplers collect only wet deposition. Thus, the potential for differences in chemistry due to differences in sampling methodology exists. If it can be demonstrated that there are no significant differences in the data sets, then they could be combined to achieve better data coverage for high-elevation areas than can be achieved through the NADP/NTN alone. Combining data sets would substantially improve the resolution of maps of atmospheric

deposition in the Rocky Mountains, and permit more accurate modelling of processes in alpine/subalpine ecosystems.

Although several comparisons of bulk versus wet deposition at low-elevation (rainfall-dominated) sites have been reported (Stedman et al., 1990; Lee and Longhurst, 1992), direct comparisons for high-elevation (snowfall-dominated) sites are rare. Heuer et al. (2000) compared snowpack and winter wet-deposition concentrations of nitrate, ammonium, and sulfate at seven NADP/NTN sites in Colorado during 1993–1997, and noted no significant differences. Concentrations of other constituents were not compared. Turk et al. (2001) compared snowpack and winter wet-deposition concentrations of major dissolved anions and cations at 10 sites in the Rocky Mountains during 1993–1997. They found that concentrations of nitrate and sulfate were similar between data sets, and that base cations were generally higher in the snowpack than in wet deposition (Turk et al., 2001).

The present study expands upon the analyses of Heuer et al. (2000) and Turk et al. (2001) by considering additional years and sites and by evaluating relations between snowpack and winter wet deposition chemistry in more detail. Concentrations of calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), chloride ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), hydrogen ( $\text{H}^+$ ), and specific conductance (SC) were compared in snowpack and winter wet-deposition samples collected during 1992–1999 at 12 high-elevation (>2400 m) sites in the Rocky Mountains, USA. Spatial patterns in differences are discussed and possible reasons for differences in chemistry are evaluated, with emphasis on an assessment of dry deposition to the snowpack. Analytical uncertainty is considered as a possible explanation for differences in reported concentrations. The ability to predict mean annual precipitation chemistry from winter measurements is evaluated.

## 2. Methods

### 2.1. Sample collection and analysis

The snowpack sampling network consists of a core of 52 high-elevation sites near the continental divide in Montana, Wyoming, Colorado, and New Mexico (Mast et al., 2001; Turk et al., 2001). Additional sites have been sampled in some years to provide increased resolution of deposition patterns and to address local concerns on atmospheric deposition. The focus of this paper is on 12 snowpack sampling sites that are co-located with high-elevation NADP/NTN sites. Elevations of the paired sampling sites range from 2400 to 3500 m. Mean daily temperatures at the sites are below freezing throughout

the winter, and mid-winter melting of the snowpack is rare.

Snowpacks were sampled just prior to the time of maximum snowpack depth, before any melting of the snow had occurred. All equipment used for sample collection and processing was cleaned in the laboratory by soaking and rinsing the equipment in 18 M $\Omega$  deionized, distilled water. Sampling personnel wore powderless vinyl gloves and non-fibrous clothing. A snow pit was dug to the ground, and a vertical column of snow was removed and placed in a Teflon bag using a plastic shovel and scoop. The top 5 cm and bottom 10 cm of snow were excluded to prevent contamination by soil or other debris. Snowpack temperature was measured in 10-cm increments to verify that the snowpack was below freezing. Samples were double bagged, transported in coolers packed with dry ice, and stored at  $-20^{\circ}\text{C}$  until they were processed. Processing involved melting the samples in the Teflon bags in which they were collected, and immediately filtering the samples through 0.45- $\mu\text{m}$  polycarbonate filters (Ingersoll, 1995).

Snowpack samples were analyzed using standard protocols designed for low-ionic strength water (Fishman, 1993) in a research laboratory operated by the USGS. Specific conductance and pH were measured on unfiltered aliquots.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^{+}$  were measured on acidified, filtered aliquots by inductively coupled plasma atomic-emission spectroscopy and  $\text{K}^{+}$  was measured on acidified, filtered aliquots by atomic absorption spectroscopy.  $\text{Cl}^{-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^{-}$  were measured on filtered aliquots by ion chromatography.  $\text{NH}_4^{+}$  was determined on a filtered aliquot by air-segmented, continuous-flow colorimetry.  $\text{H}^{+}$  was measured using an electrode designed for low-ionic strength water. SC was measured by Wheatstone bridge.  $\text{HCO}_3^{-}$  was measured by Gran titration (Gran, 1952). Quality-assurance procedures included collection and analysis of field and processing blanks and incorporation of internal and external reference standards within each analytical run. Approximately 20–40% of each analytical run was devoted to QA samples.

Weekly wet-deposition samples were collected as part of the NADP/NTN using standard protocols outlined in Peden (1986) and See et al. (1990). The NADP/NTN uses automatic samplers that open during precipitation events. Samplers are covered between precipitation events to prevent contamination and evaporation. Sample processing, analytical methods, and quality-assurance procedures also are described in Peden (1986) and See et al. (1990).

Although snowpack and NADP/NTN samples are analyzed in different laboratories, the methods used for sample processing and analysis were similar and have been consistent throughout the period of study. One exception involved a change in NADP/NTN shipping

containers in 1994. This change in protocol eliminated minor  $\text{Mg}^{2+}$  contamination from o-rings used in the lids of pre-1994 containers (Gordon, 1999). Another change in NADP/NTN protocol occurred in late 1997, when the types of filters used were switched from cellulose ester membrane to polysulfone. The cellulose ester membrane filters had been found to cause minor  $\text{Na}^{+}$  contamination, especially in low-volume samples due to lack of sample available for filter rinsing (Gordon, 1999).

## 2.2. Data analysis

Concentration data from the snowpack network were screened using two criteria: (1) ion imbalances  $> \pm 20\%$ , calculated as the total cationic charge minus the total anionic charge divided by the total charge in solution; and (2) identification of extreme outliers in a matrix of solute–solute plots. Solute–solute plots show individual solutes plotted against every other solute in separate frames. For samples where ion imbalances exceeded  $\pm 20\%$ , the solute–solute plots usually were helpful in identifying which solutes appeared to be in error, and analytical results for those solutes were excluded from the data set.

Monthly volume-weighted mean (VWM) concentrations in precipitation from the NADP/NTN for November–March were screened using the same criteria. November–March was used because that period approximates the snowpack accumulation period at the sampling sites. Less than 2% of the results were excluded from the data sets for either network.

Winter VWM concentrations were calculated for the NADP/NTN sites by multiplying monthly VWM concentrations by monthly precipitation amounts, summing the values for the 5 months, and then dividing by the total precipitation amount during the period. The winter VWM concentration at each NADP/NTN site was matched with a corresponding snowpack concentration for that site and year, yielding a data pair for each site and year. After data screening, 80 pairs of data were available for the statistical analysis.

Differences in concentrations between paired samples were tested using the paired *t*-test and the Wilcoxon signed-rank test (Helsel and Hirsch, 1992). The paired *t*-test is a parametric test, which requires that differences between the data sets be normally distributed. Frequency distribution plots of the differences indicated that the assumption of normality was not always justified. The non-parametric Wilcoxon signed-rank test was used because it does not require normally distributed data and is only slightly less powerful (Helsel and Hirsch, 1992). Results are presented for both tests.

The possibility that differences between snowpack and NADP/NTN concentrations were artifacts caused by differences in analytical bias was evaluated based on laboratory results on blind-audit performance tests

conducted by the National Laboratory for Environmental Testing, National Water Research Institute, Environment Canada (Blum and Alkema, 2000). This blind-audit program was designed for evaluation of laboratory performance on low-ionic strength waters, and consists of 10 natural audit samples during each round.

### 3. Results

The distribution of solute concentrations in snowpack and in winter NADP/NTN samples is shown in Fig. 1 (“samples” refers to the group of samples used to calculate winter VWM concentrations). Mean concentrations of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$  were higher in the snowpack than in the NADP/NTN samples (Fig. 1, Table 1). Mean concentrations of  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{H}^+$  were lower in the snowpack than in the NADP/NTN samples. Mean concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were similar in snowpack and NADP/NTN samples.

Statistical analyses indicated small, but statistically significant differences in snowpack and NADP/NTN paired sample concentrations for all solutes except  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (Table 1). The differences were highly

significant for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ , and  $\text{Cl}^-$  ( $p < 0.0001$ ), and moderately significant for  $\text{SC}$ ,  $\text{H}^+$ , and  $\text{Na}^+$  ( $p < 0.03$ ). For solutes where differences were statistically significant, the mean differences ranged from  $-0.6 \mu\text{eq l}^{-1}$  for  $\text{Na}^+$  to  $+2.3 \mu\text{eq l}^{-1}$  for  $\text{Ca}^{2+}$  (negative differences indicate NADP/NTN concentrations exceeded snowpack concentrations).

Snowpack concentrations are plotted against NADP/NTN concentrations for each of the data pairs in Fig. 2. Concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the snowpack tended to exceed those in the NADP/NTN samples throughout the range of concentrations encountered (Fig. 2). The mean difference for  $\text{Ca}^{2+}$  was  $2.3 \mu\text{eq l}^{-1}$ , and the mean difference for  $\text{Mg}^{2+}$  was  $0.5 \mu\text{eq l}^{-1}$  (Table 1). Although the differences were small when expressed as concentrations, they were fairly large when expressed as a percentage; mean concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the snowpack were 43% and 53% higher than in the NADP/NTN samples (Table 1). In some cases,  $\text{Ca}^{2+}$  in the snowpack exceeded  $\text{Ca}^{2+}$  in paired NADP/NTN samples by more than  $25 \mu\text{eq l}^{-1}$  (Fig. 2). The most likely explanation for the excess of  $\text{Ca}^{2+}$  in the snowpack compared to that in the NADP/NTN samples is that the snowpack incorporated eolian carbonates through dry deposition processes, as discussed in more

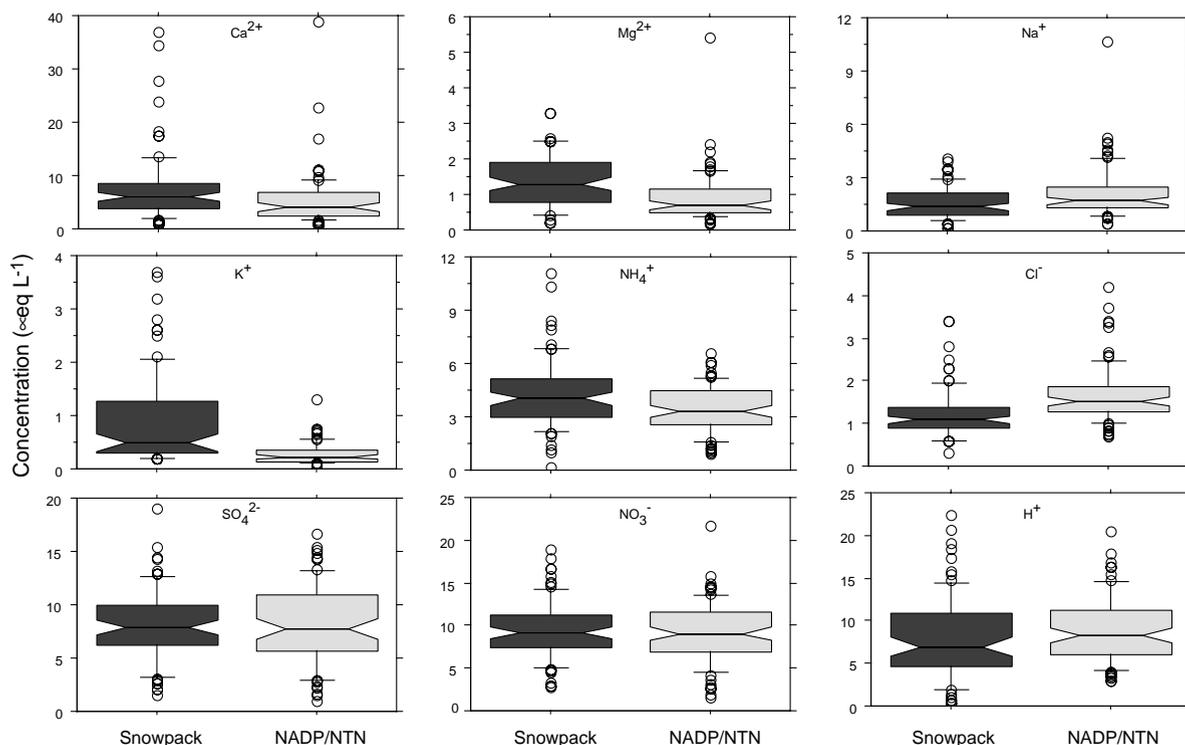


Fig. 1. Distribution of solute concentrations in the snowpack and in winter VWM wet deposition (NADP/NTN), 1992–1999. Upper and lower bounds of boxes indicate interquartile range, waist indicates median, whiskers indicate 5th and 95th percentiles, and circles indicate outliers.

Table 1  
Results of statistical comparisons between paired snowpack and winter NADP/NTN samples

Constituent	<i>p</i> -values		Concentration ( $\mu\text{eq l}^{-1}$ )			
	Paired <i>t</i> -test	Wilcoxon signed-rank test	Mean snowpack	Mean NADP/NTN	Mean difference	Percent difference
Ca <sup>2+</sup>	<0.0001	<0.0001	7.6	5.3	2.3	43
Mg <sup>2+</sup>	<0.0001	<0.0001	1.4	0.9	0.5	53
Na <sup>+</sup>	0.0006	0.0003	1.6	2.2	−0.6	−29
K <sup>+</sup>	<0.0001	<0.0001	0.9	0.3	0.6	206
NH <sub>4</sub> <sup>+</sup>	<0.0001	<0.0001	4.3	3.5	0.8	25
Cl <sup>−</sup>	<0.0001	<0.0001	1.2	1.7	−0.4	−26
SO <sub>4</sub> <sup>2−</sup>	0.7924	0.8221	8.1	8.2	n.s.	−1
NO <sub>3</sub> <sup>−</sup>	0.2537	0.1970	9.6	9.3	n.s.	4
H <sup>+</sup>	0.0201	0.0298	7.8	8.9	−1.1	−12
SC	0.0019	0.0033	5.5	6.0	−0.5	−8

n.s. indicates no significant difference.

detail in Section 4. For samples with Ca<sup>2+</sup> concentrations  $>10\mu\text{eq l}^{-1}$ , there was a strong positive correlation with HCO<sub>3</sub><sup>−</sup> concentrations ( $r^2 = 0.84$ ,  $p < 0.01$ ).

Concentrations of Na<sup>+</sup> and Cl<sup>−</sup> averaged 29% and 26% less in the snowpack than in the NADP/NTN samples (Table 1), and the magnitudes of the mean differences in Na<sup>+</sup> and Cl<sup>−</sup> were comparable (−0.6 and −0.4  $\mu\text{eq l}^{-1}$  for Na<sup>+</sup> and Cl<sup>−</sup>, respectively; Fig. 1 and Table 1). The similarity of the Na<sup>+</sup> and Cl<sup>−</sup> differences suggests a similar cause. Turk et al. (2001) and Hooper and Peters (1989) identified salt-associated solutes (Na<sup>+</sup>, Cl<sup>−</sup>, and NH<sub>4</sub><sup>+</sup>) as one of three important components affecting precipitation chemistry in the United States. The other two components included acid- (H<sup>+</sup>, SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>) and soil-associated solutes (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>). Data from the present study suggest that the salt component might be slightly more important in NADP/NTN samples than in snowpack samples. Contamination of NADP/NTN samples from the cellulose ester membrane filters used prior to 1998 may have contributed to the difference in Na concentrations between paired snowpack and NADP/NTN samples (Gordon, 1999).

Fig. 1 shows that the mean and the range of K<sup>+</sup> concentrations were significantly greater in the snowpack than in the NADP/NTN samples. The differences were greatest for data pairs in which K<sup>+</sup> concentrations in the snowpack exceed 1  $\mu\text{eq l}^{-1}$  (Fig. 2). The pattern in the K<sup>+</sup> scatter plot is indicative of an additional source for K<sup>+</sup> in the snowpack. Turk et al. (2001) noted a correlation between K<sup>+</sup> and dissolved organic carbon in snowpack samples collected at the 52 core snowpack network sites during 1993–1997 ( $r^2 = 0.37$ ). These results are consistent with dry deposition of organic

matter, such as pine needles or pollen, to the snowpack (Turk et al., 2001). The amount of particulate organic matter incorporated into the snowpack would be expected to vary according to site characteristics (forested versus alpine), as well as the strength and prevailing direction of winter winds. This may partly explain the scatter in snowpack K<sup>+</sup> concentrations.

Concentrations of NH<sub>4</sub><sup>+</sup> also tended to be higher in the snowpack than in the NADP/NTN samples (Fig. 2), with the greatest deviations occurring at the highest concentrations. Again, the mean difference was small (0.8  $\mu\text{eq l}^{-1}$ ), but the maximum difference was about 8  $\mu\text{eq l}^{-1}$  (Table 1, Fig. 2). The average difference was about 25%. Higher NH<sub>4</sub><sup>+</sup> concentrations in the snowpack probably is due to loss of NH<sub>4</sub><sup>+</sup> in the NADP/NTN samples due to biological uptake after melting (i.e., during transport and storage prior to analysis).

Concentrations of SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup> in the snowpack were in close agreement with those in the NADP/NTN samples (Fig. 2). Statistical tests indicate no significant differences in concentrations ( $p > 0.1$ ; Table 1). Linear regressions of snowpack against NADP/NTN concentrations for SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup> indicated strong correlations ( $r^2 \geq 0.6$ ), and the slopes of the regression equations were close to one. These results indicate that snowpack measurements of SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup> provide data that are comparable to data from the NADP/NTN. The data also indicate that dry deposition of SO<sub>4</sub><sup>2−</sup> and NO<sub>3</sub><sup>−</sup> to the snowpack does not have a substantial effect on snowpack chemistry.

The mean H<sup>+</sup> concentration in the snowpack was lower than that in the NADP/NTN samples (7.8 versus 8.9  $\mu\text{eq l}^{-1}$ ; Table 1), but the most noticeable differences

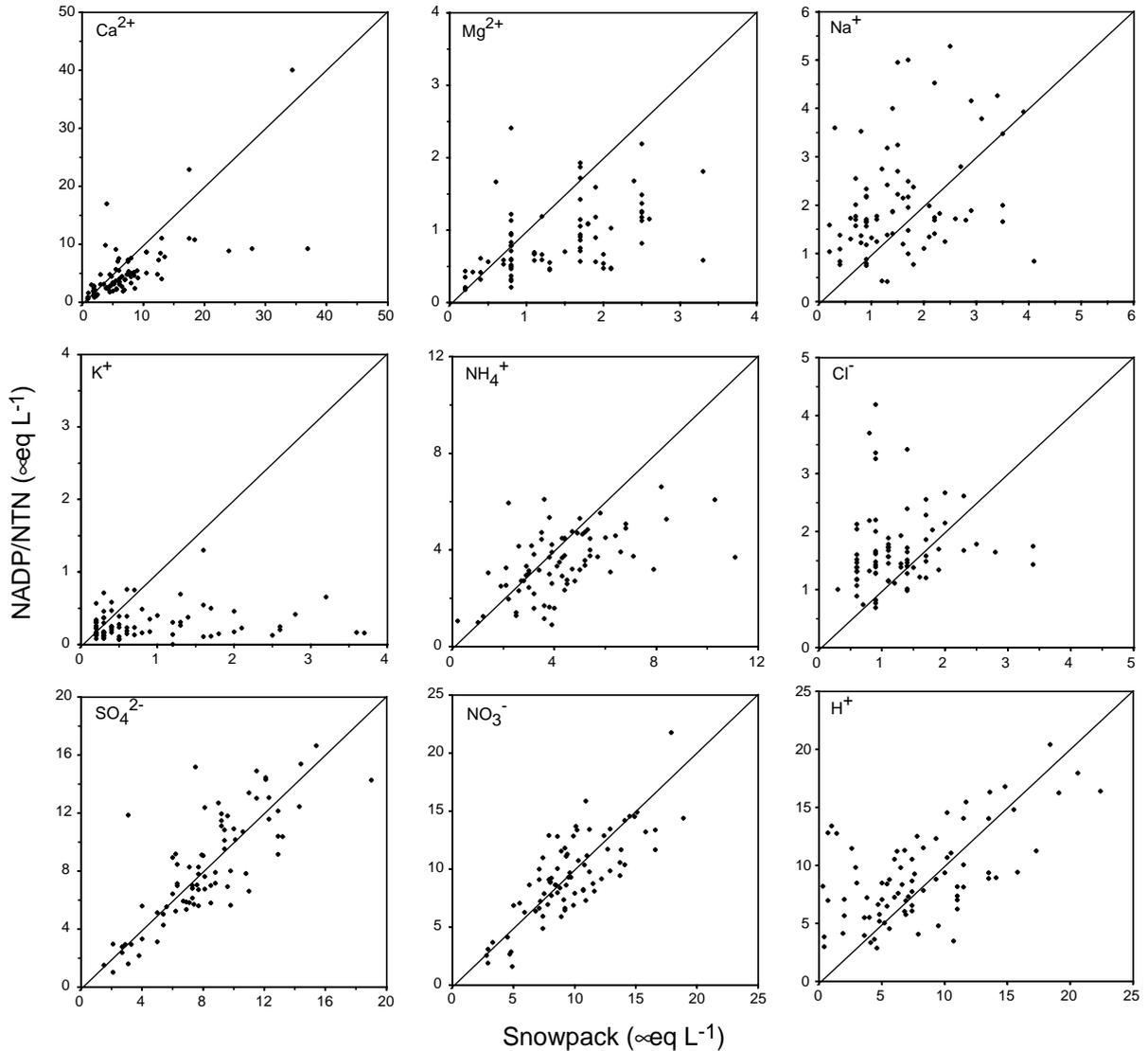


Fig. 2. Solute concentrations in paired snowpack and NADP/NTN (winter volume-weighted mean) samples, 1992–1999.

occurred in a group of samples having low snowpack  $H^+$  concentrations (Fig. 2); for this group of samples,  $H^+$  in the NADP/NTN samples exceeded that in the snowpack by as much as  $12 \mu\text{eq l}^{-1}$ . The samples that had the largest  $H^+$  deficit (snowpack  $<$  NADP/NTN) tended to be those with the largest excess of  $Ca^{2+}$  (snowpack  $>$  NADP/NTN).

Results of the blind-audit performance tests indicated that both laboratories produced high-quality data, accurate to within  $\pm 8\%$  for all constituents. Regressions of concentrations reported by each of the two laboratories against the mean concentration reported by

all laboratories that participated in the blind-audit test ( $n = 34$ ) had Pearson  $r^2$  values  $\geq 0.996$  for all constituents, and slopes that ranged from 0.92 to 1.06 (Fig. 3). Slopes of the regressions for the two laboratories differed by  $< 0.02$ , except for  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $NH_4^+$  indicating that for most constituents differences in analytical bias were minor. For  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $NH_4^+$ , slopes of the regressions for the USGS research lab were higher than for the NADP/NTN lab by up to 0.09, indicating a positive bias by the USGS research lab, a negative bias by the NADP/NTN lab, or a combination of the two (Fig. 3). These results indicate

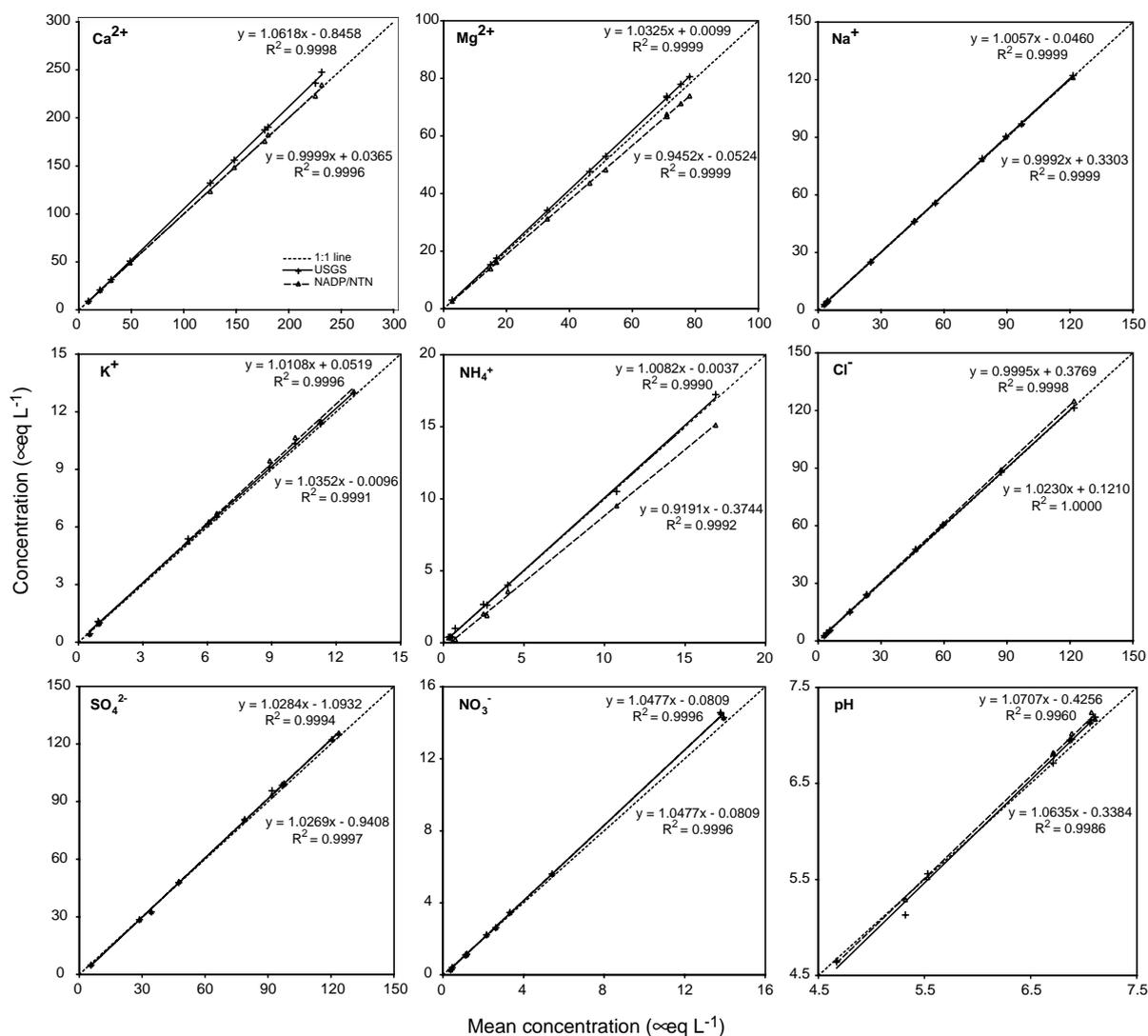


Fig. 3. Concentrations reported by laboratories that analyzed snowpack and NADP/NTN samples versus the mean of concentrations reported by participating laboratories ( $n = 34$ ) during Fall 2000 round of the Environment Canada blind-audit performance test.

that differences in analytical bias may explain up to 36% of the difference in reported concentrations in  $\text{NH}_4^+$  and up to 15% of the differences in reported concentrations in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

#### 4. Discussion

The lack of significant differences in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations between the snowpack network and the NADP/NTN indicates the data from the two networks can be combined to provide better estimates of winter atmospheric deposition of these constituents across the

Rocky Mountain region. This will be particularly helpful for filling in the data gap for high-elevation areas, where NADP/NTN sites are scarce due to the logistical difficulties of operating sites at high-elevations. The appropriateness of combining data from the two networks for other solutes will depend on the solute and on the intended application of the data. Although the differences generally were small in terms of concentration, differences for some solutes were large when expressed as a percentage. In the following discussion, reasons for the differences are explored and implications for winter dry deposition are evaluated. Understanding the reasons for the differences might help

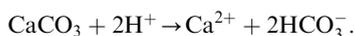
users evaluate the suitability of combining data for individual solutes.

#### 4.1. Variations according to latitude

There are regional patterns in snowpack concentrations of  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{H}^+$  that reflect variations in the strength of sources of these solutes. Concentrations of  $\text{Ca}^{2+}$  show a strong increase going from north to south, probably reflecting an increase in the influence of carbonate dust to the south. Strong acid anions also show an increasing trend from north to south, but overlaid on the regional trend is a local peak in concentrations in northern Colorado that may be related to local sources of pollution (Fig. 4, Mast et al., 2001). There is no strong north to south gradient in  $\text{H}^+$ , probably because of the offsetting regional trends in  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  (Fig. 4). However, the peak in  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  in northern Colorado is clearly reflected in a peak in  $\text{H}^+$  concentrations at the same latitude. Turk et al. (2001) found that snowpack acidity in the Rockies was strongly related to  $\text{Ca}^{2+}$  (negative relation), and  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  (positive relations). The regional patterns in  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{H}^+$  snowpack concentrations illustrate how  $\text{H}^+$  concentrations reflect a balance between contributions from carbonate dust and strong acids.

By analyzing regional patterns in differences between snowpack and NADP/NTN concentrations it is possible to separate the effects of wet and dry deposition on snowpack chemistry. Although most solutes did not show regional patterns in differences in concentrations between snowpack and NADP/NTN samples, several did. Differences in  $\text{Ca}^{2+}$  concentrations increased substantially from north to south; the average difference was  $0.4 \mu\text{eq l}^{-1}$  at the northernmost site and  $5.0 \mu\text{eq l}^{-1}$  at the southernmost site (Fig. 5).

The spatial pattern in  $\text{Ca}^{2+}$  concentration differences is consistent with an increasing influence from carbonate dust from north to south. In the mid-continent region of the United States, the dominant source of  $\text{Ca}^{2+}$  in precipitation is eolian carbonate dust (Sequeira, 1993), which is entrained in the atmosphere primarily by wind erosion associated with convective activity or the passage of weather fronts (Gillette et al., 1992). Carbonate dust is composed mostly of  $\text{CaCO}_3$ , which is soluble in rain and melting snow. As it dissolves,  $\text{Ca}^{2+}$  and  $\text{CO}_3$  are released to solution and the  $\text{CO}_3$  reacts with  $\text{H}^+$  to neutralize acidity in the snowmelt, as shown in the following reaction:



The hypothesized regional pattern in carbonate dust influence is supported by a north to south increase in  $\text{Ca}^{2+}$  concentration in both the snowpack and

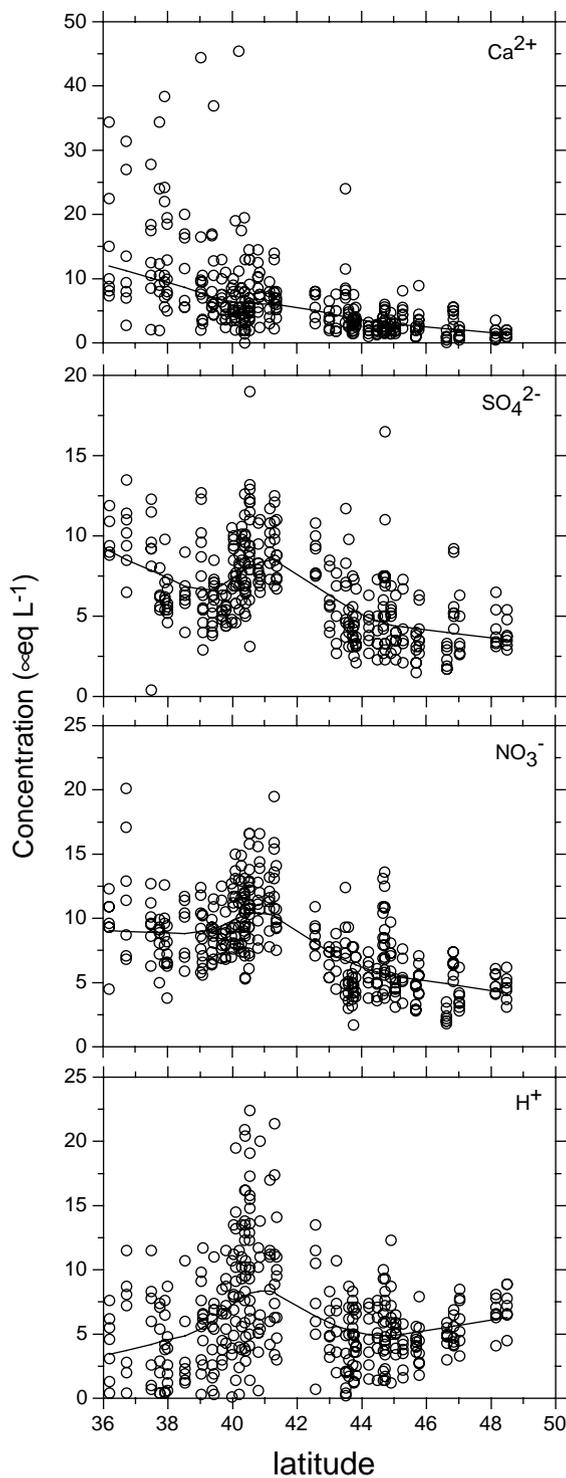


Fig. 4. Solute concentrations in snowpack at 52 core sampling sites, 1992–1999. Lowess regression line shows trends according to latitude. Plot modified from Mast et al. (2001).

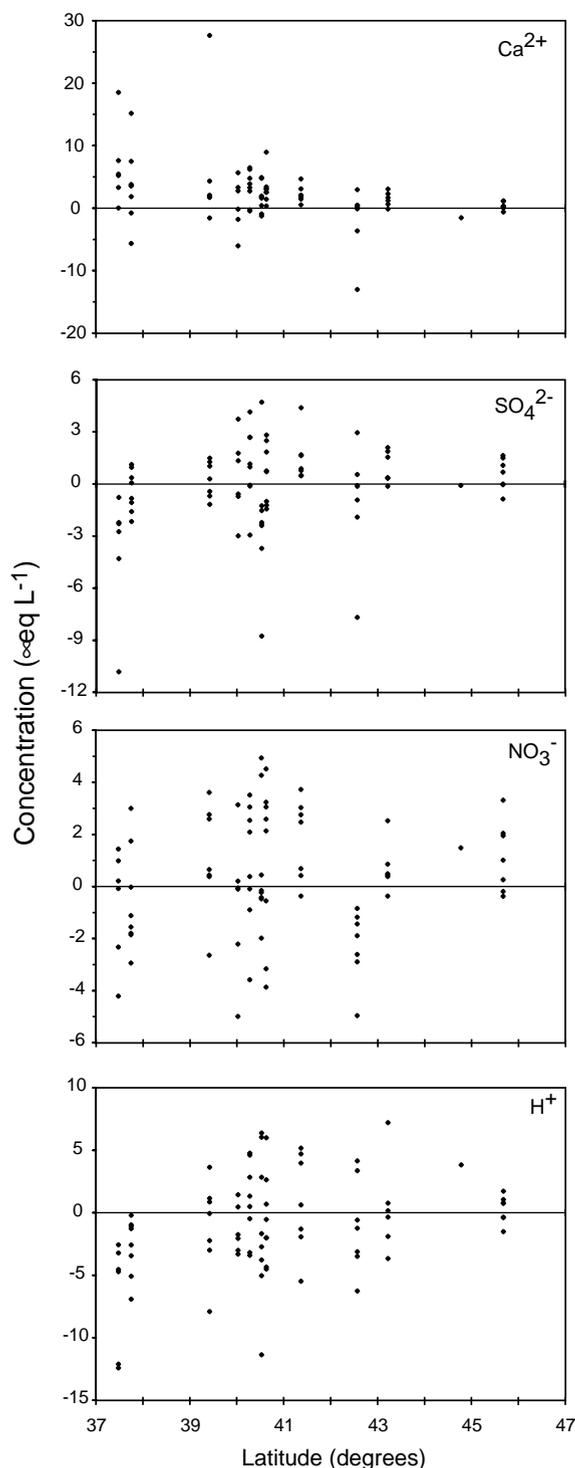


Fig. 5. Differences in solute concentration between snowpack and winter wet deposition (NADP/NTN) for individual sites and years according to latitude, 1992–1999. Positive values indicate snowpack concentrations were greater than NADP/NTN concentrations.

NADP/NTN data sets (Mast et al., 2001; Turk et al., 2001), and by direct measurements of particulate calcite in the snowpack in 1992. These measurements indicated increasing amounts of carbonate dust from north to south (Clow and Ingersoll, 1994). The north to south gradient in carbonate dust influence probably is related to the proximity of southern sites to large arid basins in the southwestern United States. Frontal storms tend to move from west to east during winter in the Rocky Mountain region, and prevailing winds transport carbonate dust eastward. Significant outcrops of limestone, which are prevalent in southwestern Colorado, may provide an additional local source of carbonate dust. Gypsum dust ( $\text{CaSO}_4$ ) does not appear to be an important contributor to snowpack chemistry based on the lack of geographic patterns in differences between snowpack and NADP/NTN  $\text{SO}_4^{2-}$  concentrations (Fig. 4, Turk et al., 2001). The strong correlation between  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations for samples with  $\text{Ca}^{2+} > 10 \mu\text{eq l}^{-1}$ , supports the hypothesis that carbonate, rather than gypsum, is the dominant source of  $\text{Ca}^{2+}$  in the snowpack.

Differences in  $\text{H}^+$  concentrations between the snowpack and NADP/NTN data sets were close to zero except in the south, where NADP/NTN concentrations exceeded snowpack concentrations by an average of  $6.9 \mu\text{eq l}^{-1}$  (Fig. 5). The spatial pattern in  $\text{H}^+$  differences, which is opposite to the spatial pattern in  $\text{Ca}^{2+}$  differences, is consistent with the hypothesized influence of dry deposition of eolian carbonates to the snowpack in the south. The magnitude of the  $\text{H}^+$  differences provides an indication of the buffering capacity added to the snowpack by dry deposition of eolian carbonates. The mean difference in  $\text{H}^+$  at the 10 northernmost sites was only  $0.2 \mu\text{eq l}^{-1}$ , and was not statistically significant ( $p > 0.5$ ). The average difference in  $\text{H}^+$  at the two southernmost sites was  $6.9 \mu\text{eq l}^{-1}$  and in several cases differences for individual years and sites reached  $12 \mu\text{eq l}^{-1}$ .

#### 4.2. Comparison of winter and annual precipitation chemistry

An important assumption in the design and operation of the snowpack monitoring network is that measurement of snowpack chemistry may permit estimation of average annual precipitation chemistry. This assumption is based on the fact that, in the Rocky Mountains, the majority of yearly precipitation falls during the winter as snow. The validity of this assumption can be evaluated by comparing winter VWM chemistry (November–March) to annual VWM chemistry at NADP/NTN sites, which operate year around. For solutes that exhibit strong relations between winter and annual precipitation chemistry, snowpack concentrations may be used to estimate annual precipitation chemistry, even

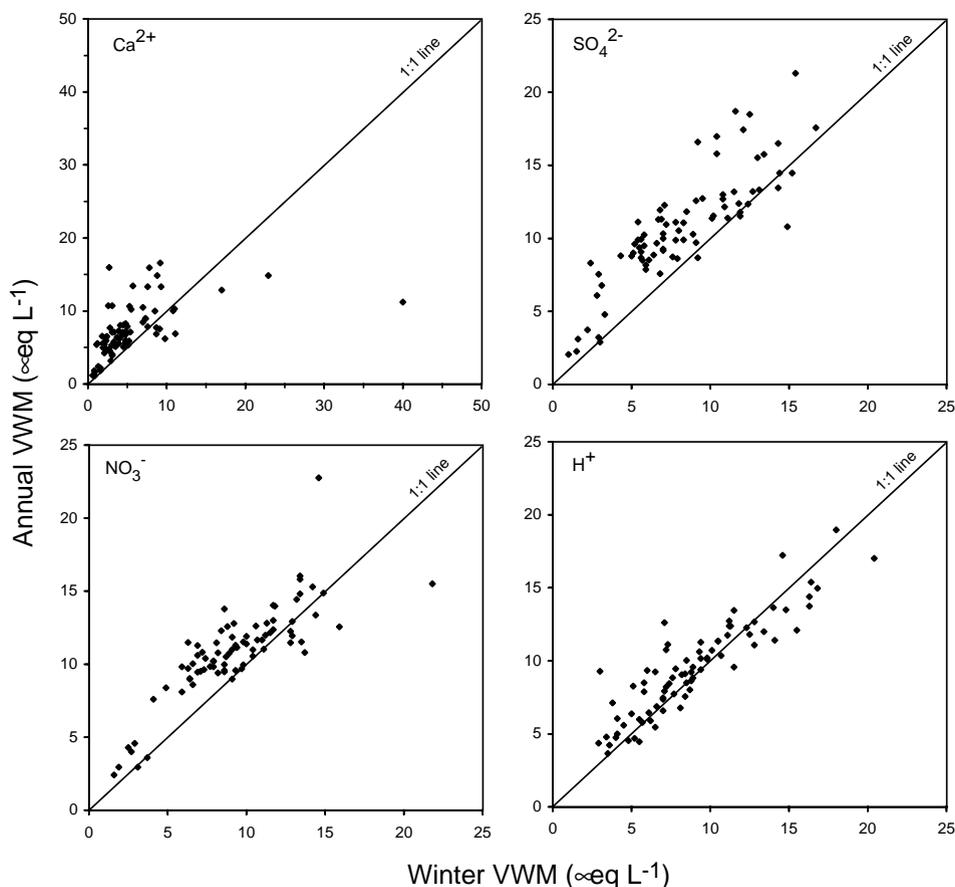


Fig. 6. Relations between annual and winter VWM concentrations at 12 high-elevation NADP/NTN sites, 1992–1999.

if the slopes of the regression equations are not equal to one. By combining chemistry data with precipitation volume information gathered through monitoring or by precipitation modelling, an estimate of annual deposition may be obtained. This information is needed for models used to predict ecosystem sensitivity to atmospheric deposition. Such information is particularly important for improving estimates of deposition to high-elevation (> 2400 m) ecosystems because they are particularly sensitive to atmospherically deposited pollutants.

Regressions of winter VWM concentrations versus annual VWM concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{H}^+$  at the 12 NADP/NTN sites used in this study had Pearson  $r^2$  values of 0.71, 0.69, and 0.80, indicating good agreement between winter and annual VWM concentrations for those constituents (Fig. 6). The agreement was not as good for  $\text{Ca}^{2+}$  ( $r^2 = 0.28$ ), largely because of several extreme  $\text{Ca}^{2+}$  concentrations during the winter period (Fig. 6).

For  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , annual VWM concentrations commonly exceeded winter VWM concentrations

(Fig. 6). Regressions of winter VWM concentrations versus annual VWM concentrations with intercepts set to zero had slopes of 1.17, 1.24, and 1.11 for  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , respectively. Slopes > 1 are reasonable because concentrations in summer precipitation tend to be higher than in winter precipitation (Kuhn et al., 1998). Higher concentrations in summer precipitation are due to enhanced mixing of air in mountainous terrain with air in adjacent valleys, which tends to have higher concentrations of particulates,  $\text{NO}_x$ , and  $\text{SO}_2$  (Nickus et al., 1998). For  $\text{H}^+$ , no bias was evident between winter and annual VWM concentrations, suggesting that the effects of seasonal variability in  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  largely offset each other.

## 5. Conclusions

Statistical analyses indicated no significant difference in concentrations of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  between snowpack and winter NADP/NTN samples collected at 12

high-elevation sites in the Rocky Mountains during 1992–1999. Small, but statistically significant differences were indicated for all other solutes analyzed ( $p < 0.05$ ). Differences were greatest for  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^{+}$ , probably due to incorporation of eolian carbonate dust and organic matter in the snowpack by dry deposition processes. Dry deposition of carbonate dust was most important at the southernmost sites, where it neutralized an average of  $6.9 \mu\text{eq l}^{-1}$  and a maximum of  $12 \mu\text{eq l}^{-1}$  of snowpack acidity. Results of this study indicate that strong acids in the snowpack are derived mostly from wet deposition, but  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are derived from a combination of wet and dry deposition in an approximate ratio of 2:1.

Strong relations were identified between winter precipitation chemistry and average annual precipitation chemistry for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{H}^+$ , indicating that measurements of concentrations in winter precipitation can be used to estimate average annual precipitation chemistry. Furthermore, because there is generally good agreement between snowpack and NADP/NTN measurements of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{H}^+$  during the winter, the results of this study indicate that single measurements of snowpack chemistry taken just prior to the time of maximum snowpack depth can provide an estimate of average annual solute concentrations in precipitation. Although these estimates will not be as accurate as weekly monitoring of precipitation chemistry, they are a substantial improvement over other options (i.e., no data). Snowpack measurements are the only practical method of characterizing precipitation chemistry at many remote, high-elevation sites and thus are valuable for improving estimates of solute deposition in those areas.

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