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Trends in snowpack chemistry and comparison to National Atmospheric Deposition Program results for the Rocky Mountains, US, 1993–2004

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Abstract

Seasonal snowpack chemistry data from the Rocky Mountain region of the US was examined to identify long-term trends in concentration and chemical deposition in snow and in snow-water equivalent. For the period 1993–2004, comparisons of trends were made between 54 Rocky Mountain Snowpack sites and 16 National Atmospheric Deposition Program wetfall sites located nearby in the region. The region was divided into three subregions: Northern, Central, and Southern. A non-parametric correlation method known as the Regional Kendall Test was used. This technique collectively computed the slope, direction, and probability of trend for several sites at once in each of the Northern, Central, and Southern Rockies subregions. Seasonal Kendall tests were used to evaluate trends at individual sites.

Significant trends occurred during the period in wetfall and snowpack concentrations and deposition, and in precipitation. For the comparison, trends in concentrations of ammonium, nitrate, and sulfate for the two networks were in fair agreement. In several cases, increases in ammonium and nitrate concentrations, and decreases in sulfate concentrations for both wetfall and snowpack were consistent in the three subregions. However, deposition patterns between wetfall and snowpack more often were opposite, particularly for ammonium and nitrate. Decreases in ammonium and nitrate deposition in wetfall in the central and southern rockies subregions mostly were moderately significant ($p<0.11$) in constrast to highly significant increases in snowpack ($p<0.02$). These opposite trends likely are explained by different rates of declining precipitation during the recent drought (1999–2004) and increasing concentration. Furthermore, dry deposition was an important factor in total deposition of nitrogen in the region. Sulfate deposition decreased with moderate to high significance in all three subregions in both wetfall and snowpack. Precipitation trends consistently were downward and significant for wetfall, snowpack, and snow-telemetry data for the central and southern rockies subregions ($p<0.03$), while no trends were noted for the Northern Rockies subregion.
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1. Introduction

Snowfall that accumulates in seasonal snowpacks provides about 50–70 percent of the annual precipitation in headwater basins of the Rocky

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Mountains (Western Regional Climate Center, 2007). As these snowpacks accumulate during the winter and spring, chemicals deposited from the atmosphere are stored until snowmelt begins each year. Because snowmelt dominates the annual water budget in mountain lakes, streams, and wetlands in the area, monitoring the water quality of snow is important for quantifying atmospheric deposition to these systems.

Alpine and subalpine environments in the region are sensitive to changes in chemical composition of the water because thin soils and dilute water bodies in these ecosystems typically have limited capacity to buffer acidity from deposition of ammonium, nitrate, and sulfate (Campbell et al., 1995). As the seasonal snowpack melts and the accumulated atmospheric deposition is released to these watersheds, aquatic and wildlife populations may be affected. Concerns about adverse effects associated with nitrogen or sulfur deposition in North America historically have focused on eastern areas of the continent (US Environmental Protection Agency, 2005). Recent work, however, indicates watersheds in the Rocky Mountains of the Western US, particularly along the Front Range of Colorado, are exhibiting nitrogen saturation (Campbell et al., 2000; Burns, 2002; Fenn et al., 2003a).

Although several watershed-scale studies have investigated atmospheric deposition of nitrogen and sulfur in small headwater watersheds in the Rocky Mountains (Turk and Campbell, 1987; Caine and Thurman, 1990; Baron, 1992; Campbell et al., 1995; Williams et al., 1996; Williams and Tonnessen, 2000), regional-scale atmospheric deposition data are sparse (Nanus et al., 2003). The National Atmospheric Deposition Program (NADP) provides nationwide estimates of atmospheric deposition (Nilles, 2000; National Atmospheric Deposition Program, 2007). Coverage for high-elevation areas [generally between 2000 and 3500 m, but decreasing with latitude] in the Rocky Mountains, however, is limited. Although 10 NADP sites have been monitoring atmospheric deposition above 2400 m since 1993 in Colorado, few sites are operated in high-elevation areas of Idaho, Montana, Wyoming, and New Mexico, where snowpacks persist throughout the snowfall season with negligible melt. The high-elevation snowpack is important because it accumulates 2–3 times the annual precipitation measured at lower elevations where regular monitoring is more easily accomplished and more commonly done (National Atmospheric Deposition Program, 2005). Estimates of regional deposition mainly are based on lower-elevation sites where precipitation amounts are typically lower than those at higher elevations (Western Regional Climate Center, 2007) and may underestimate overall regional deposition. And if estimates of deposition fall short of actual levels, regional increases or decreases may become more difficult to identify.

To estimate precipitation and chemical deposition to the region, and to identify spatial and temporal trends in chemical deposition to the high-elevation snowpack, the US Geological Survey (USGS), in cooperation with the National Park Service, US Department of Agriculture Forest Service, and other organizations, has been monitoring snow chemistry at a network of more than 50 high-elevation snowpack sites in the Rocky Mountains since 1993 (Ingersoll et al., 2002). Designed to complement the NADP network of wet-deposition collectors in the region, major-ion concentrations such as ammonium, nitrate, and sulfate have been analyzed each year for each snowpack site (Fig. 1). Snow-chemistry data obtained from these annual snowpacks offer reliable estimates of atmospheric deposition chemistry for a substantial fraction of yearly precipitation and are comparable to results reported from the NADP network (Heuer et al., 2000; Clow et al., 2002).

Although statistically robust tests for national trends in precipitation chemistry in the US have been done (Lynch et al., 1996; Nilles and Conley, 2001; Lehmann et al., 2005), little work on trends in chemical deposition at high-elevation sites in the Rocky Mountain region has been done. Further, few statistical trend tests work well for atmospheric deposition that includes variability in mountain precipitation. Also, the recent drought (1999–2004) in the region may have affected chemical deposition because of reduced snowfall. Combined snow-chemistry and snow-water equivalent (SWE) results from 12 years (1993–2004) for a network of 54 snowpack-sampling sites in the Rocky Mountain region, and wetfall chemistry and precipitation for 16 NADP sites were used to determine temporal and spatial trends in precipitation chemistry. This paper presents trends in regional snowpack chemistry and water content and compares them to NADP wetfall results.

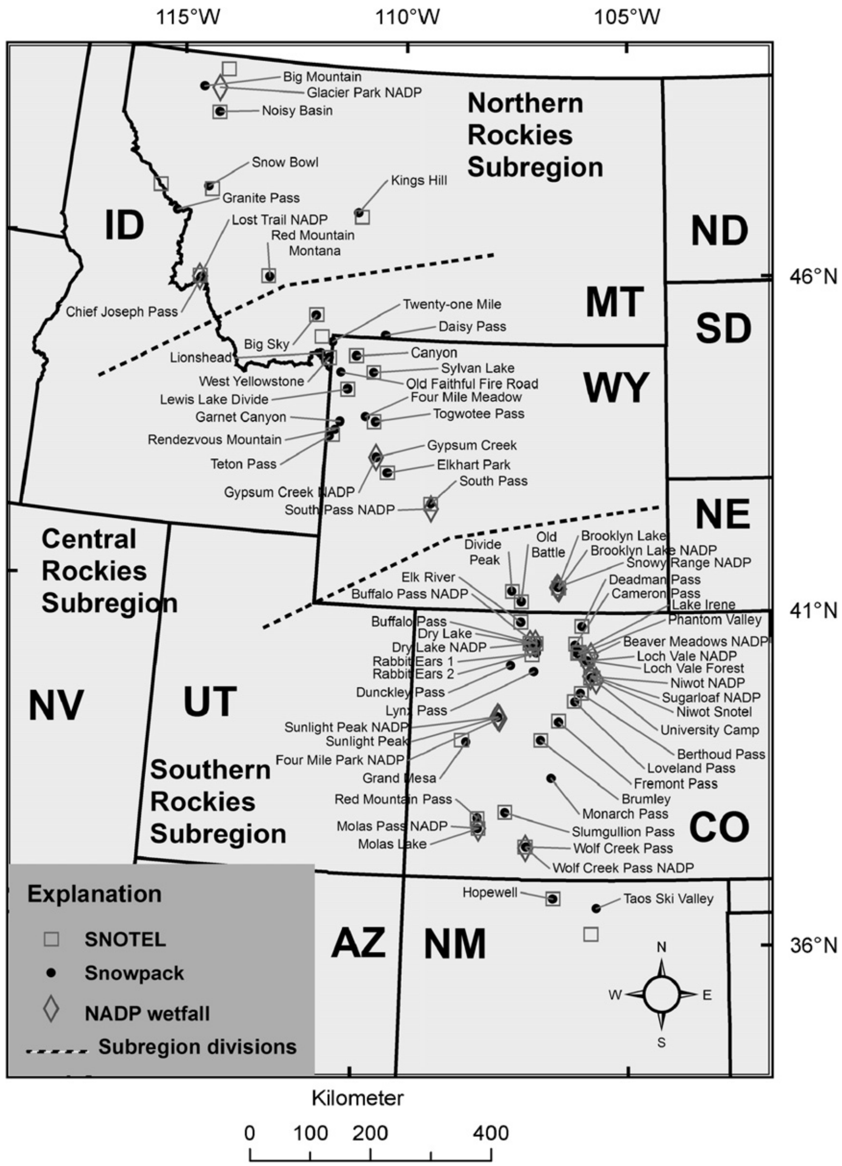

Fig. 1. Study area in Rocky Mountain region of western United States.

2. Methods

2.1. Data and analysis

To develop long-term trends for the period 1993–2004, 54 snowpack-sampling sites were chosen where chemical analyses had been performed consistently during the period with data available for at least 11 of the 12 years. Fifty-one sites had the full 12 years of record, and 3 of 54 sites lacked the 12th year of record. Chemical concentrations and SWE values were combined in the following manner to estimate deposition amounts. SWE was measured at sites during 1993 and 2002–2004 and was estimated from measured snow depths during the other years. Estimates of SWE were justified by observations of low variability of snow densities throughout the region, and the strong correlation of depth versus SWE ($r = 0.96$, $n = 208$). Mean densities derived from measured SWE values for each site during 1993 and 2002–2004 were multiplied by snow depths to estimate SWE for the years 1994–2001. The product of SWE (or precipitation volume) times chemical concentration yields chemical deposition expressed herein as kilograms per hectare.

The 54 snowpack sites in the Rocky Mountain Region were subdivided into 3 subregions to separate influences of different physiography and likely storm tracks (Fig. 1). The Northern Rockies subregion ($n = 7$) consists of snowpack sites in western and northwestern Montana where maritime-climate effects occur (National Oceanic and Atmospheric Administration, 2007). Sites in the Central Rockies subregion ($n = 17$) in northwestern Wyoming were influenced by a drier, continental climate. Sites in the Southern Rockies subregion ($n = 30$) in southern Wyoming, Colorado, and northern New Mexico were in a higher-elevation continental climate affected either by westerly storms originating from the Pacific Ocean or by upslope storms on the eastern slope of the Rocky Mountains that derive moisture from the Gulf of Mexico.

NADP wetfall sites in the region were selected wherever possible near snowpack-sampling sites for comparison to trends observed with snowpack chemistry and SWE (Fig. 1). NADP sites generally were chosen if they were located at snowfall-dominated elevations exceeding 2400 m, and the period of record spanned 1993–2004. Most of the 16 sites that met that criteria were located in Colorado (10), whereas eligible sites were scarce in Montana (2), Wyoming (4), and New Mexico (0). One NADP site in northwestern Montana was chosen for comparison to nearby snowpack-sampling sites although the elevation was less than 2400 m because the seasonal snowpack persists at lower elevations at this northernmost latitude of the study area. Twelve NADP sites in Colorado and southern Wyoming represented the Southern Rockies, 2 NADP sites in western Wyoming represented the Central Rockies, and 2 NADP sites in western Montana represented the Northern Rockies (Fig. 1). Although data for only two sites at high elevations were available for each of the Central and Northern Rockies subregions, trend tests were done for consistent comparisons to the 3 snowpack subregions.

National Resources Conservation Service snow-telemetry (SNOTEL) data (Western Region Climate Center, 2007) from 43 selected sites in the region were compared to snowpack- and wetfall-precipitation data for further verification of precipitation trends. Similar selection criteria for elevation and period of record previously mentioned were used in choosing SNOTEL sites in this comparison. Annual SWE totals for 1 April at SNOTEL sites representing the three subregions in the study were tested for trends for individual sites and for subregional groups. Twenty-six SNOTEL sites represented the Southern Rockies, 10 SNOTEL sites represented the Central Rockies, and 7 SNOTEL sites represented the Northern Rockies.

Data-collection methods and field quality-assurance procedures for the snowpack-sampling sites are described in Ingersoll et al. (2002). NADP methods are detailed at http://nadp.sws.uiuc.edu/, and SNOTEL methods are given at http://www.wcc.nrcs.usda.gov/factpub/sntlfct1.html.

2.2. Statistical analysis

A non-parametric correlation method known as the Regional Kendall Test (RKT) was used (Helsel et al., 2006; Helsel and Frans, 2006) for 12-year trend analyses of subregions. This method was designed specifically to assess temporal trends in spatially distributed data such as snowpack chemistry and SWE at numerous locations. The tests were arranged to evaluate groups of sites in the three subregions and to determine the slope, directions, and probability of trends for the subregions. Trends in each constituent (ammonium, nitrate, sulfate, and precipitation) were evaluated independently within each subregion for snowpack and wetfall data. The RKT has the distinct advantage of combining trends at several locations in a given domain to display generalized trend information for the area (Helsel and Frans, 2006).

Seasonal values from NADP sites for winter and spring wetfall, generally corresponding to the snowfall season, were used in this comparison. In a two-sided test, pair wise annual trend slopes were computed for each year at each individual site, and then an overall trend for all sites was computed to represent the subregion. For each constituent in each subregion, the program output yielded single values for the magnitude (slope) and direction of trend and its associated probability. Further computation of trends at individual sites for the study period was done using two-sided Seasonal Kendall tests at all snowpack and wetfall sites for the same constituents and at SNOTEL sites for SWE. A significant trend in this paper is defined as having 95 percent probability ($p < = 0.05$). In comparisons where $0.05 < p < 0.15$, trends are considered to be moderately significant.

Considering the effects of the recent drought on snowpacks in the Rocky Mountain region, the

Wilcoxon Rank-sum test was used instead of the RKT to determine differences between population means for SWE for two periods during the study (1993–1998 and 1999–2004). Although the RKT is useful in reporting monotonic trends over a temporal gradient, the rank-sum test more clearly contrasted the two periods before and during the drought. Because the drought in the Rocky Mountain region began at about the midpoint of the study period, and persisted through 2004, an opportunity arose to test for drought effects on precipitation at high-elevation sites for the two equal periods of time. Accordingly, the two groups of years 1993–1998 and 1999–2004 were compared to represent wetter and drier periods, respectively, for 54 snowpack sites.

3. Results and discussion

For the period 1993–2004, both subregional and local trends were developed for snowpack chemistry and SWE, wetfall chemistry and precipitation, and SNOTEL SWE (Figs. 2–4). Local trends at individual sites were shown to further evaluate subregional trends and to give site-specific information. In some cases a moderately or highly significant trend at a site within a given subregion was overshadowed by insignificant trends in the opposite direction at several neighboring sites. This is because RKT test results representing a set of sites in a subregion were sensitive to overall positive slopes or overall negative slopes among individual sites. For example, Fig. 4b shows that for the seven snowpack sites in the Northern Rockies subregion, a significant downward trend in SWE was detected at one site ($p<0.05$) while no trend was noted for the subregion as a whole. The comparisons between the three monitoring networks are discussed in the following sections.

3.1. *Trends in snowpack chemistry and water content*

Significant trends occurred in snowpack concentrations and deposition of ammonium, nitrate, and sulfate, and in SWE (Table 1). This finding is especially true in the Central and Southern Rockies subregions where both ammonium and nitrate concentrations and deposition increased with a high level of significance ($p<0.02$). However, sulfate concentrations and deposition decreased in all three subregions. Snowpack SWE showed no significant trend in the Northern Rockies, but decreased significantly in the Central and Southern Rockies. Location information and median values for snowpack SWE, and concentrations and deposition of ammonium, nitrate, and sulfate are shown in Table 2. Similar information for NADP wetfall data and SNOTEL data may be found on the respective websites (National Atmospheric Deposition Program, 2005; Western Regional Climate Center, 2007).

No trends in either ammonium or nitrate concentrations or deposition in snow were observed in the Northern Rockies subregion over the 12-year period. This likely can be attributed to the relatively small population and development in the subregion and surrounding areas. In contrast, significant increases in both ammonium and nitrate concentrations and deposition in snow occurred in the Central and Southern Rockies subregions. This probably is due to both the growing populations (particularly in the states of Arizona, Colorado, New Mexico, and Utah [US Census Bureau, 2008]); and the expanding energy development in the two subregions. Mobile emissions sources associated with such population growth and development have been shown to account for up to two thirds of nitrogen oxides (NO_x) emissions in the western USA (Fenn et al., 2003b). National Emissions Inventories data through 2002 show that the largest amount of NO_x emissions in the region occurred in Arizona, Colorado, and New Mexico (US Environmental Protection Agency, 2006a)(Fig. 5a). Because of uncertainty in regional estimates, ammonium emissions are not shown in Fig. 5. However, it is important to note that a discrepancy exists between apparent increases in snowpack nitrogen deposition and decreases in NO_x emissions in as shown in Fig. 5. Decreasing NO_x emissions are not reflected in snowpack nitrate deposition. The general decreasing emission trends perhaps are due to a focus on point-source emissions data in Fig. 5, and the unaccountability of mobile-source NO_x emissions. This discrepancy also has been noted for somewhat similar time periods in other work (Porter and Johnson, 2007).

Sulfate concentrations and deposition in snow showed quite different patterns with downward trends in all three subregions. These trends in snowpack sulfate concentrations were consistent with emission decreases reported for the region (Fig. 5b). The largest reduction in sulfate concentration and second-largest reduction in sulfate deposition occurred in the Northern Rockies

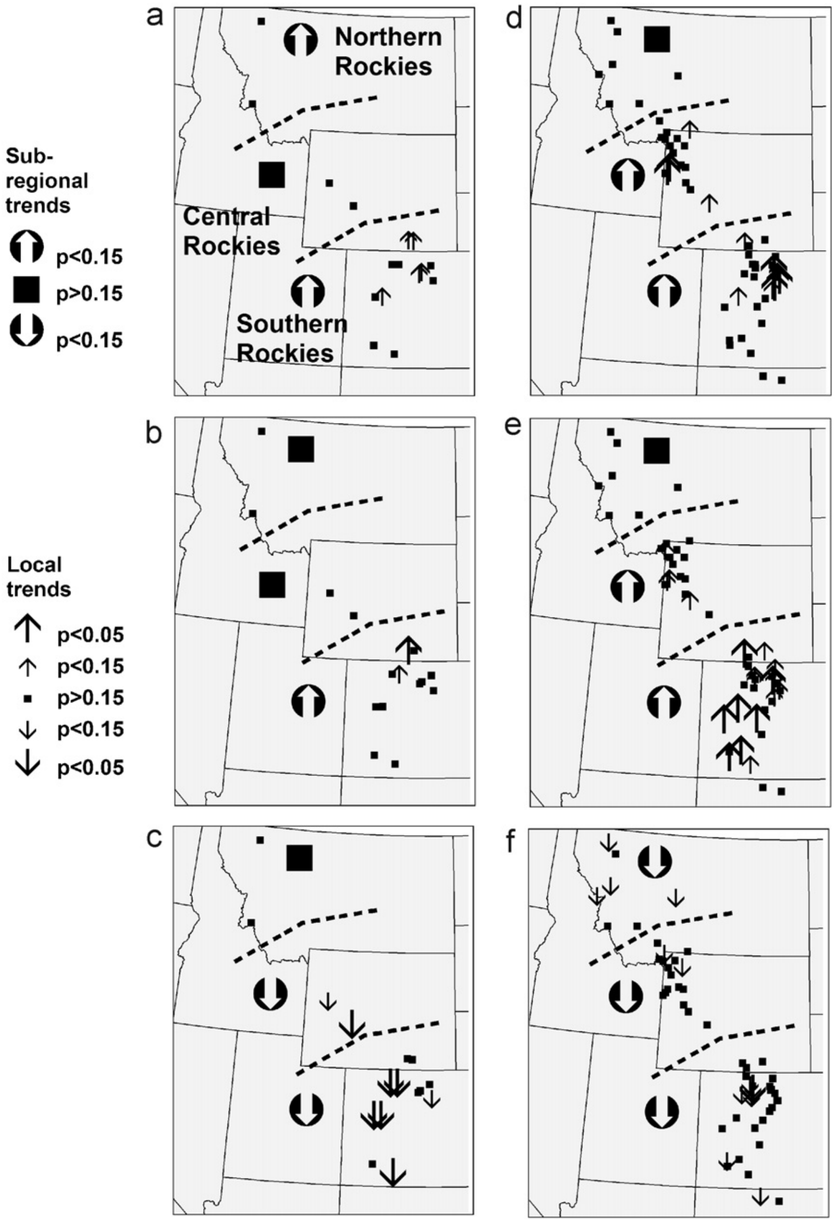

Fig. 2. Concentration trends at (a–c) NADP wetfall sites and (d–f) snowpack sites in Rocky Mountain region. Dashed lines divide subregions. Arrows indicate trend directions. Solid squares indicate no significant trend.

subregion, where typical concentrations of sulfate were lowest in the entire Rocky Mountain region. The reason for this greater reduction in sulfate in the Northern Rockies subregion is uncertain, but could be due to substantial reductions in sulfur-dioxide emissions at the largest point source in the northwestern United States, the Centralia power plant in western Washington (US Environmental Protection Agency, 2006b, c). Elsewhere in the Rocky Mountain region, reduction in sulfate concentration in the Central Rockies subregion was lowest while sulfate-concentration reduction in the Southern Rockies subregion was intermediate, although significant. Despite the presence of substantially more coal-burning power plants in the Central Rockies and Southern Rockies subregions than in the Northern Rockies subregion (US Environmental Protection Agency, 2006b), sulfate deposition also decreased.

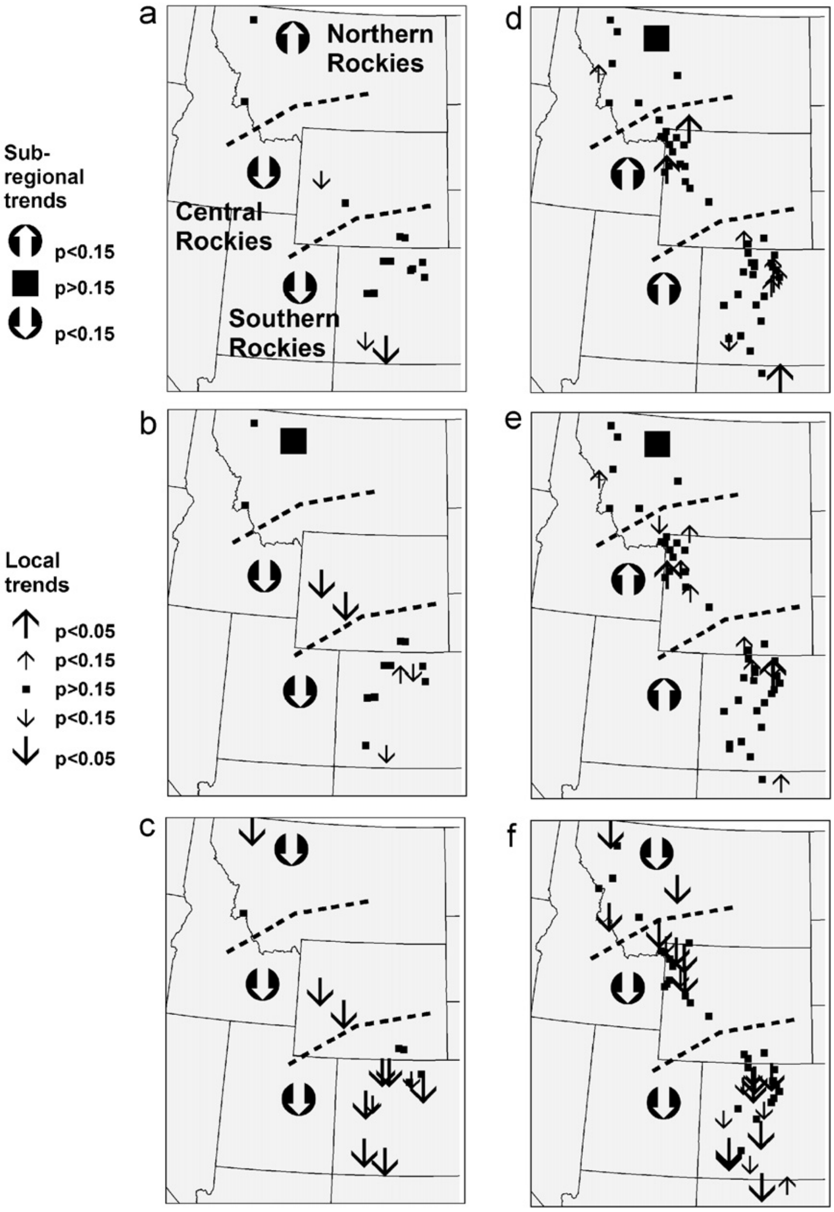

Fig. 3. Deposition trends at (a–c) NADP wetfall sites and (d–f) snowpack sites in Rocky Mountain region. Dashed lines divide subregions. Arrows indicate trend directions. Solid squares indicate no significant trend.

While little change in snowpack and SNOTEL SWE was observed in the Northern Rockies subregion, SWE decreased significantly in the Central and Southern Rockies subregions. These decreases in SWE in the Central and Southern Rockies are consistent with the regional drought that began near the middle of the study period, during 1998 or 1999, depending on the area of the Rocky Mountain Region. Wilcoxon rank-sum tests compared SWE at all 54 snowpack-sampling sites in three subregions for the periods 1993–1998 versus 1999–2004. Results showed a significant decrease ($p = 0.001$) during the latter period, supporting the RKT trend results for the Central and Southern Rockies subregions. These findings are consistent with other work monitoring snowpack SWE in the Western US (Knowles et al., 2006). Annual snowpacks in the Rocky Mountain Region were well below average at many SNOTEL sites when snow samples were collected during 1999–2004

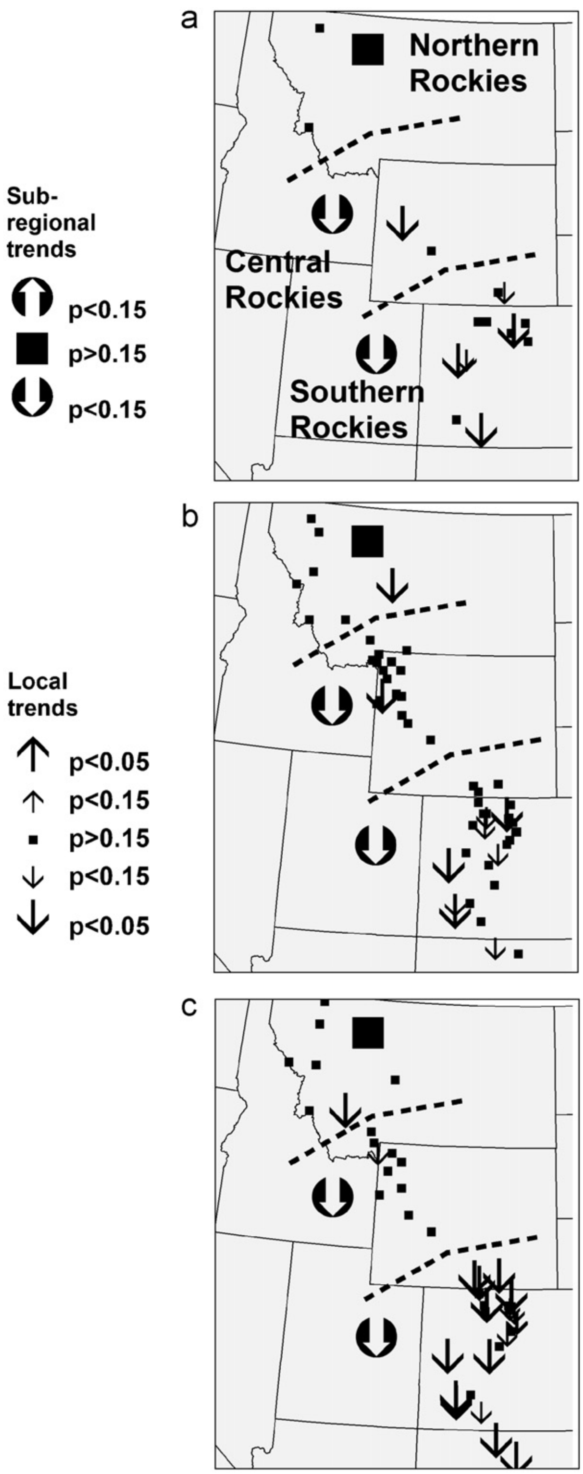

Fig. 4. Precipitation trends at (a) NADP wetfall sites, (b) snowpack sites, and (c) SNOTEL sites. Dashed lines divide subregions. Arrows indicate trend directions. Solid squares indicate no significant trend. SWE is SWE.

(Western Regional Climate Center, 2007). Further, significant downward trends in SWE at SNOTEL sites occurred during 1993–2004. As observed at snowpack-sampling sites in the Northern Rockies subregion, there was no trend in SWE at 7 SNOTEL sites in that subregion. However, at 10 SNOTEL sites in the Central Rockies subregion, and at 26 SNOTEL sites in the Southern Rockies subregion, highly significant downward trends in SWE occurred ($p<0.003$) (Table 1).

3.2. Comparisons of trends in snowpack and wetfall chemistry

To evaluate results of snowpack chemistry- and SWE trends, trend analyses were done for NADP network wetfall-concentration and precipitation data at 16 sites for comparison. Concentrations and deposition of ammonium, nitrate, and sulfate, as well as precipitation amounts were tested for trends across the three subregions of the Rocky Mountains by using the RKT. These results showed many significant trends for the period 1993–2004 (Table 1), similar to those observed in the snowpack data. However, there are noteworthy differences in precipitation and deposition trends for wetfall sites when compared to the trends for snowpack sites previously mentioned.

Ammonium concentrations at wetfall sites showed a moderately significant upward trend in the Northern Rockies subregion ($p = 0.15$), showed no trend in the Central Rockies subregion, and an upward trend with high significance in the Southern Rockies subregion ($p = 0.0018$). These concentration trends are consistent in direction with those observed in the snowpack. However, trends in wetfall ammonium deposition contradict trends shown for the snowpack, particularly in the Central and Southern Rockies subregions. Although trends in ammonium deposition at wetfall sites were upward in the Northern Rockies, they were downward in the Central and Southern Rockies subregions. Downward trends in wetfall ammonium deposition in the Central ($p = 0.062$) and Southern ($p = 0.11$) Rockies subregions were less significant than upward trends in snowpack ammonium deposition in the same areas ($p = 0.011$ and $p = 0.005$, respectively).

Nitrate concentrations at wetfall sites showed no trend in the Northern and Central Rockies subregions and significant upward trends in the Southern Rockies subregion. This increase in

Table 1
Trends in concentrations and deposition of ammonium, nitrate, and sulfate, and in precipitation in the Northern, Central, and Southern Rockies subregions

	Northern Rockies (2 sites)			Central Rockies (2 sites)			Southern Rockies (12 sites)		
	μeq L^{-1} yr^{-1}	*p*-Value	Median	μeq L^{-1} yr^{-1}	*p*-Value	Median	μeq L^{-1} yr^{-1}	*p*-Value	Median
NADP concentration									
Ammonium	**0.13**	0.15	3.5	0.067	0.41	5.2	**0.130**	0.0018	5.8
Nitrate	0.057	0.21	5.0	−0.073	0.70	9.1	**0.17**	<0.0010	11.8
Sulfate	−0.029	0.72	4.5	**−0.26**	0.0057	7.8	**−0.23**	<0.0010	9.3
	kg ha^{-1} yr^{-1}	*p*-Value	Median	kg ha^{-1} yr^{-1}	*p*-Value	Median	kg ha^{-1} yr^{-1}	*p*-Value	Median
NADP deposition									
Ammonium	**0.0063**	0.12	0.20	**−0.0050**	0.062	0.15	**−0.0060**	0.11	0.41
Nitrate	0.0060	0.64	1.3	**−0.051**	<0.0010	1.3	**−0.030**	0.078	3.7
Sulfate	**−0.020**	0.12	0.92	**−0.063**	<0.0010	0.90	**−0.096**	<0.0010	2.3
	mm yr^{-1}	*p*-Value	Median	mm yr^{-1}	*p*-Value	Median	mm yr^{-1}	*P*-Value	Median
NADP precipitation	0.0	0.92	530	**−10**	0.0096	230	**−12**	<0.0010	510

	Northern Rockies (7 sites)			Central Rockies (17 sites)			Southern Rockies (30 sites)		
	μeq L^{-1} yr^{-1}	*p*-Value	Median	μeq L^{-1} yr^{-1}	*p*-Value	Median	μeq L^{-1} yr^{-1}	*p*-Value	Median
Snowpack concentration									
Ammonium	0.012	0.62	3.5	**0.020**	<0.0010	5.2	**0.17**	<0.0010	4.5
Nitrate	0.047	0.21	4.8	**0.12**	0.0010	6.7	**0.35**	<0.0010	10.8
Sulfate	**−0.14**	<0.0010	3.3	**−0.044**	0.097	4.80	**−0.10**	<0.0010	7.7
	kg ha^{-1} yr^{-1}	*p*-Value	median	kg ha^{-1} yr^{-1}	*p*-Value	median	kg ha^{-1} yr^{-1}	*p*-Value	Median
Snowpack deposition									
Ammonium	−0.0029	0.39	0.33	**0.0067**	0.011	0.37	**0.0064**	0.0050	0.40
Nitrate	0.0021	0.86	1.6	**0.020**	0.0039	1.7	**0.032**	0.019	3.3
Sulfate	**−0.034**	<0.0010	0.89	**−0.020**	<0.0010	1.0	**−0.050**	<0.0010	1.8
	mm yr^{-1}	*p*-Value	Median	mm yr^{-1}	*p*-value	Median	mm yr^{-1}	*p*-Value	Median
snowpack SWE[a]	−1.9	0.53	570	**−5.2**	0.023	450	**−8.6**	<0.0010	490

	Northern Rockies (7 sites)			Central Rockies (10 sites)			Southern Rockies (26 sites)		
	mm yr^{-1}	*p*-Value	Median	mm yr^{-1}	*p*-Value	Median	mm yr^{-1}	*p*-Value	Median
SNOTEL SWE	−3.4	0.54	730	−9.1	0.0022	470	−17	<0.0010	440

Results are grouped for National Atmospheric Deposition Program (NADP), snowpack, and National Resources Conservation Service snow telemetry (SNOTEL) sites in Rocky Mountain region, 1993–2004
Significant slopes (*p*-value less than or equal to 0.15) are shown in bold.
[a]SWE, snow-water equivalent.

concentration in the Southern Rockies subregion is consistent with the increase observed in snowpack in that area. Nitrate deposition showed no trend in the Northern Rockies (as with snowpack), but significant downward trends in the Central and Southern Rockies subregions. As mentioned previously for ammonium deposition, trends in wetfall nitrate deposition also are opposite trends shown for snowpack in the Central and Southern Rockies subregions.

Possible causes for these differences in trend directions include the much smaller number of

Table 2
Location information and median concentrations, deposition, and snow-water equivalent (SWE) at selected snowpack sites in Rocky Mountain region, 1993–2004

Subregion and site name	Latitude[a] (north)	Longitude (west)	Elevation (m a.s.l.)	SWE (m)	NH_4^+ (μeq L^{-1})	NH_4^+ (kg ha^{-1})	NO_3^- (μeq L^{-1})	NO_3^- (kg ha^{-1})	SO_4^{2+} (μeq L^{-1})	SO_4^{2+} (kg ha^{-1})
Northern Rockies Subregion										
Big Mountain	48.508	114.345	2073	0.88	3.3	0.46	4.8	2.4	3.6	1.3
Chief Joseph Pass	45.687	113.932	2195	0.46	3.1	0.24	3.2	0.9	2.3	0.6
Granite Pass	46.640	114.611	2050	0.63	1.6	0.18	2.3	0.9	2.0	0.7
Kings Hill	46.850	110.700	2286	0.42	6.9	0.45	6.9	1.8	5.2	1.0
Noisy Basin	48.155	113.943	1865	0.82	4.2	0.56	5.5	2.9	3.5	1.5
Red Mountain	45.792	112.492	2743	0.33	5.3	0.32	5.6	1.3	3.7	0.8
Montana										
Snow Bowl	47.036	113.995	2335	0.57	2.5	0.27	3.5	1.3	3.0	0.9
Central Rockies Subregion										
Big Sky	45.275	111.433	2871	0.46	4.2	0.32	5.1	1.6	3.4	0.9
Canyon	44.717	110.533	2466	0.28	4.9	0.26	6.5	1.2	3.3	0.5
Daisy Pass	45.050	109.950	2987	0.69	4.5	0.46	4.9	2.0	3.6	1.1
Elkhart Park	43.000	109.750	2865	0.35	4.3	0.27	7.2	1.5	5.7	0.9
Four Mile Meadow	43.817	110.267	2438	0.23	3.8	0.17	6.2	0.9	3.6	0.4
Garnet Canyon	43.724	110.783	2743	0.63	5.2	0.59	5.7	2.3	5.4	1.7
Gypsum Creek	43.223	109.991	2435	0.29	3.4	0.15	7.1	1.3	5.0	0.7
Lewis Lake Divide	44.217	110.667	2396	0.70	5.9	0.79	6.1	2.7	4.6	1.4
Lionshead	44.717	111.283	2438	0.48	14.1	1.04	11.1	3.2	7.6	1.8
Old Faithful Fire Road	44.456	110.834	2225	0.26	7.5	0.35	7.6	1.4	5.1	0.6
Rendezvous Mountain	43.602	110.873	3094	0.75	4.1	0.65	4.5	2.2	4.4	1.7
South Pass	42.572	108.842	2755	0.38	5.0	0.32	8.5	2.1	8.6	1.5
Sylvan Lake	44.483	110.150	2566	0.47	5.3	0.47	5.2	1.7	3.7	0.9
Teton Pass	43.500	110.983	2359	0.45	6.5	0.54	7.8	2.1	6.9	1.4
Togwotee Pass	43.750	110.050	2926	0.50	3.3	0.30	4.9	1.5	3.8	1.0
Twenty-one Mile	44.900	111.050	2179	0.37	6.9	0.39	7.7	1.8	4.8	0.8
West Yellowstone	44.667	111.100	2042	0.24	9.0	0.37	10.6	1.6	5.6	0.6
Southern Rockies Region										
Berthoud Pass	39.800	105.783	3444	0.58	3.6	0.40	9.0	3.2	5.1	1.4
Brooklyn Lake	41.375	106.245	3231	0.64	4.5	0.50	10.2	3.7	8.4	2.4
Brumley	39.083	106.542	3231	0.30	3.2	0.19	8.9	1.7	5.3	0.7
Buffalo Pass	40.533	106.667	3139	1.13	5.6	1.10	12.3	8.1	11.0	6.5
Cameron Pass	40.517	105.900	3110	0.54	4.5	0.44	10.0	3.3	8.0	1.8

Table 2 (*continued*)

Subregion and site name	Latitude[a] (north)	Longitude (west)	Elevation (m a.s.l.)	SWE (m)	NH_4^+ (μeq L^{-1})	NH_4^+ (kg ha^{-1})	NO_3^- (μeq L^{-1})	NO_3^- (kg ha^{-1})	SO_4^{2+} (μeq L^{-1})	SO_4^{2+} (kg ha^{-1})
Deadman Pass	40.800	105.767	3109	0.46	6.0	0.43	11.4	3.6	8.3	1.8
Divide Peak	41.305	107.160	2634	0.41	6.3	0.45	15.8	3.9	10.2	1.9
Dry Lake	40.533	106.783	2560	0.47	6.1	0.49	16.8	4.7	10.3	2.5
Dunckley Pass	40.200	107.150	2987	0.49	4.5	0.41	10.8	3.1	6.9	1.7
Elk River	40.850	106.967	2621	0.44	4.6	0.33	14.0	3.5	7.6	1.6
Fremont Pass	39.367	106.200	3475	0.37	3.0	0.22	8.8	1.9	4.5	0.8
Grand Mesa	39.033	107.978	3103	0.50	5.7	0.54	11.0	3.3	9.2	2.1
Hopewell	36.709	106.248	3048	0.42	5.1	0.37	12.2	2.9	8.5	1.9
Lake Irene	40.415	105.820	3256	0.51	3.9	0.32	9.7	3.0	6.5	1.5
Loch ValeForest	40.289	105.668	3216	0.76	6.1	0.75	12.3	6.3	8.2	3.2
Loveland Pass	39.667	105.892	3597	0.60	3.7	0.38	8.6	3.4	5.2	1.6
Lynx Pass	40.113	106.700	2731	0.38	3.4	0.21	12.1	2.8	6.0	1.2
Molas Lake	37.750	107.700	3261	0.50	3.0	0.25	9.1	2.4	5.6	1.4
Monarch Pass	38.517	106.325	3200	0.43	4.8	0.32	10.2	2.8	6.2	1.3
Niwot SNOTEL	40.033	105.533	3021	0.26	9.3	0.40	13.7	2.3	9.1	1.2
Old Battle	41.154	106.969	3024	0.72	5.1	0.66	11.7	5.3	9.3	3.4
Phantom Valley	40.397	105.848	2752	0.20	4.9	0.18	11.9	1.6	7.9	0.8
Rabbit Ears 1	40.399	106.657	2938	0.75	5.3	0.75	11.4	5.3	9.3	3.5
Rabbit Ears 2	40.400	106.657	2938	0.73	5.3	0.73	11.8	5.4	9.6	3.8
Red Mountain Pass	37.900	107.717	3353	0.58	2.9	0.29	8.5	3.0	5.7	1.6
Slumgullion Pass	37.992	107.200	3505	0.24	2.4	0.11	7.0	1.2	5.3	0.7
Sunlight Peak	39.421	107.375	3200	0.48	4.8	0.42	10.0	3.1	7.0	1.7
Taos Ski Valley	36.575	105.458	3603	0.39	5.5	0.42	10.0	2.5	9.4	1.9
University Camp	40.033	105.567	3139	0.53	7.1	0.63	11.0	3.5	8.9	2.2
Wolf Creek Pass	37.483	106.783	3307	0.65	4.6	0.53	11.0	4.2	9.2	3.2

[a]Latitude and longitude are in decimal degrees.

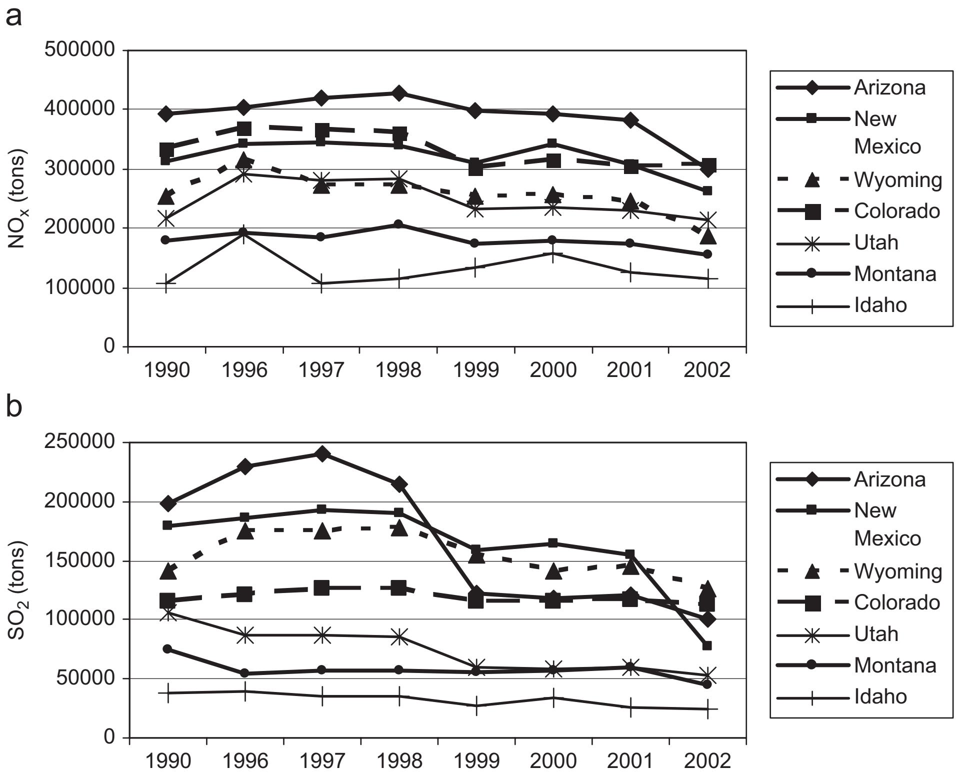

Fig. 5. (a) Total NO_x emissions in Rocky Mountain region, 1990–2002, and (b) total SO_2 emissions in Rocky Mountain region, 1990–2002. Units are in short tons (1 short ton = 907.18474 kg). Ammonium emissions trends were not available. Source: National Emissions Inventory (NEI), Emissions Inventory & Analysis Group; Air Quality Assessment Division, Office of Air Quality Planning and Standards, US EPA, Research Triangle Park, NC, USA.

wetfall sites being compared to snowpack sites, particularly in the Northern and Central Rockies subregions (Table 1). For example, trend patterns for several sites covering a larger part of the subregion can overwhelm subregional patterns based on just two sites representing a relatively smaller area. Another explanation for these differing trend directions in the case of ammonium and nitrate, may be due to the changes observed in the two key factors in deposition calculations, concentration and precipitation amount. First, more positive slopes of ammonium- and nitrate-concentration trends for snowpack versus wetfall occurred (increasing snowpack deposition), and second, more negative slopes of precipitation trends for wetfall versus snowpack were observed (decreasing wetfall deposition) during the same period. Further explanation of this effect is provided below in the discussion of differences in nitrogen deposition trends.

Contrary to the results for ammonium and nitrate, sulfate deposition has decreased at wetfall and snowpack sites. Sulfate concentrations showed significant downward trends for wetfall sites in the Central and Southern Rockies subregions and for snowpack sites in all subregions ($p<0.001$). Although no trend was seen in sulfate concentrations for the two wetfall sites in the Northern Rockies subregion, decreasing sulfate deposition for those two sites occurred on a subregional basis (with moderate significance, $p = 0.12$). Elsewhere in the region, sulfate deposition trends between wetfall and snowpack were in very strong agreement. Downward trends in sulfate deposition are consistent with other work in the region (Mast et al., 2005) and with national trends (US Environmental Protection Agency, 2006d).

Downward trends in sulfate concentration and deposition are encouraging during a time of large-scale development and population growth in the Rocky Mountain region. Accordingly, demand for electricity generation is increasing in the region, and electric services recently are responsible for the large majority of sulfur emissions (US Environmental

Protection Agency, 2006e). It is unknown if this downward trend in sulfate deposition will continue, with widespread development likely in the Western US.

Precipitation collected in gages at wetfall sites showed no trend in the Northern Rockies (as with the snowpack), but showed downward trends of high significance ($p<0.003$) in the Central and Southern Rockies subregions. These downward trends in precipitation at wetfall-collection sites generally are consistent with the downward trends in SWE at snow-sampling sites, however, greater rates of decrease occurred at wetfall sites (Table 1). This is noteworthy because of the substantial effect precipitation amounts have on the calculation of deposition.

3.3. Differences in nitrogen deposition trends

Although trends in sulfate deposition and precipitation for wetfall were similar to trends for snowpack, trends for ammonium and nitrate were quite different. Estimates of nitrogen deposition (from combined ammonium and nitrate) are highly dependent upon precipitation amounts, and representative measurements of precipitation can be difficult to obtain, especially in mountainous areas. Both the wetfall- and the snowpack-sampling methods for collection of precipitation chemistry and snowfall chemistry, respectively, are subject to natural variability and error. This is particularly true regarding precipitation amounts.

There are several potential reasons for differences in total precipitation amounts (and resultant chemical deposition) when comparing precipitation gages and adjacent wetfall collectors to nearby annual snowpacks. Primarily, snowfall collection in gages or other collection devices is a difficult challenge in mountainous areas (Goodison et al., 1998). Further, the catch efficiency of unshielded precipitation gages is known to be a problem at high-elevation sites (Yang et al., 2000) and may be less than the annual snowpack. Presumably, unshielded wetfall buckets also would be expected to undercatch snowfall.

The snowpack-sampling method also has disadvantages that may affect results. First, because SWE was estimated for 8 of the 12 years of study (and measured for the other 4 years), potential error exists in that estimator of chemical deposition in snowpack. Second, additional variation was introduced at a minority of the snowpack-sampling locations because the samples were not collected at the same site for each of the 12 years of the study. The change in sampling locations was due to difficulty in reaching the locations and (or) drought conditions and warm weather melted the snowpack earlier than usual. In these cases, valid snow samples were collected at the nearest possible locations to the original sampling location. The term "valid," in this case, means that the snowpack was representative of the area, and no substantial snowmelt occurred before sampling. In most cases, sampling locations generally were selected within the same hectare each year at each site. Additionally, some snow-depth variability may have been introduced subjectively because samples were not collected from exactly the same point each year. Finally, the difference in time periods analyzed for wetfall seasons (fall and winter) versus snowfall seasons may have introduced error because significant precipitation may have been included in snowpack but excluded in wetfall, or vice versa.

Results for the Northern Rockies subregion showed the fewest differences in nitrogen deposition between snowpack and wetfall sites. Although ammonium concentration and deposition at wetfall sites in the Northern Rockies subregion increased with moderate significance, there were no subregional trends in snowpack ammonium. And no subregional trends for nitrate deposition were found for either wetfall or snowpack in that area. Further, no subregional trends in precipitation occurred in the Northern Rockies subregion at wetfall, snowpack, or SNOTEL sites. Occasional local trends were observed opposing subregional trends in all three subregions, however.

Differences in nitrogen deposition trends between the two networks were more pronounced in the Central and Southern Rockies subregions likely because of the different rates of declining precipitation and increasing concentrations observed at wetfall and snowpack sites. Precipitation at wetfall sites was decreasing at a greater rate than SWE in snowpack while ammonium and nitrate concentrations in wetfall were increasing at a lesser rate than in snowpack. This relation was especially noticeable in the Southern Rockies subregion, where 12 wetfall sites were compared to 30 snowpack sites. For example, wetfall precipitation was decreasing at a 40 percent greater rate ($12\,mm\,yr^{-1}$) at wetfall sites than SWE ($8.6\,mm\,yr^{-1}$) at snowpack sites. At the same time, rates of increasing ammonium and nitrate concentrations in wetfall were 76 percent and 49 percent, respectively, of the rate of increase at snowpack sites. These combined effects explain the occurrence of decreasing nitrogen deposition in wetfall with corresponding increasing nitrogen deposition in snowpack.

Another contributing factor for the greater ammonium and nitrate deposition to snowpack is the added dry deposition accumulated throughout the snowfall season. The separation of wet and dry deposition by wetfall collectors eliminated this component of total atmospheric deposition. Although dry deposition has been observed to be a substantial fraction of total deposition in eastern and central areas of the US, it is estimated that wet deposition has dominated in the Western US during the study period (National Park Service, 2006). Because monitoring locations are sparse in the Rocky Mountain region, few data are available to determine regional or temporal patterns of dry deposition to Rocky Mountain snowpacks (Burns, 2002). However, dry-deposition data from 6 sites in the region operated by the Clean Air Status and Trends Network (CASTNet) were available for most of the 12 years of this study (US Environmental Protection Agency, 2006f). Data from the CASTNet sites, that were in operation at similar elevations and within 60 km of wetfall and snowpack sites in this study, help explain differences in nitrogen deposition observed in wetfall samples versus snowpack samples. Those CASTNet data indicate dry deposition accounted for generally about one-fourth to one-third of the total annual nitrogen deposition. Of those six CASTNet sites, seasonal data for winter and spring dry deposition composed about 35 to 40 percent of annual dry-deposition totals at five sites located in the Central and Southern Rockies subregions. About 50 percent of annual dry-deposition occurred during winter and spring at the sixth site in the Northern Rockies subregion. Thus, a considerable fraction of total nitrogen deposition has been collected as dry deposition at locations in the general vicinity of snowpack-sampling sites in the region.

When CASTNet data for these six sites were examined across the three subregions defined in this study, a latitudinal gradient emerged. Seasonal dry-deposition fluxes of nitrogen were greatest in the Southern Rockies subregion when compared to the Central and Northern subregions. This pattern of dry-deposition fluxes increasing from north to south in the region generally is consistent with the greater levels of nitrogen emissions for states in the southern part of the study area. For example, the highest total NO_x emissions during the study were reported in Arizona, Colorado, and New Mexico, whereas the lowest NO_x emissions were reported in Montana and Idaho (US Environmental Protection Agency, 2006a) (Fig. 5a). These data support the notion that dry deposition is an important factor in total deposition of nitrogen in the Southern Rockies subregion because of the greater emissions associated with greater population and development.

The general downward trend of SWE in the snowpack during a period of increasing deposition of nitrogen as either ammonium or nitrate indicates that there may be more nitrogen available in the atmosphere during fewer snowfall events. If increased emissions of nitrogen occur in the Western US (Fenn et al., 2003b), then increased atmospheric deposition is likely to follow—in spite of decreasing precipitation. This occurrence is especially likely in the Southern Rockies subregion of the Rocky Mountain region (Porter et al., 2005) where the largest concentrations of nitrogen-emitting activities in the study area occur. Large coal-fired powerplants, widespread non-point sources, large-scale energy development, dense urban and suburban development, and substantial farming and livestock operations in this subregion all combine to make nitrogen available for atmospheric deposition.

4. Summary and conclusions

The RKT was used to identify trends in chemical concentration and deposition and in precipitation in high-elevation snowpack in the Rocky region of the western USA. Snowpack chemistry and snow-water-equivalent data from 1993 to 2004 were compared to wetfall chemistry and precipitation data for during the same period. SNOTEL data also were compared to snowpack and wetfall-precipitation data for verification of precipitation trends. Two periods before and during the recent drought were contrasted.

Significant trends in snowpack concentrations and deposition of ammonium, nitrate, and sulfate, and in SWE occurred during the study. Trends were particularly pronounced in the Central and Southern Rockies subregions where ammonium and nitrate concentrations and deposition increased significantly ($p<0.02$). During the same period, significant trends in concentrations and deposition of ammonium, nitrate, and sulfate, and in precipitation also were observed at nearby NADP wetfall sites. Although concentrations of ammonium, nitrate, and sulfate for the two networks were in fair agreement, trends in ammonium and nitrate deposition at wetfall sites were opposite those shown for snowpack in the Central and Southern Rockies subregions. This likely can be attributed to the more steeply downward trends in precipitation for wetfall sites compared to snowfall sites, resulting in more ammonium and nitrate from the atmosphere to be deposited at snowpack sites than at wetfall sites. Further, additional nitrogen deposition to snowpack was added as dry deposition throughout the snowfall season while the separation of wet and dry deposition by wetfall collectors eliminated this component of total atmospheric deposition. Contrary to the results for ammonium and nitrate deposition, sulfate deposition clearly decreased at both wetfall and snowpack sites. Precipitation showed downward trends at wetfall-, snowpack-, and SNOTEL sites in the Central and Southern Rockies subregions ($p<0.02$). No trends in precipitation were identified in the Northern Rockies subregion. A comparison of 54 regional snowpack sites representing the periods before and during the recent drought (1993–1998 versus 1999–2004) showed a significant decrease in SWE during the latter period ($p = 0.001$).

Finally, for increased nitrogen deposition in snowpacks to occur while precipitation is decreasing, concentrations must increase at a greater rate. Such an increase was shown in snowpack data and indicates regional emissions of nitrogen compounds are on the rise. This assertion is supported by the large-scale development and population of the Rocky Mountain region, which suggests that more atmospheric nitrogen likely will be available for deposition to the region in the future.

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