AE International – North America

Atmospheric Environment 37 (2003) 4881–4892

ATMOSPHERIC ENVIRONMENT

www.elsevier.com/locate/atmosenv

Atmospheric deposition maps for the Rocky Mountains

Leora Nanus*, Donald H. Campbell, George P. Ingersoll, David W. Clow, M. Alisa Mast

US Geological Survey, Water Resources Division, Federal Center, Denver, CO 80225, USA

Received 8 December 2002; accepted 9 August 2003

Abstract

Variability in atmospheric deposition across the Rocky Mountains is influenced by elevation, slope, aspect, and precipitation amount and by regional and local sources of air pollution. To improve estimates of deposition in mountainous regions, maps of average annual atmospheric deposition loadings of nitrate, sulfate, and acidity were developed for the Rocky Mountains by using spatial statistics. A parameter-elevation regressions on independent slopes model (PRISM) was incorporated to account for variations in precipitation amount over mountainous regions. Chemical data were obtained from the National Atmospheric Deposition Program/National Trends Network and from annual snowpack surveys conducted by the US Geological Survey and National Park Service, in cooperation with other Federal, State and local agencies. Surface concentration maps were created by ordinary kriging in a geographic information system, using a local trend and mathematical model to estimate the spatial variance. Atmospheric-deposition maps were constructed at 1-km resolution by multiplying surface concentrations from the kriged grid and estimates of precipitation amount from the PRISM model. Maps indicate an increasing spatial trend in concentration and deposition of the modeled constituents, particularly nitrate and sulfate, from north to south throughout the Rocky Mountains and identify hot-spots of atmospheric deposition that result from combined local and regional sources of air pollution. Highest nitrate (2.5–3.0 kg/ha N) and sulfate (10.0–12.0 kg/ha SO_4) deposition is found in northern Colorado.

Published by Elsevier Ltd.

Keywords: Atmospheric deposition; GIS; Kriging; Precipitation chemistry; Rocky Mountains

1. Introduction

Many high-elevation ecosystems in the Rocky Mountain region are within the boundaries of Class I wilderness areas, national parks, and wildlife refuges that are protected from air-pollution damage under provisions of the Clean Air Act Amendments of 1977. These areas may be effected by pollutants in atmospheric deposition from local and regional sources (Peterson et al., 1998). A number of Rocky Mountain ecosystems have been identified as being affected by atmospheric deposition of nitrogen (Williams et al., 1996; Baron et al., 2000; Campbell et al., 2000) and acidity (Turk and Campbell, 1997). However, in many high-elevation areas, above 3000 m, of the western United States, data on atmospheric deposition and its effects on ecosystems are sparse or nonexistent. To protect sensitive ecosystems from potential damage from atmospheric deposition and accommodate population growth and manage energy development, a better understanding of the spatial distribution of pollutant loading to high-elevation ecosystems is needed.

Several regional deposition models (Vautz et al., 2003; Fenn et al., 2003; Ollinger et al., 1993) identified the lack of data at high elevations as a problem when modeling regional deposition trends, but none have focused specifically on high elevation regions. Vautz et al. (2003) developed a regional model to estimate spatial

*Corresponding author. Tel.: +1-303-236-4882x250; fax: +1-303-236-4912.

E-mail address: lnanus@usgs.gov (L. Nanus).

1352-2310/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.atmosenv.2003.08.024

distributions of wet deposition in Germany and states that the influence of snow has to be investigated in further detail at increasing elevations above sea level. Fenn et al. (2003) modeled chemical transformations and deposition of nitrogen in the western United States for 1996 using the Models-3/Community Multiscale Air Quality Model and found several hotspots including parts of Colorado and eastern Idaho. However, it is stated that there is a high level of uncertainty in the model simulations of nitrogen deposition because of uncertainty of nitrogen inputs, as well as the lack of data in the highest elevation areas, where ecosystems are likely to be of highest sensitivity (Fenn et al., 2003). Ollinger et al. (1993) developed a spatial model of both wet and dry deposition for the northeastern United States, using a combination of statistics and Geographic Information System (GIS). Regional trends in ion concentration were evaluated by linear regression analyses of concentration against latitude and longitude, and deposition maps were developed in GIS by incorporating ion concentration and precipitation, then adding dry deposition (Ollinger et al., 1993). Ollinger et al. (1993) did not include elevational trends in the concentration model, due to the fact that the limited elevational distribution of National Atmospheric Deposition Program/National Trends Network (NADP/NTN) sites were thought to be inadequate for meaningful analysis. In addition, elevation was not included in the precipitation amount because few long-term precipitation collecting stations were established at high elevations. Thus, Ollinger et al. (1993) assumed constant concentration and precipitation at all elevations. It was noted that greater attention should be given to monitoring deposition at high elevation and establishing the relationship between elevation and ion concentrations in precipitation. Ollinger et al. (1993) concluded that statistically meaningful trends could be established after long-term averages of deposition variables are obtained.

High-elevation areas in the Rocky Mountains annually receive large amounts of precipitation, most of which accumulates in a seasonal snowpack. During spring snowmelt, all of the accumulated atmospheric deposition is delivered to the surface-water ecosystem during just a few months. Chemical concentrations of pollutants in early snowmelt may be magnified by the ionic pulse effect. Many high-elevation watersheds are underlain by thin soils and resistant bedrock that provide little acid-neutralizing capacity, which makes the watersheds highly sensitive to chemical inputs (Clow and Sueker, 2000). Burns (2003) states that nitrogen loads in atmospheric wet deposition have increased since the mid-1980s at several high elevation sites in the Rocky Mountains of Colorado and southern Wyoming, and demonstrates the need for continued monitoring of atmospheric deposition at high elevations.

A major source of atmospheric deposition data for the Rocky Mountain region is the NADP/NTN, which provides uniform, quality assured data for atmospheric deposition of the major acid anions and base cations, plus ammonium, hydrogen ion and specific conductance. These data are used to construct nationwide maps with isopleths of atmospheric deposition amounts for major chemical constituents (NADP/NTN, 1999), and are useful for comparing levels of atmospheric deposition among regions. NADP/NTN sites are sparsely distributed at high elevations in the Rocky Mountains due to the fact that they are logistically difficult to maintain (Turk et al., 2001), and generally do not have sufficient resolution to identify hot-spots of deposition within a region.

The US Geological Survey (USGS), National Park Service (NPS), US Department of Agriculture (USDA) Forest Service, and other agencies, initiated the Rocky Mountain snowpack survey (RMS) in the early 1990s, to complement NADP/NTN at high elevations in the Rocky Mountains (Ingersoll et al., 2002). Turk et al. (2001) conducted principal component analysis on the RMS snowpack chemistry data and determined that there are three solute associations, acid, soil and salt. Acid solute concentrations, including nitrate, sulfate, and acidity, were identified as being similar to concentrations in nearby wetfall collectors while soil solutes were found to be higher in snowpack than wetfall, thus it was concluded that dryfall of acid solutes during snow season is insignificant (Turk et al., 2001).

Clow et al. (2002) compared data from the two networks at 12 co-located sampling sites ranging from elevations of 2400 to 3500 m in the Rocky Mountains and determined that they could be combined to achieve better spatial resolution of acid solute concentrations for high elevations (Fig. 1, copied from Clow et al., 2002). Statistical tests indicated no significant differences in concentrations (p-value >0.1) for nitrate and sulfate at the 12 co-located sites in snowpack compared with NADP/NTN (winter volume-weighted mean) (Clow et al., 2002). Linear regressions of snowpack against NADP/NTN for sulfate and nitrate indicated strong correlations ($r^2 \geqslant 0.6$), and the slopes of the regression equations were close to 1 (Clow et al., 2002). These results indicate that for nitrate and sulfate snowpack data are comparable with data from NADP/NTN, and also indicates that dry deposition (which is included in snowpack but not wetfall) of these anions to the snowpack does not have a substantial effect on these particular solute concentrations (Clow et al., 2002). Differences in snowpack and NADP/NTN acidity concentrations were close to zero, except south of 39° latitude, where significant carbonate inputs occur (Clow et al., 2002). The mean difference in acidity at the ten northern co-located sites was only 0.2 μeq/l and was not statistically significant ($p > 0.5$) between the NADP/

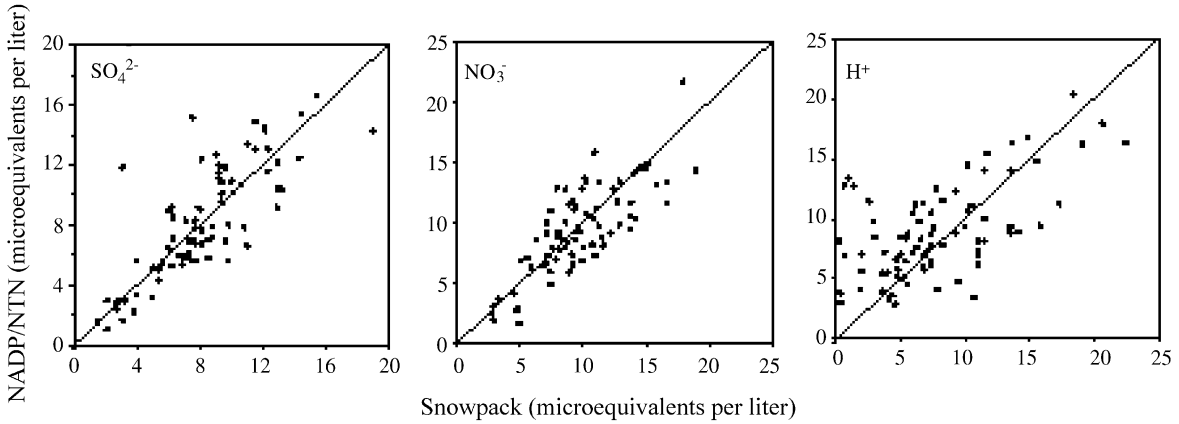

Fig. 1. Solute concentrations in paired snowpack and NADP/NTN (winter volume-weighted mean) samples, 1992–1999 (from Clow et al., 2002).

NTN and snowpack data (Clow et al., 2002) (Fig. 1). It was determined that the two datasets could also be combined for acidity north of 39° latitude. Comparability of the data for ammonium was also evaluated, and results indicate statistically significant differences between the two data sets (Clow et al., 2002). The average ammonium difference was 25% greater concentration in the snowpack vs. NADP/NTN samples and could be resulting from loss of ammonium in NADP/NTN samples after melting, or dry deposition in the snowpack (Fig. 1, from Clow et al., 2002). Because of this bias towards higher concentrations in snow, the two data sets cannot be combined for ammonium to produce concentration and deposition maps at this scale.

The objective of this study was to include effects of elevation on precipitation amount and ion concentration, and provide improved estimates of nitrate, sulfate, and acidity deposition for the Rocky Mountain region. Monthly precipitation chemistry data from the NADP/NTN were combined with USGS and NPS snowpack chemistry data to produce high-resolution average annual precipitation chemistry and deposition maps. Chemical concentration maps were produced by using ordinary kriging spatial statistics in a GIS and were overlaid with maps of precipitation amount, calculated by using the parameter-elevation regressions on independent slopes model (PRISM) (Daly et al., 1994). The PRISM model combines data on precipitation amount from hundreds of sites with digital elevation models (DEM) to account for spatial variability of precipitation amount in topographically complex, mountainous terrain. The resulting deposition maps of nitrate, sulfate, and acidity incorporate the best available data sets for chemical concentration and precipitation amount and model atmospheric deposition of these constituents on a 1-km grid.

2. Methods

Chemical-concentration data were obtained from the NADP/NTN (NADP/NTN, 1999) wetfall database and from the RMS snowpack database for sites located in Montana, Idaho, Colorado, Utah, Wyoming, Arizona, and New Mexico. For consistency between the two networks, only sites at elevations > 1830 m and with 3 or more years of data between the period of 1992 and 1999 were included in this study. Twenty-seven NADP/NTN sites and 71 RMS sites met the criteria and were used in the modeling (Tables 1 and 2). The majority of the sites are located near the Continental Divide (Fig. 2). Precipitation data based on a 30-year annual average were obtained from the PRISM model (Fig. 3).

2.1. National atmospheric deposition program national trends network

NADP/NTN deposition samples are collected weekly throughout the year. Deposition samples represent only wet deposition because the automatic collectors only open during precipitation events. NADP/NTN standard sampling protocols, sample processing, analytical methods, and quality-assurance procedures are outlined in Peden (1986) and See et al. (1990). NADP/NTN completeness criteria 1-4 (NADP/NTN, 1999) were addressed prior to data analysis.

NADP/NTN wetfall chemistry collectors are prone to under catch snowfall compared to snowfall collected by the co-located weighing precipitation gages installed at all NADP/NTN sites. Differences can be attributed to delays in activation of the wetfall collector sensor during light and/or dry snow events (Gordon, 1999), and also the capacity of the wetfall collector (approximately one foot of snowfall) may be exceeded at some sites over the 1-week sampling interval (Gordon, 1999). Although,

Table 1
Average annual chemical concentrations for selected NADP/NTN wetfall sampling sites, 1992–99

Site Name	Site	Latitude	Longitude	Elev (m)	Nitrate (μeq/l)	Sulfate (μeq/l)	H^+ (μeq/l)
Bandelier National Monument	NM007	354654	1061603	1999	14.3	13.7	11.2
Cuba	NM009	360227	1065817	2125	16.7	16.6	12.6
Grand Canyon National Park	AZ003	360418	1120918	2153	14.1	13.3	5.78
Mesa Verde National Park	CO099	371153	1082925	2173	16.6	19.3	13.5
Alamosa	CO000	372629	1055155	2299	13.3	14.6	4.54
Wolf Creek Pass	CO091	372807	1064725	3293	11.2	12.3	11.4
Bryce Canyon National Park	UT099	373707	1121022	2478	15.7	13.7	8.10
Molas Pass	CO096	374505	1074107	3250	10.8	9.99	9.16
Manitou Springs	CO021	390604	1050531	2363	21.5	17.5	16.0
Four Mile Park	CO008	392411	1072028	2503	11.6	10.2	7.30
Sunlight Peak	CO092	392538	1072247	3207	10.7	10.2	7.36
Sugarloaf	CO094	395938	1052848	2525	19.3	15.2	11.4
Niwot Saddle	CO002	400319	1053518	3521	14.3	11.0	9.69
Loch Vale	CO098	401716	1053946	3160	12.1	10.8	9.44
Beaver Meadows	CO019	402151	1053455	2491	17.0	12.6	9.15
Sand Spring	CO015	403027	1074207	1999	15.6	14.5	10.3
Dry Lake	CO093	403205	1064648	2528	14.6	16.9	15.6
Buffalo Pass	CO097	403216	1064035	3235	11.5	14.8	12.2
Murphy Ridge	UT008	412127	1110255	2147	19.7	16.1	8.55
Brooklyn Lake	WY095	412153	1061427	3213	10.2	8.86	7.69
Snowy Range	WY000	412234	1061534	3287	11.4	10.5	7.78
South Pass City	WY097	422941	1084945	2512	12.6	11.7	9.28
Sinks Canyon	WY002	424402	1085100	2165	9.2	9.63	6.14
Pinedale	WY006	425544	1094712	2389	13.8	12.5	10.4
Gypsum Creek	WY098	431322	1095928	2429	9.51	8.68	6.63
Tower Falls	WY008	445502	1102513	1913	8.71	7.11	4.79
Lost Trail Pass	MT097	454130	1135756	2415	3.55	3.10	4.72

NADP/NTN volume-weighted precipitation chemistry calculations and deposition calculations are made using precipitation amounts from the co-located precipitation gage, measurements may still be biased if the wetfall collector does not collect a representative sample of a snow event. The co-located precipitation gage at NADP/NTN sites may be a source of bias at windy, snow-dominated sites due to either under-or over-collection from blowing snow (Williams et al., 1996).

Simple regression analysis of paired high- (>3000 m) versus low-elevation (<3000 m) NADP/NTN sites yielded no relationship for acid solute concentrations, nitrate ($r^2 = 0.2$), sulfate ($r^2 = 0.4$) or acidity ($r^2 = 0.5$), indicating that changes in deposition are not based independently on variation in elevation between sites. In alpine areas, precipitation, largely influenced by elevation change is still important. Thus, precipitation amount needs to be included in the spatial analysis of atmospheric deposition.

Winter volume-weighted-mean (VWM) concentrations for the NADP/NTN data were calculated by multiplying monthly VWM concentration by monthly precipitation amounts, summing the values for the 5-month period of November to March, then dividing by total precipitation (Clow et al., 2002). Winter VWM concentrations correlated well with annual VWM concentrations for nitrate, sulfate, and acidity with Pearson R^2-values of 0.69, 0.71, and 0.80. This correlation suggests that RMS snowpack chemistry measurements can provide a good estimate of average annual precipitation chemistry for nitrate, sulfate, and acidity (Clow et al., 2002). Long-term annual averages were determined by calculating the geometric mean for the period of record (1992–99). The data are normally distributed.

2.2. Rocky Mountain snowpack chemistry synoptic data

The seasonal snowpack was sampled once annually at maximum accumulation at northern sites in early spring prior to snowmelt by the USGS/NPS and represents a combination of wet and dry winter deposition captured in a single snow sample (Ingersoll et al., 2002). Samples were melted in Teflon bags and processed within 12 h. Samples were filtered using 0.45 μm polycarbonate filters. Snowpack sample analysis followed protocols for low-ionic strength water (Ingersoll et al., 2002). Methods used for sample processing and analysis were similar between the two laboratories and have been consistent throughout the period, additionally blind

Table 2
Average annual chemical concentrations, USGS/NPS Rocky Mountain snowpack chemistry, 1992–99

Site Name	Site	Latitude	Longitude	Elev (m)	Nitrate (μeq/l)	Sulfate (μeq/l)	H^+ (μeq/l)
Gallegos Peak	SS021	361100	1053300	2988	11.1	12.5	5.37
Horse Theif Peak	SS026	364300	1061600	3049	12.0	12.5	6.39
Wolf Creek Pass SS	SS065	372900	1064700	3308	11.4	12.6	6.05
Molas Lake	SS036	374500	1074200	3262	10.2	9.76	4.90
Red Mountain Pass	SS048	375400	1074300	3354	10.9	10.2	4.64
Slumgullion Pass	SS053	375930	1071200	3506	8.80	9.35	4.82
Monarch Pass	SS037	383100	1061930	3201	10.9	9.69	5.01
Grand Mesa	SS023	390158	1075839	3104	11.0	12.3	6.10
Brumley	SS006	390500	1063230	3232	9.67	7.81	7.17
Fremont Pass	SS020	392200	1061200	3476	10.3	8.15	5.20
Sunlight Peak	SS058	392516	1072230	3201	11.0	10.5	6.39
Loveland Pass	SS034	394000	1055330	3598	10.9	8.91	6.32
Berthoud Pass	SS002	394800	1054700	3445	10.4	8.69	8.28
Ned Wilson	SS040	395800	1071900	3384	7.45	9.48	6.53
Trappers Lake	SS085	395930	1071430	3050	11.1	9.41	5.34
University Camp	SS063	400200	1053400	3140	11.8	11.8	9.10
Niwot Snotel	SS066	400200	1053200	3022	12.7	11.9	8.55
Lynx Pass	SS035	400645	1064200	2732	12.5	9.97	9.79
Ripple Creek Pass	SS083	400700	1071800	3201	10.7	10.5	5.35
Dunckley Pass	SS015	401200	1070900	2988	12.2	10.9	6.01
Loch Vale	SS046	401724	1054000	3217	6.89	11.4	8.29
Phantom Valley	SS043	402350	1055054	2753	12.0	11.3	10.4
Rabbit Ears Pass	SS044	402355	1063924	2939	12.6	12.7	12.0
Rabbit Ears 2	SS045	402359	1063925	2939	12.6	12.9	11.9
Lake Irene	SS030	402440	1054847	3244	10.2	9.82	8.38
Hogan Peak	SS080	402723	1064247	3098	12.5	13.7	11.5
Cameron Pass	SS008	403100	1055400	3111	11.2	11.2	9.26
Buffalo Pass SS	SS007	403200	1064000	3140	12.3	11.8	10.1
Dry Lake SS	SS014	403200	1064700	2561	14.3	13.5	13.8
Trial Lake	SS095	404052	1105707	3000	9.46	9.01	7.08
Little Brush Creek	SS090	404227	1092946	2445	13.1	11.4	9.16
Deadman Pass	SS012	404800	1054600	3110	12.2	11.7	6.72
Elkhart Park	SS016	405100	1065800	2622	13.8	11.7	10.6
Old Battle	SS042	410900	1075800	3025	12.3	12.3	9.85
Divide Peak	SS013	411800	1071000	2702	14.0	12.6	10.1
Brooklyn Lake	SS005	412200	1061400	3116	11.3	11.3	8.92
Beaver Mountain	SS087	415803	1113319	2683	10.1	10.0	7.55
South Pass	SS057	423400	1085000	2756	10.7	11.9	7.93
Willow Creek	SS096	424912	1105007	2415	9.32	9.93	7.79
Fish Hawk Snow	SS017	430000	1094500	2866	8.56	9.35	6.71
Gypsum Creek SS	SS025	431322	1095927	2436	5.32	7.98	5.93
Teton Pass	SS060	433000	1105900	2360	9.24	9.66	3.89
Rendevous Mountain	SS049	433606	1105222	3095	6.57	7.91	6.00
Garnet Canyon	SS022	434326	1104659	2744	6.89	7.78	7.11
Togwotee Pass	SS061	434500	1100300	2927	6.14	6.98	5.35
Four Mile Meadow	SS019	434900	1101600	2439	7.70	5.97	5.66
Lewis Lake Divide	SS032	441300	1104000	2397	7.69	7.02	5.97
Old Faithful Fire Road	SS073	442720	1105003	2226	9.15	7.28	6.02
Old Faithful in Road	SS082	442721	1105003	2256	4.32	10.2	6.70
Old Faithful East Lot	SS075	442725	1104928	2238	9.28	6.51	6.04
Old Faithful Crew Corrals	SS074	442727	1105055	2257	8.98	4.12	5.02
Biscuit Basin	SS071	442840	1105120	2223	9.06	7.98	5.09
Sylvan Lake	SS059	442900	1100900	2567	6.89	7.02	6.35
Sylvan Lake in Road	SS084	442900	1100901	2567	3.17	8.43	7.13
Monida Pass	SS091	443600	1121000	2147	11.8	8.53	6.49
West Yellowstone in Road	SS086	443900	1110500	2033	4.40	12.6	5.23
West Yellowstone	SS064	444000	1110600	2043	10.3	7.71	6.26

Table 2 (*continued*)

Site Name	Site	Latitude	Longitude	Elev (m)	Nitrate (μeq/l)	Sulfate (μeq/l)	H^+ (μeq/l)
Canyon	SS009	444300	1103200	2467	7.63	6.37	5.69
Lionshead	SS033	444300	1111700	2439	12.0	11.3	6.56
Twenty-One Mile	SS062	445400	1110300	2180	9.36	7.68	7.31
Daisy Pass	SS011	450300	1095700	2988	6.34	6.34	6.42
Big Sky	SS004	451630	1112600	2872	7.54	5.61	5.26
Chief Joseph Pass	SS010	454113	1135556	2196	5.33	4.04	5.97
Red Mountain Montana	SS047	454730	1122930	2744	7.54	6.65	5.55
Sunlight Creek	SS094	460700	1102500	2147	8.36	7.14	5.59
Grassy Mountain	SS089	462100	1110400	1891	10.2	9.64	7.27
Cement Gulch Divide	SS088	463800	1112300	1879	10.1	9.65	7.22
Mount Belmont	SS092	464000	1123000	2135	7.71	8.71	6.52
Kings Hill	SS028	465100	1104200	2287	8.59	9.47	6.53
Snow Bowl	SS054	470211	1135943	2336	5.50	5.86	7.21
Noisy Basin	SS041	480919	1135636	1866	7.07	6.81	7.66

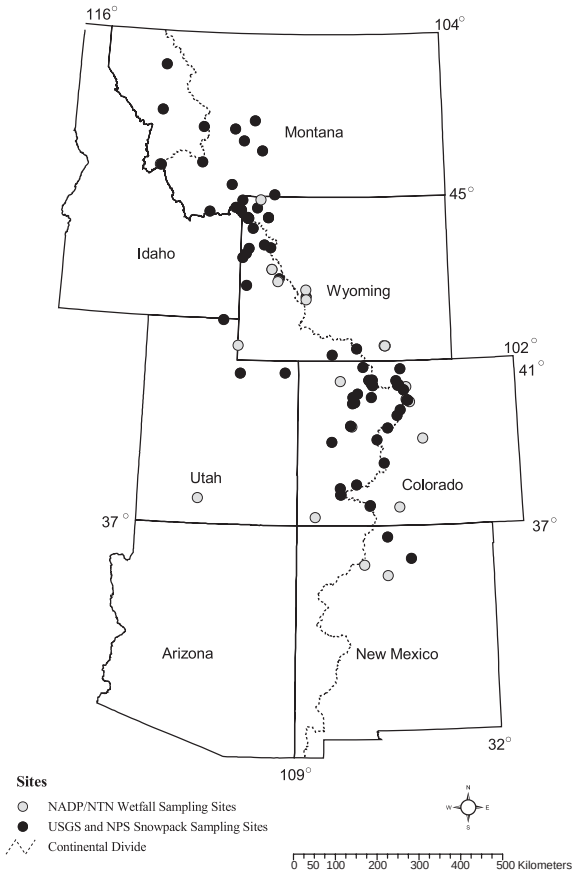

Fig. 2. NADP/NTN wetfall and USGS/NPS snowpack sampling sites in the Rocky Mountains.

audit performance tests indicated that both labs produced high-quality data (Clow et al., 2002). Analytical bias for most constituents was determined to be minor, slopes of the regressions for the two laboratories differed by <0.02 for all constituents except Ca, Mg, and NH_4 which had regressions slopes higher in the snowpack samples than NADP/NTN by up to 0.09% (Clow et al., 2002).

2.3. Parameter regression on independent slopes model data

Climate mapping with PRISM, developed by Oregon State University, in cooperation with the USDA, Natural Resource Conservation Service (NRCS) to improve spatial estimates of climate data. For PRISM, observed precipitation data were collected from 9110 stations across the Nation including the National Weather Service cooperative network, the NRCS SNOTEL network, storage gages, and measurements from snow courses (Daly et al., 1994). The goal of the PRISM model is to explain extreme, complex variations in precipitation that occur in mountainous regions by addressing the spatial scale and pattern of orographic precipitation (Daly et al., 1994) using a digital-elevation model and 30-year-average annual-precipitation values. The PRISM model is recognized by the USDA as the official precipitation map for the United States. The Rocky Mountain region portion of the PRISM model is shown in Fig. 3.

2.4. Spatial statistical data analysis

Measured NADP/NTN and estimated RMS average annual VWM chemical concentrations were combined into a single database, and used to produce maps of nitrate, sulfate, and acidity. Maps of chemical concentration were constructed based on nearest available NADP/NTN wetfall data and estimates of bulk deposition from RMS data.

Surface concentration maps were developed for nitrate, sulfate, and acidity (north of 39° latitude).

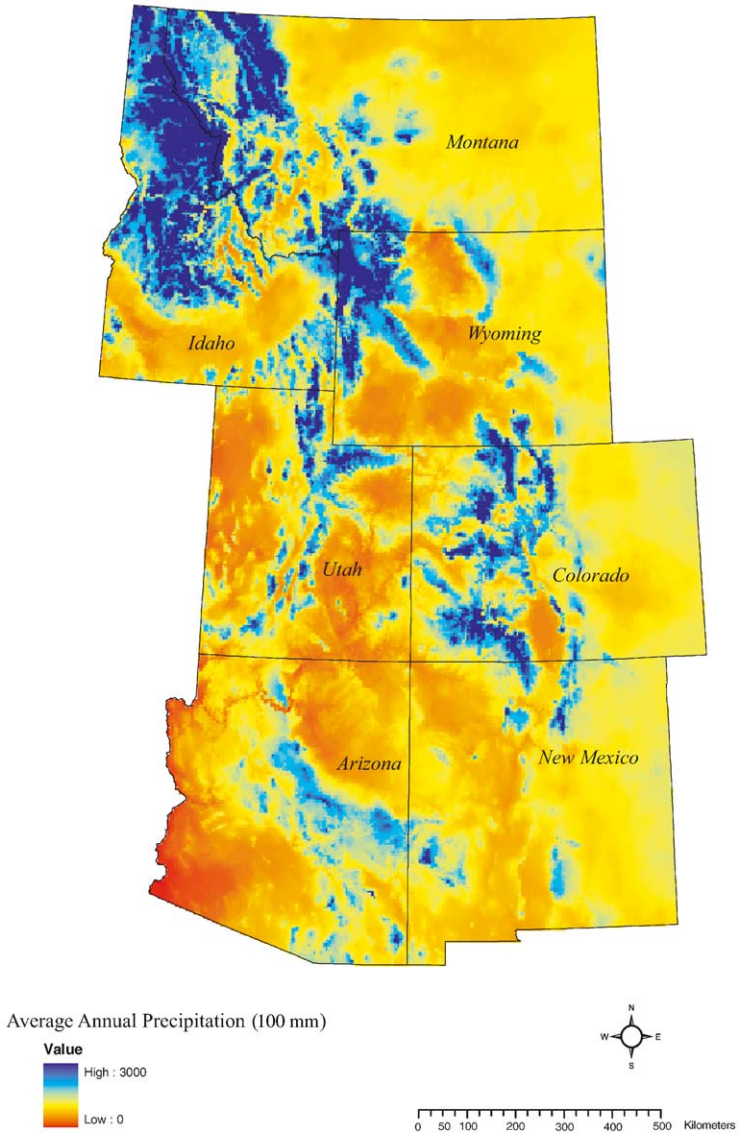

Fig. 3. Thirty-year average annual precipitation data obtained from the PRISM model (modified from Parameter-elevation Regressions on Independent Slopes Model, 2000).

Ordinary kriging, which models the trend surface and incorporates local spatial correlation, was chosen as the interpolation model for the concentration map over other models such as the inverse distance-weighted method, which is more point specific. Kriging produces a trend surface and then attempts to develop more detail at various point locations. When kriging a data set with a low skewness coefficient, a smaller search radius can be used, which produces a more locally accurate trend-surface model. For this particular data set, kriging was selected because concentrations at known locations for nitrate, sulfate, and acidity should be accurate predictors of those nearby.

The normal distribution of data allowed for the application of ordinary kriging in ArcGrid GIS (ESRI, 1999) to generate an estimated surface from known concentrations. Kriging was performed with latitude and longitude as the explanatory factors. Spatial variation is quantified through the development of a semivariogram. The exponential model yielded the best fit between variance and distance. Cross-validation, which uses all of the data to estimate the trend and autocorrelation models, then removes each data location one at a time and predicts the associated value was used to evaluate the results. All data points within a 250-km radius were used to perform interpolation. After

interpolation was performed, artifacts that were created and existed beyond 250-km east and west of the divide were modified to reflect the general trend at that distance. Final average annual atmospheric-deposition maps for each chemical constituent were constructed by multiplying the kriged surface-concentration maps by the precipitation amount estimated from the PRISM model.

3. Results and discussion

3.1. Results

Average annual precipitation amounts in the Rocky Mountains increase as a function of elevation and latitude (Fig. 3). Higher precipitation amounts are observed at higher latitudes. Greater than 1500 mm of precipitation per year are observed in the northwestern mountains of Montana, Idaho, and Wyoming. The mountains in Colorado, Utah, and New Mexico at lower latitudes, receive precipitation amounts of <1500 mm per year. Mountainous areas above 3000 m elevation generally receive at least 800 mm precipitation per year, whereas lower elevation areas nearby may receive as little as 200 mm precipitation per year (Fig. 3).

Concentration maps indicate generally increasing concentration gradients from northwest to southeast along the Continental Divide in the Rocky Mountains for nitrate and sulfate. Acidity shows a more complex pattern. The highest nitrate concentration, 21.5 μeq/l, is at Manitou Springs, in eastern Colorado (Tables 1 and 2), and the range in concentrations is 3.17–21.5 μeq/l. Other high nitrate levels, >15.0 μeq/l, are found in southwest Colorado, southern Utah, northern New Mexico and northern Colorado along the continental divide, northwest Colorado, and the border of Wyoming and Utah.

High sulfate concentrations, >12.0 μeq/l, occur in northwest, southwest, and eastern Colorado, southwest Wyoming, and in the Four Corners region of southern Utah, northern Arizona, northern New Mexico, and southern Colorado (Tables 1 and 2). The range in sulfate concentrations is 3.10–19.3 μeq/l, and a maximum concentration of 19.3 μeq/l was found at Mesa Verde, southwestern Colorado.

Acidity ranges from 3.89 to 16.0 μeq/l; highest concentrations north of 39° latitude were measured at Manitou Springs, in central Colorado (Tables 1 and 2). High concentrations, >12.5, also exist in northern New Mexico, and southwestern Colorado (Tables 1 and 2), but were not included in the deposition map because of lack of comparability between the NADP/NTN and RMS acidity data south of 39° latitude (Clow et al., 2002).

The average annual deposition maps (for 1992–1999) indicate that there are regions of high atmospheric deposition in the Rocky Mountains (Figs. 4–6). Highest nitrate (2.50–3.00 kg/ha N) and sulfate (10.0–12.0 kg/ha SO_4) deposition is in the Park Range, northwest Colorado. High nitrate (2.00–2.50 kg/ha N) and sulfate (8.00–10.0 kg/ha SO_4) deposition is found along the Front Range of Colorado and the Wasatch Front in northeastern Utah (Figs. 4 and 5), which are both adjacent to large urban corridors. Other areas of high nitrate and sulfate include southwestern Colorado and northern Montana (Figs. 4 and 5). Relatively high acid deposition (0.10–0.25 kg/ha H^+) is present in northwestern Colorado, the Colorado Front Range, south-central and northwestern Wyoming, and northwestern Montana (Fig. 6).

3.2. Evaluation of methods: modeling

The use of the RMS snowpack-chemistry data improved the spatial distribution of concentration data and deposition estimates for high-elevation areas for which little or no NADP/NTN data are available. The combined data set is not greatly skewed. The skewness coefficient for annual concentrations is 0.26 for nitrate, 0.05 for sulfate, and 0.75 for acidity. Furthermore, there is minimal variation along short distances, particularly because the majority of the samples are near the Continental Divide. One difficulty in producing an accurate surface-trend model stems from trying to interpolate points a large distance east or west of the mountain ranges where little to no data are available. Although there is less than optimal precision along the outlying edges of the concentration maps, when compared with NADP/NTN concentration maps (NADP/NTN, 1999), there was a good agreement. Boundary conditions are a problem with all spatial modeling and, in this case, the large region selected for the model allowed for variation along the edges in low-lying areas adjacent to mountain ranges. The resultant deposition trend along the Continental Divide where there is high deposition and high sensitivity to deposition was minimally affected by variability along boundaries and is the most accurate.

Cross validation results for nitrate, sulfate and acidity measured versus predicted concentrations yielded correlations $r^2 \geqslant 0.5$. The models are the most accurate predictors where the variability is low across short distances, however, where extreme elevation differences exist, incorporating precipitation and elevation into the final model decreases local variability caused by rapid changes in elevation. In other words, concentration data may be somewhat variable or unrepresentative near boundaries, but natural geographic and topological factors may be accommodated by multiplying the kriged

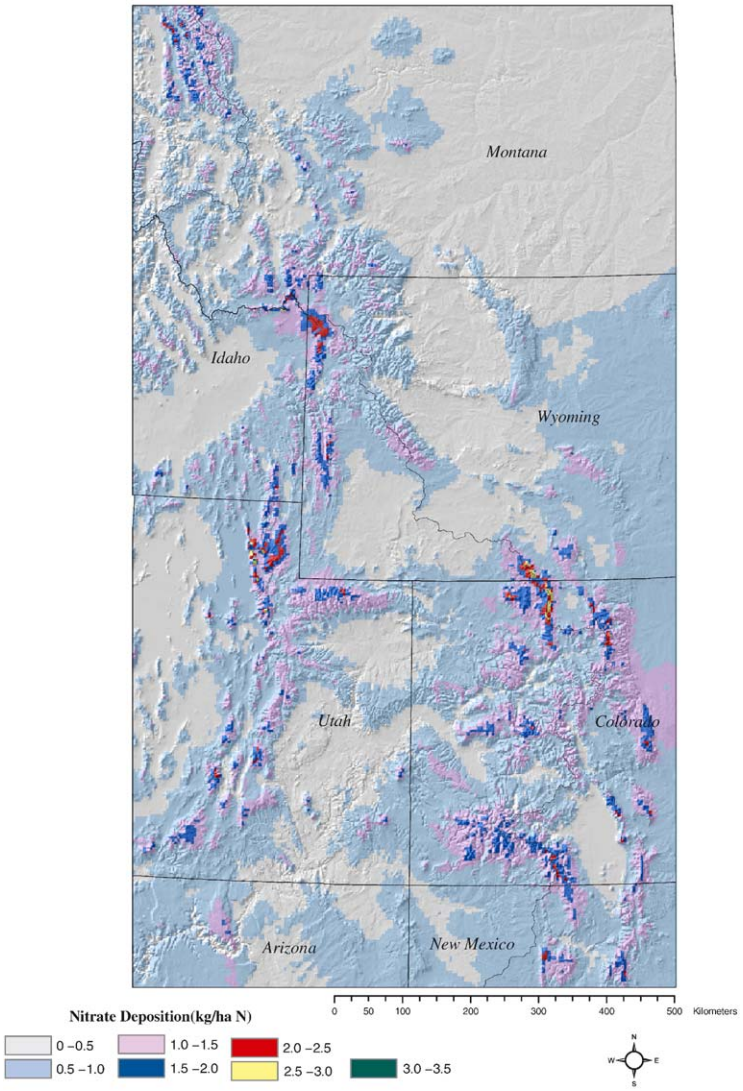

Fig. 4. Average annual nitrate deposition for the Rocky Mountains, 1992–1999.

concentration data with precipitation data from the PRISM model.

3.3. Regional variation in atmospheric deposition

Spatial variations in atmospheric deposition of acid solutes are driven by precipitation amount and superimposed on that is concentration, thus deposition does not necessarily reflect variations in concentration alone. Deposition maps indicate that acid solute deposition is greater at high elevations than mid- to low elevations, likely due to orographically enhanced precipitation amounts at high elevations. Sources contributing to high deposition include local and regional sources. Local sources of pollution may cause some small variation in trends, while regional pollution may result in a larger trend variation.

A number of factors confound reliable interpolation of atmospheric deposition using only the NADP/NTN data available for the Rocky Mountain region. The low density of NADP/NTN sites in the Rocky Mountains fails to capture spatial patterns in precipitation amount (caused by elevation) which has an impact on total deposition. The use of PRISM greatly improves precipitation estimates by incorporating many more precipitation sites in the model and including elevation in the interpolation. In addition, the density of data is greatly improved by adding RMS concentrations, as there are only 29 NADP/NTN sites >3000 m in the entire Rocky Mountain region with more than 3 years of

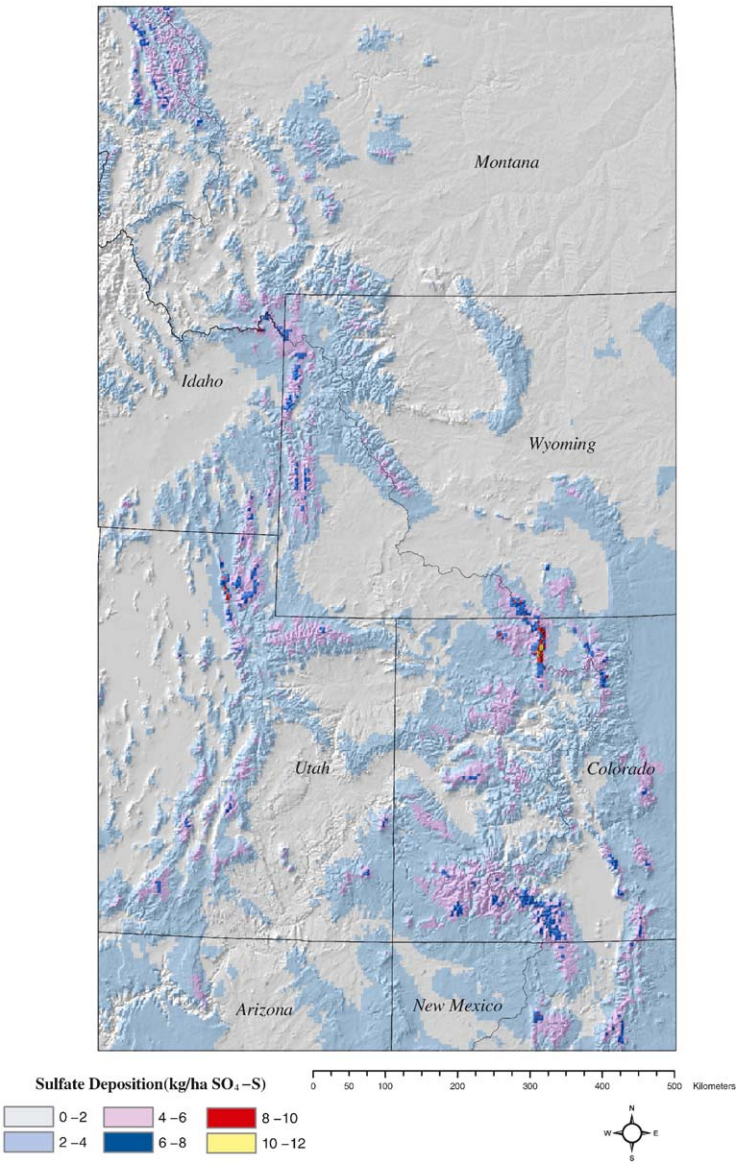

Fig. 5. Average annual sulfate deposition for the Rocky Mountains, 1992–1999.

data, especially in areas where there are only 1–3 NADP sites >3000 m with a long-term record for an entire state.

There is a regional pattern in acid solute deposition, with increasing deposition from the northwest to southeast. Concentration maps also indicate an increasing regional trend from northwest to southeast. Results are consistent with those of Turk et al. (2001), who found an increasing concentration trend from north to south. The data set used by Turk et al. (2001) did not incorporate the NADP/NTN sites, which tend to be at lower elevations, nor did it incorporate a detailed precipitation map. This regional pattern reflects regional patterns in emissions (Mast et al., 2001).

Large nitrate and sulfate concentrations and deposition (hot-spots) tend to be in northern Colorado and are probably a result of emissions of SO_2 and NO_x from coal-fired power plants in northwestern Colorado (Turk and Campbell, 1997) and southwestern Wyoming (Mast et al., 2001). Large amounts of deposition of nitrate, sulfate, and acidity also are found in southwestern Montana and South Pass, close to the divide in central Wyoming.

Overall, determination of the spatial distribution of atmospheric deposition for the Rocky Mountain region

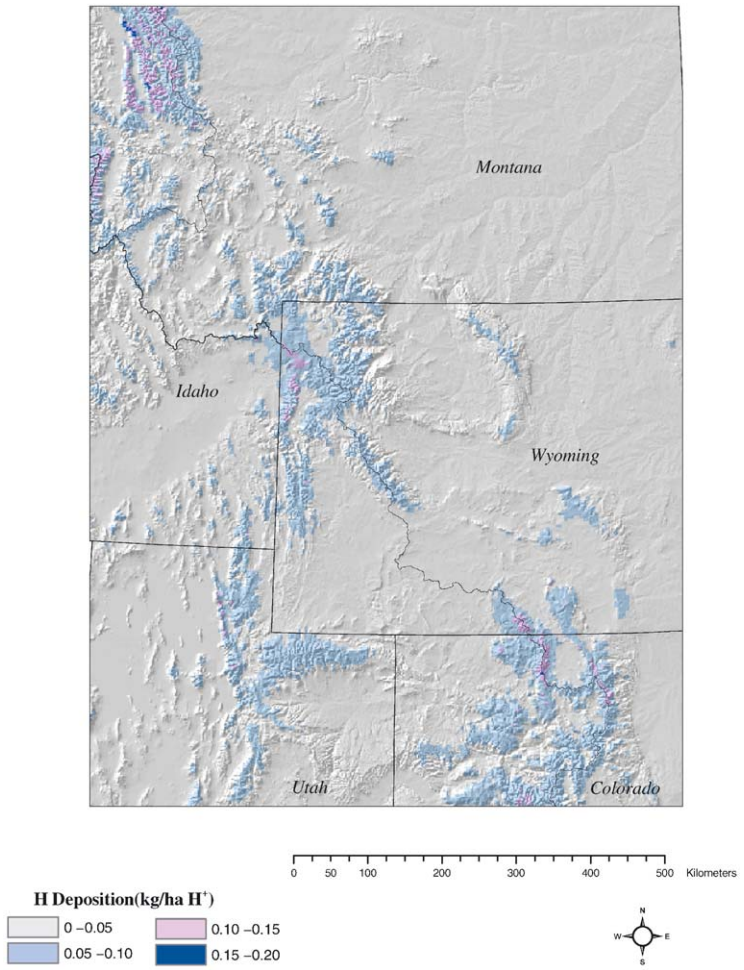

Fig. 6. Average annual H^+ deposition North 39° latitude for the Rocky Mountains, 1992–1999.

was substantially improved by combining three ancillary data sets to address problems that have been identified but not resolved in previous studies that used only a single data set. Maps are provided on a 1-km grid that estimates atmospheric deposition for areas with little deposition chemistry data by identifying overall spatial trends in data. These maps can provide resource managers with visual, high-resolution, estimates of regional patterns in atmospheric deposition and highlight areas where concern about atmospheric deposition may warrant additional investigations.

References

Baron, J.S., Rueth, H.M., Wolfe, A.M., Nydick, K.R., Allstott, E.J., Minear, J.T., Moraska, B., 2000. Ecosystem responses to nitrogen deposition in the Colorado Front Range. Ecosystems 36, 89–99.

Burns, D.A., 2003. Atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming—a review and new analysis of past study results. Atmospheric Environment 37, 921–932.

Campbell, D.H., Baron, J.S., Tonnessen, K.A., Brooks, P.D., Schuster, P.F., 2000. Controls on nitrogen flux in alpine/subalpine watersheds of Colorado. Water Resources Research 36, 37–47.

Clow, D.W., Sueker, J.K., 2000. Relations between basin characteristics and stream-water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado. Water Resources Research 36, 49–61.

Clow, D.W., Ingersoll, G.P., Mast, M.A., Turk, J.T., Campbell, D.H., 2002. Comparison of snowpack and winter wet-deposition chemistry in the Rocky Mountains, USA: implications for winter dry deposition. Atmospheric Environment 36, 2337–2348.

Daly, C., Neilson, R.P., Phillips, D.L., 1994. A statistical-topographic model for mapping climatological precipitation over mountainous terrain. Journal of Applied Meteorology 33, 140–158.

Environmental Systems Research Institute (ESRI), 1999. Using Grid with Arc/Info, Vol. 2. ESRI, Inc.

Fenn, M.E., Haeuber, R., Tonnessen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., Sickman, J.O., 2003. Nitrogen emissions, deposition, and monitoring in the Western United States. BioScience 53 (4), 391–403.

Gordon, J.D., 1999. External quality-assurance results for the National Atmospheric Deposition Program/National Trends Network, 1995–1996. US Geological Survey Water-Resources Investigations Report 99-4072, 69pp.

Ingersoll, G.P., Turk, J.T., Mast, M.A., Clow, D.W., Campbell, D.H., Bailey, Z.C., 2002. Rocky Mountain snowpack chemistry network: history, methods, and the importance of monitoring mountain ecosystems. US Geological Survey Open-File 01-466.

Mast, M.A., Turk, J.T., Ingersoll, G.P., Clow, D.W., Kester, C.L., 2001. Use of stable sulfur isotopes to identify sources of sulfate in Rocky Mountain snowpacks. Atmospheric Environment 35, 3303–3313.

National Atmospheric Deposition Program/National Trends Network (NADP/NTN), 1999. Illinois State Water Survey, Urbana, IL. http://nadp.sws.uiuc.edu/.

Ollinger, S.V., Aber, J.D., Lovett, G.M., Millham, S.E., Lathrop, R.G., Ellis, J.M., 1993. A spatial model of atmospheric deposition for the northeastern US. Ecological Applications 3 (3), 459–472.

Parameter-elevation Regressions on Independent Slopes Model, 2000. Oregon Climate Center, Oregon State University, Oregon. http://www.ocs.orst.edu/prism/.

Peden, M.E., 1986. Development of standard methods for collection and analysis of precipitation. Methods for collection and analysis of precipitation, Champaign, Illinois State Water Survey Contract Report 381, pp. 19–21.

Peterson, D.L., Sullivan, T.J., Eilers, J.M., Brace, S., 1998. Assessment of air quality and air pollutant impacts in National Parks of the Rocky Mountains and Northern Great Plain. NPS Air Resources Division, Denver, CO.

See, R.B., Willoughby, T.C., Brooks, M.H., Gordon, J.D., 1990. Programs and analytical methods for the US Geological Survey Acid Rain Quality-Assurance Project. US Geological Survey Water-Resources Investigations Report 90–4029.

Turk, J.T., Campbell, D.H., 1997. Are aquatic resources of the Mt. Zirkel wilderness area affected by acid deposition and what will emissions reductions at the local power plants do? USGS Factsheet 043–97.

Turk, J.T., Taylor, H.E., Ingersoll, G.P., Tonnessen, K.A., Clow, D.W., Mast, M.A., Campbell, D.H., Melack, J.M., 2001. Major-ion chemistry of the Rocky Mountain snowpack, USA. Atmospheric Environment 35, 3957–3966.

Vautz, W., Busch, A.U., Urfer, W., Klockow, D., 2003. A statistical approach to estimate spatial distributions of wet deposition in Germany. Water, Air, and Soil Pollution 145, 215–238.

Williams, M.W., Baron, J., Caine, N., Sommerfeld, R., 1996. Nitrogen saturation in the Rocky Mountains. Environmental Science and Technology 30, 640–646.