Effects of Emission Reductions at the Hayden Powerplant on Precipitation, Snowpack, and Surface-Water Chemistry in the Mount Zirkel Wilderness Area, Colorado, 1995–2003

By M. Alisa Mast, Donald H. Campbell, and George P. Ingersoll

Prepared in cooperation with the
Colorado Department of Public Health and Environment

Scientific Investigations Report 2005–5167

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
Gale A. Norton, Secretary

U.S. Geological Survey
P. Patrick Leahy, Acting Director

U.S. Geological Survey, Reston, Virginia: 2005

For sale by U.S. Geological Survey, Information Services
Box 25286, Denver Federal Center
Denver, CO 80225

For more information about the USGS and its products:
Telephone: 1-888-ASK-USGS
World Wide Web: http://www.usgs.gov/

Suggested citation:
Mast, M.A., Campbell, D.H., and Ingersoll, G.P., 2005, Effects of emission reductions at the Hayden powerplant on precipitation, snowpack, and surface-water chemistry in the Mount Zirkel Wilderness Area, Colorado, 1995–2003: U.S. Geological Survey Scientific Investigations Report 2005–5167, 32 p.

Contents

Figures

Tables

Conversion Factors

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
hectare (ha)	2.471	acre
liter (L)	0.2642	gallon
kilogram (kg)	2.205	pound

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Elevation, as used in this report, refers to distance above the vertical datum.

Concentrations of chemical constituents in water are presented in microequivalents per liter (µeq/L).

Effects of Emission Reductions at the Hayden Powerplant on Precipitation, Snowpack, and Surface-Water Chemistry in the Mount Zirkel Wilderness Area, Colorado, 1995–2003

By M. Alisa Mast, Donald H. Campbell, and George P. Ingersoll

Abstract

Precipitation, snowpack, and surface-water samples collected during 1995–2003 were analyzed to evaluate environmental effects of emission reductions at the Hayden powerplant on the Mount Zirkel Wilderness Area. The Hayden powerplant, one of two large coal-fired powerplants in the Yampa Valley, was retrofitted with control systems during late 1998 and 1999 to reduce emissions of sulfur dioxide and nitrogen oxide—the primary precursors of haze and acidic precipitation. The U.S. Geological Survey, in cooperation with the Colorado Department of Public Health and Environment, evaluated three water-chemistry data sets: wet-only precipitation chemistry from the National Atmospheric Deposition Program, snowpack chemistry from the Rocky Mountain snowpack network, and surface-water chemistry from a U.S. Geological Survey long-term lakes monitoring program. Concentrations and deposition rates of selected constituents were compared for the periods before and after emission reductions at the Hayden powerplant. Data collected during 1995–98 were used to represent the pre-control period, and data collected during 2000–2003 were used to represent the post-control period.

Ten stations in the National Atmospheric Deposition Program were evaluated including two that were directly downwind from the Hayden powerplant (Dry Lake and Buffalo Pass) and eight that were upwind or distant (more than 100 kilometers) from the powerplant. Precipitation amount at all 10 stations was lower in the post-control period than the pre-control period as a result of a regional drought that persisted during the post-control period. In contrast to precipitation amount, there was no consistent pattern of change in sulfate concentrations between periods, indicating that the drought did not have a concentrating effect on sulfate or that trends in regional sulfur dioxide emissions masked its influence. Sulfate concentrations increased at three stations between periods, remained the same at three stations, and decreased at four stations. The largest change in average annual sulfate concentrations occurred at the two precipitation stations downwind from the Hayden powerplant, decreasing by 3.3 microequivalents per liter at Dry Lake and by 2.2 microequivalents per liter at Buffalo Pass. Declines in annual sulfate deposition also were greater at Dry Lake (3.4 kilograms per hectare) and Buffalo Pass (3.3 kilograms per hectare) than at the other stations, which ranged from 0.2 to 1.7 kilograms per hectare. These results indicate that emission reductions at the Hayden powerplant have been a factor in declines in atmospheric deposition of sulfate downwind from the powerplant. In contrast to sulfate, nitrate, ammonium, and base-cation concentrations were higher in the post-control period than the pre-control period at all 10 stations, most likely due to a concentrating effect of the drought.

Twenty-two snowpack sites in the Rocky Mountain snowpack network were evaluated including 4 sites that were located directly downwind from the Hayden powerplant and 18 sites that were upwind or distant (as much as 200 kilometers) from the powerplant. The water content of the snowpack at maximum accumulation was lower in the post-control period than the pre-control period, reflecting the regional drought. Although there were small declines in snowpack sulfate concentrations at the downwind stations between the pre- and post-control periods, the difference was not statistically significant, indicating emission reductions had a weaker effect on snowpack chemistry than precipitation chemistry. Sulfate deposition decreased at all four downwind sites in the post-control period, primarily reflecting both lower water content and concentrations in the snowpack. As observed at the precipitation stations, nitrate, ammonium, and base-cation concentrations at all 22 sites were significantly higher in the post-control period than the pre-control period, reflecting drier conditions caused by drought.

The chemistry at six surface-water sites in and near the Mount Zirkel Wilderness Area and five control sites in the Flat Tops Wilderness Area was examined. No response to emission reductions was detectable in chemistry of the surface water in the Mount Zirkel Wilderness Area. Detection of a response to changes in emissions and deposition in the lake-chemistry data may have been confounded by drought conditions during the period after emission reductions occurred. The magnitude of reduced sulfate in atmospheric deposition indicates that at some time in the future, a reduction in lake sulfate attributable

to Yampa Valley emission reduction should be detectable. The trend of decreasing sulfur dioxide emissions throughout western North America over the past 20 years is reflected in reduced concentrations of sulfate in lakes that were part of this study, as well as other lakes in the Rocky Mountains. However, detection of the surface-water response to changes in deposition requires a sufficiently long record to minimize effects of climate variability and to allow for lag time as sulfate moves through storage in soil, ground water, and lake reservoirs.

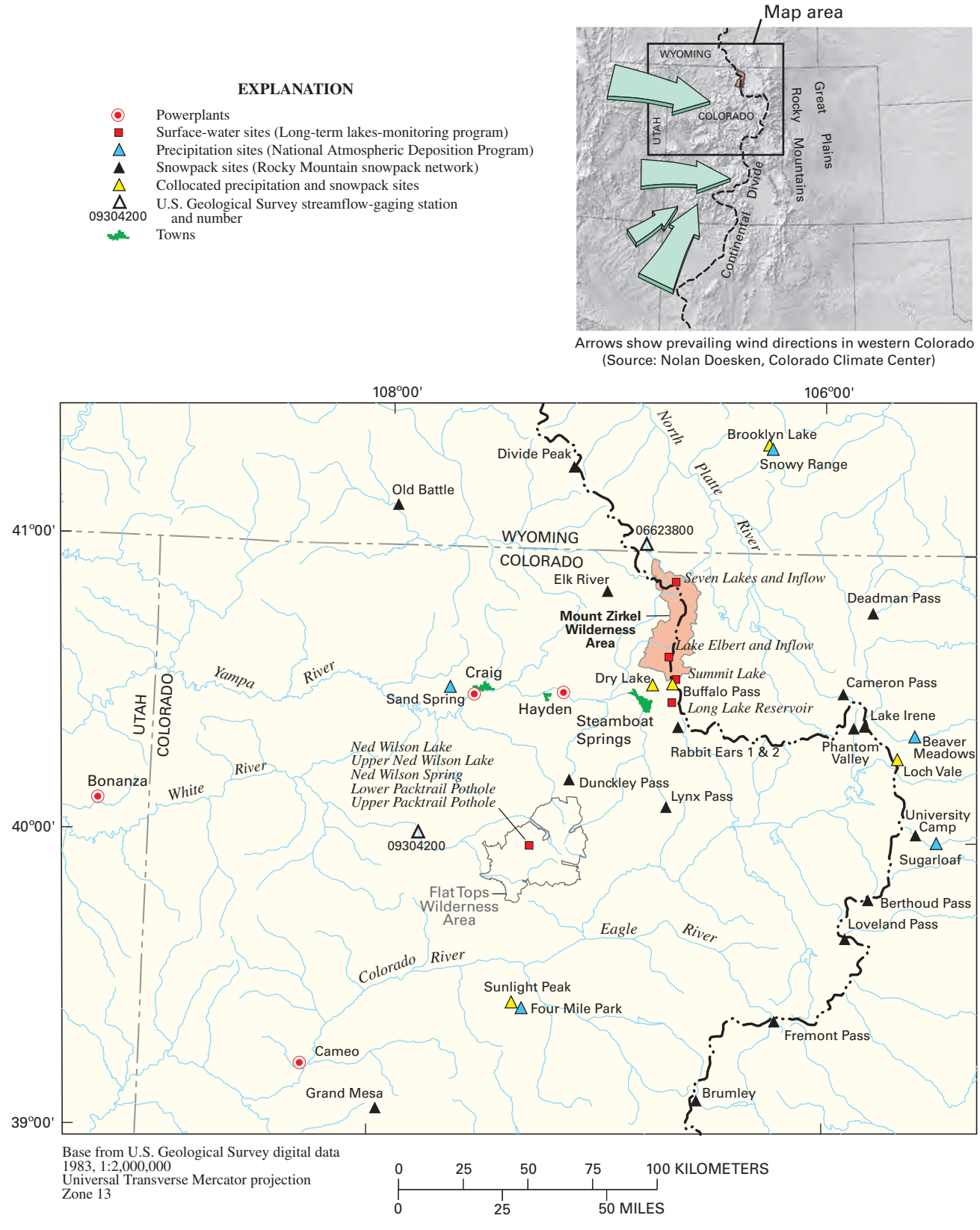
Introduction

The Mount Zirkel Wilderness Area (MZWA) straddles the Continental Divide in the Routt National Forest in northwestern Colorado (fig. 1). The MZWA lies at the headwaters of the Yampa Valley, which extends to the west approximately 165 km along the course of the Yampa River. The Yampa Valley lies within Routt and Moffat Counties and contains the towns of Steamboat Springs, Hayden, and Craig. The permanent population of the Yampa Valley is about 27,100 (Colorado Department of Public Health and Environment, written commun., 2004) but is augmented substantially during winter by skiers and during summer by outdoor enthusiasts. The major economic interests in the Yampa Valley include tourism, cattle ranching, coal mining, and electric power generation. Most of the power is generated at two large coal-fired powerplants that, because of the prevailing westerly winds, are located upwind from the MZWA (fig. 1). The Hayden powerplant, which consists of one 184-megawatt (MW) generating unit and one 262-MW generating unit, is located near the town of Hayden and is approximately 30 km west from the closest wilderness boundary. The Craig powerplant, which consists of three 450-MW generating units, is located near the town of Craig and is approximately 60 km west from the closest wilderness boundary.

In 1993, the U.S. Department of Agriculture (USDA) Forest Service asserted that sulfur dioxide and nitrogen oxide emissions from the Craig and Hayden powerplants were contributing to visibility impairment in the MZWA (Colorado Department of Health and Environment, 2004). The MZWA is 1 of 156 Class I wilderness areas in the United States in which visibility is protected by law under the Clean Air Act Amendments of 1977. Visibility impairment typically is attributable to a mix of small particles consisting of sulfate and nitrate aerosols, which are formed in the atmosphere from gaseous sulfur dioxide and nitrogen oxide emissions, with larger particulates such as organic and elemental carbon (soot) and road dust. In 1994, the Colorado Department of Public Health and Environment commissioned the Mount Zirkel Visibility Study to determine the cause of visibility impairment in the MZWA (Watson and others, 1996). The study concluded that the major and most frequent contributors to visibility impairment in the MZWA were from a combination of motor vehicle exhaust, vegetative burning, and regional secondary ammonium sulfate. These contributors were for the most part of regional origins, resulting from a mixture of emissions from source areas, which could be hundreds of kilometers distant from the MZWA. Watson and others (1996) also concluded that sulfate haze from the Hayden and Craig powerplants occasionally entered the MZWA and, along with regional haze, contributed to visibility impairment.

The USDA Forest Service also had concerns that powerplant emissions might be associated with acidic precipitation, which could cause aquatic and terrestrial ecosystem effects in the MZWA. Oxidation of gaseous sulfur dioxide and nitrogen oxide in the atmosphere forms sulfuric and nitric acids, which are the primary components of acidic precipitation (Driscoll and others, 2001). Turk and Campbell (1997) reported that for snowpack chemistry sites in Colorado, Wyoming, and Montana, the highest concentrations of sulfate, nitrate, and acidity were measured at sites in and near the MZWA, perhaps due to emissions from the upwind powerplants. Although lakes and streams in the MZWA currently (2005) are not acidic, they are especially sensitive to acidic precipitation because they drain bedrock and soil types that have little capacity to buffer acidic inputs. In addition, snowmelt-dominated ecosystems such as those in the MZWA are subject to periods of episodic acidification during the early stages of snowmelt when high concentrations of acidity can be released from the snowpack (Turk and Campbell, 1997). Acidic precipitation also results in excess nitrogen deposition to high-elevation ecosystems, which can eventually lead to nitrogen saturation, a condition where ecosystems can no longer utilize excess nitrogen (Williams and others, 1996). Possible ecological effects of acidification and nitrogen saturation include changes in surface-water chemistry, shifts in the abundance and diversity of aquatic species, and changes in soil and forest biogeochemistry (Burns, 2002).

Due to concerns about impairment of air-quality-related values in the MZWA, an agreement was made between the owners of the Hayden powerplant and the USDA Forest Service, the State of Colorado, the Sierra Club, and the U.S. Environmental Protection Agency (USEPA) to install new emissions control equipment on the two generating units at the powerplant. Installation of gas and particulate control systems for one of the units began during fall of 1998, and installation of systems for the other unit began during the spring of 1999. Both generating units were back online by November 1999. Following installation of emission controls at the Hayden powerplant, there were substantial decreases in both sulfur dioxide and nitrogen oxide emissions (Colorado Department of Public Health and Environment, written commun., 2005). Average annual sulfur dioxide emissions at the Hayden powerplant declined by nearly 83 percent after emission controls were installed, and combined emissions from the Hayden and Craig powerplants were reduced by 48 percent (fig. 2). Decreases in nitrogen oxide emissions were more modest than those for sulfur dioxide. Average annual nitrogen oxide emissions were reduced by about 41 percent at the Hayden powerplant but only 7 percent for the combined emissions due to a slight increase in nitrogen oxide emissions at the Craig powerplant. In 2001, a similar



Arrows show prevailing wind directions in western Colorado
(Source: Nolan Doesken, Colorado Climate Center)

Figure 1. Location of study area with precipitation, snowpack, and surface-water sites.

agreement was finalized to install new control equipment at two of the three generating units at the Craig powerplant. The tie-in of the upgrades at the Craig powerplant began in September 2003 and is scheduled to be completed in 2005. The Colorado Department of Public Health and Environment anticipates that recent emission reductions at the Hayden powerplant and future reductions at the Craig powerplant should reduce visibility impairment in the MZWA and improve the chemistry of precipitation and surface water in areas downwind from the powerplants (Colorado Department of Public Health and Environment, 2004).

Purpose and Scope

In 2004, the U.S. Geological Survey (USGS), in cooperation with the Colorado Department of Public Health and Environment, conducted a study to evaluate the effects of emission reductions at the Hayden powerplant on the chemistry of precipitation, snowpack, and surface water in areas downwind from the powerplant including the Mount Zirkel Wilderness Area. Precipitation chemistry data were obtained from the National Atmospheric Deposition Program (NADP), which is a national network that has been in operation since the early 1980s and has more than 220 precipitation stations. Snowpack chemistry data were obtained from the Rocky Mountain Snowpack (RMS) network, which is a monitoring network of over 50 snow-sampling sites in the Rocky Mountain region and has been operated by the USGS since 1993 (Turk and others, 1992; Ingersoll, 1995; Ingersoll and others, 2002). Surface-water chemistry data were obtained from a USGS long-term lakes-monitoring program that has monitored lake chemistry in several wilderness areas in Colorado since the mid-1980s (Turk and others, 1993). This report compares chemical constituent concentrations and deposition rates (for precipitation and snowpack) for periods before and after installation of emission controls at the Hayden powerplant at selected sites from each of the three monitoring networks. Data collected during 1995–98 were used to represent the "pre-control" period and data collected during 2000–2003 were used to represent the

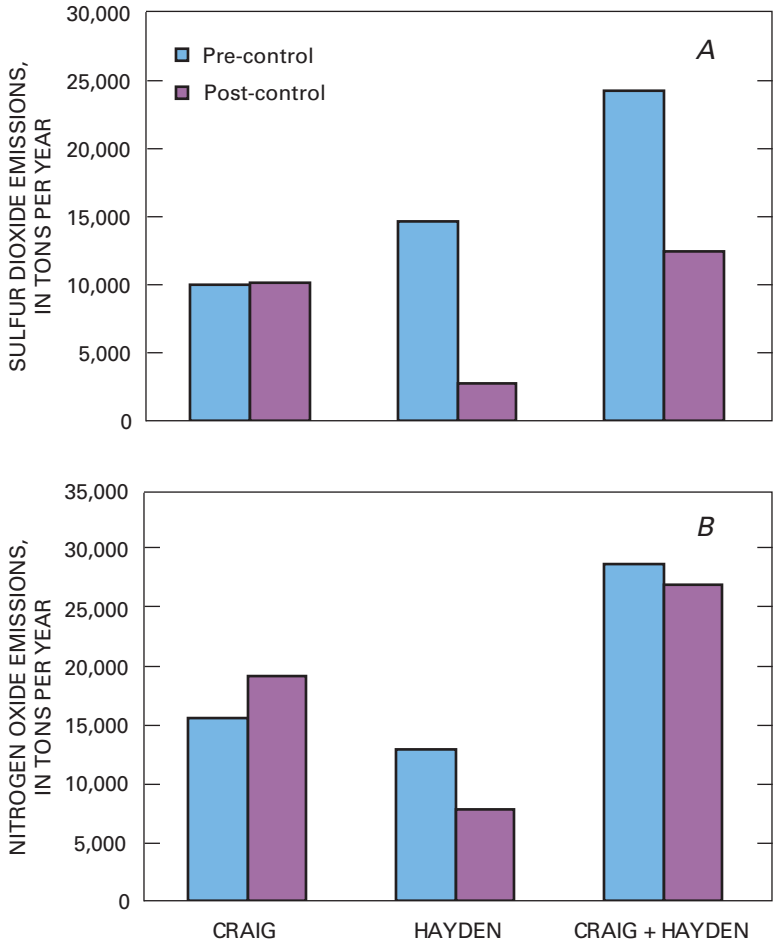


Figure 2. Average annual (*A*) sulfur dioxide and (*B*) nitrogen oxide emissions at the Hayden and Craig powerplants in Colorado before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

"post-control" period. The primary focus of this report is on sulfate and nitrate, which are the dominant oxidation products of sulfur dioxide and nitrogen oxide in the atmosphere. The report also discusses ammonium, base cations (calcium plus magnesium), hydrogen ion (precipitation only), and acid-neutralizing capacity (surface water only), which are constituents and properties that are indicative of the acid/base status of precipitation and surface water.

Acknowledgments

The authors thank Dan Ely and Patrick Reddy of the Colorado Department of Public Health and Environment for their support of this project. The authors also acknowledge the contributions of the following USGS employees for assistance in completing this report. John T. Turk (retired) and Dave W. Clow for technical reviews, Mary A. Kidd for editorial review, Robert Olmstead for preparation of figures, and Joy Monson for preparation of layout and text. Additional support for this project was provided by the USDA Forest Service.

Effects of Emission Reductions on Precipitation, Snowpack, and Surface-Water Chemistry

Previously collected chemical data for precipitation, snowpack, and surface water from three monitoring networks were used in this study. Methods of data collection and results of the data analysis for each of the three networks are discussed in separate sections of this report. Site names and locations for all three networks are given in table 1 and figure 1.

Precipitation Chemistry

This section compares precipitation chemistry at NADP stations before (1995–98) and after (2000–2003) emission reductions at the Hayden powerplant. Chemical data were analyzed for 10 NADP stations located within 150 km of the Hayden powerplant (fig. 1 and table 1). Dry Lake and Buffalo Pass, which are along the southern boundary of the MZWA, are directly downwind from the powerplant and should be the most sensitive to changes in emissions. The Sand Spring station also is close (45 km) to the powerplant but is situated upwind from Hayden and receives much less precipitation than Dry Lake and Buffalo Pass because of its lower elevation (table 1). The remaining seven stations are more distant from the Hayden powerplant (more than 120 km) and should be minimally affected by the powerplant emissions. These stations were selected as background sites to evaluate regional patterns in precipitation chemistry over the same period of study. Brooklyn Lake and Snowy Range are northeast of the Hayden powerplant on the east side of the Snowy Range in

Table 1. Site names and locations of precipitation, snowpack, and surface-water sampling sites in Colorado and Wyoming included in the study.

[NADP, National Atmospheric Deposition Program; RMS, Rocky Mountain Snowpack network; elevation in meters; latitude and longitude in decimal degrees; site locations in figure 1]

Site name	Latitude	Longitude	Elevation
Precipitation stations (NADP)			
Beaver Meadows	40.364	105.582	2,490
Brooklyn Lake[a]	41.365	106.241	3,212
Buffalo Pass[a]	40.538	106.676	3,234
Dry Lake[a]	40.535	106.780	2,527
Four Mile Park	39.403	107.341	2,502
Loch Vale[a]	40.288	105.663	3,159
Sand Spring	40.508	107.702	1,998
Snowy Range	41.376	106.259	3,286
Sugarloaf	39.994	105.480	2,524
Sunlight Peak[a]	39.427	107.380	3,206
Snowpack sites (RMS)			
Berthoud Pass	39.800	105.783	3,444
Brooklyn Lake[a]	41.367	106.233	3,115
Brumley	39.083	106.542	3,231
Buffalo Pass[a]	40.533	106.667	3,139
Cameron Pass	40.517	105.900	3,110
Deadman Pass	40.800	105.767	3,109
Divide Peak	41.300	107.167	2,701
Dry Lake[a]	40.533	106.783	2,560
Dunckley Pass	40.200	107.150	2,987
Elk River	40.850	106.967	2,621
Fremont Pass	39.367	106.200	3,475
Grand Mesa	39.033	107.978	3,103
Lake Irene	40.411	105.813	3,243
Loch Vale[a]	40.290	105.666	3,216
Loveland Pass	39.667	105.892	3,597
Lynx Pass	40.113	106.700	2,731
Old Battle	41.150	107.967	3,024
Phantom Valley	40.397	105.848	2,752
Rabbit Ears 1	40.399	106.657	2,938
Rabbit Ears 2	40.400	106.657	2,938
Sunlight Peak[a]	39.421	107.375	3,200
University Camp	40.033	105.567	3,139
Surface-water sites			
Lake Elbert	40.634	106.708	3,289
Lake Elbert Inflow	40.634	106.708	3,289
Long Lake Reservoir	40.476	106.691	3,002
Seven Lakes	40.896	106.681	3,271
Seven Lakes Inflow	40.896	106.681	3,271
Summit Lake	40.546	106.681	3,144
Lower Packtrail Pothole	39.968	107.324	3,379
Ned Wilson Lake	39.962	107.324	3,383
Ned Wilson Spring	39.958	107.325	3,365
Upper Ned Wilson Lake	39.963	107.324	3,386
Upper Packtrail Pothole	39.966	107.324	3,380

[a]Collocated NADP stations and RMS sites.

southeastern Wyoming. Loch Vale, Sugar Loaf, and Beaver Meadows are east of the Hayden powerplant on the east side of the Colorado Front Range. Four Mile Park and Sunlight Peak are south of the Hayden powerplant at the northern end of the Elk Mountains in central Colorado. Five of the NADP stations (Brooklyn Lake, Buffalo Pass, Dry Lake, Loch Vale, and Sunlight Peak) also are collocated with RMS sites (fig. 1) discussed in the "Snowpack Chemistry" section of this report.

Data Collection and Analysis

Each NADP station is equipped with a wet-only precipitation collector and an event-recording rain gage. The wet-only collector samples precipitation only when it rains or snows and is closed to the atmosphere during dry periods. A weekly composite sample is collected each Tuesday by an NADP site operator and shipped to the Illinois Central Laboratory in Champaign, Illinois, for analysis of pH, specific conductance, and concentrations of sulfate, nitrate, ammonium, chloride, calcium, magnesium, potassium, and sodium. More detailed information on sample-collection protocols, analytical methods, and quality-assurance procedures used by the NADP can be obtained from the NADP Web site at *http://nadp.sws.uiuc.edu/*.

Chemical concentration data and precipitation amount for the 10 stations selected for this study were retrieved from the NADP Web site in June 2004. Average annual and seasonal concentrations in microequivalents per liter (μeq/L) and average annual deposition in kilograms per hectare (kg/ha) were calculated for the pre-control and post-control periods at each of the 10 NADP stations and compared graphically. Concentrations were averaged by volume-weighting based on the precipitation amount associated with each weekly sample. Annual deposition rates were calculated by multiplying annual precipitation amount by the average annual concentration and a factor to convert the results to units of kilograms per hectare. All annual data were computed over the water year, defined as October 1 through September 30. The seasonal periods were defined as fall (September–November), winter (December–February), spring (March–May), and summer (June–August). Statistical comparisons of precipitation amount and concentrations in the pre- and post-control periods were made using the nonparametric Wilcoxon signed-rank test (Helsel and Hirsch, 1992). The p-value is reported to provide information on the level of significance of the statistical test. The difference in concentration or precipitation between the two groups was considered to be statistically significant if the p-value of the test was less than 0.05.

Precipitation Amount

Average annual precipitation amount was lower during the post-control period compared to the pre-control period at all 10 NADP stations (fig. 3*A*). The difference was statistically significant (p=0.002) and was caused by above-normal precipitation in the pre-control period combined with drier conditions in the post-control period caused by regional drought. In the pre-control period, average annual precipitation at all stations was 21 percent above the long-term average (1988–2003) compared to 11 percent below the long-term average in the post-control period (long-term data obtained from *http://nadp.sws.uiuc.edu/*). At the individual stations, precipitation in the post-control period was lower than the pre-control period by as little as 15 percent at the Snowy Range station in southeastern Wyoming to as much as 36 percent at the Loch Vale station in the Colorado Front Range. At the two downwind stations, annual precipitation was 31 percent lower at Dry Lake and 24 percent lower at Buffalo Pass in the post-control period. Precipitation amount broken out by season (fall, winter, spring, summer) showed a pattern similar to annual precipitation, indicating the drought persisted through all seasons of the year (fig. 3*B–E*). The only exceptions were the Sand Spring and Snowy Range stations, which had slightly higher winter precipitation in the post-control period compared to the pre-control period. At most NADP stations, the drought had the strongest effect during the summer months. At Dry Lake, for example, summer precipitation was 46 percent lower in the post-control period than in the pre-control period compared to winter precipitation, which was 24 percent lower. Buffalo Pass showed a similar pattern with 41 percent less summer precipitation in the post-control period compared to 15 percent less during winter.

Chemical Constituent Concentrations and Deposition Rates

Sulfate.—In contrast to precipitation amount, there was no significant difference (p=0.492) in annual sulfate concentrations between the pre- and post-control periods for the 10 NADP stations (fig. 4*A*). Because chemical constituent concentrations in precipitation commonly are inversely correlated with precipitation amount, the observed pattern in sulfate concentrations may indicate that the drought did not have a concentrating effect on sulfate concentrations in the post-control period. Alternatively, it is possible that other factors may have masked the concentrating effect of the drought. Data from the USEPA Clean Air Markets Program (*http://cfpub.epa.gov/gdm/*) indicates sulfur dioxide emissions from powerplants and other large stationary sources in Colorado declined by about 20 percent statewide between 1995 and 2003. These regional declines in sulfur dioxide emissions may have caused sulfate concentrations in precipitation to decrease, thus offsetting the increase in concentrations caused by the drought during the post-control period.

Examination of annual sulfate concentrations at the individual stations showed that three stations (Loch Vale, Snowy Range, and Brooklyn Lake) had higher concentrations in the post-control period compared to the pre-control period and that three stations (Beaver Meadows, Sugar Loaf, and Sand Spring) showed little difference in concentrations. Four stations, however, showed decreases in sulfate concentrations including Dry Lake (3.3 μeq/L), Buffalo Pass (2.2 μeq/L), Four Mile Park (0.8 μeq/L), and Sunlight Peak (1.2 μeq/L). Because the largest decreases in sulfate concentrations were at the two downwind stations (Dry Lake and Buffalo Pass), some

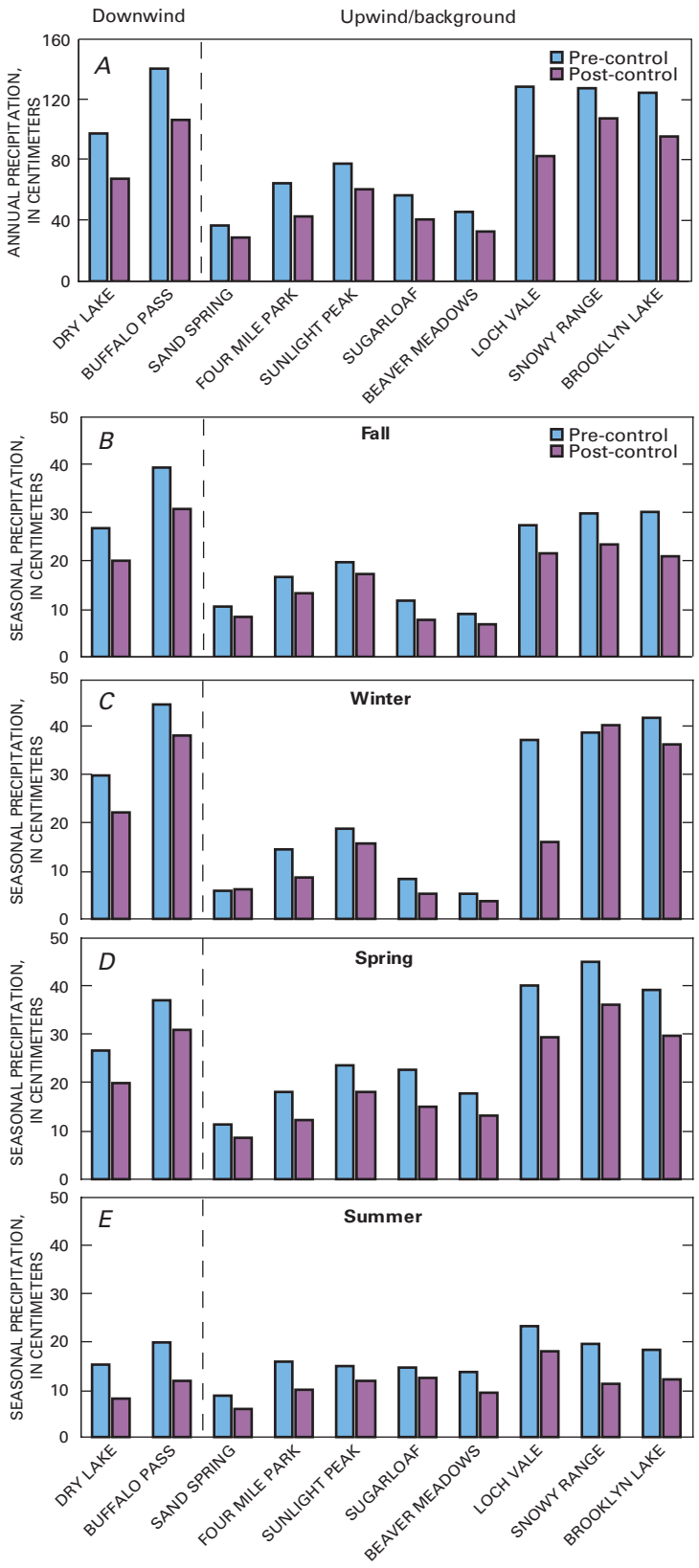


Figure 3. Average (*A*) annual and seasonal precipitation amount during (*B*) fall, (*C*) winter, (*D*) spring, and (*E*) summer at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

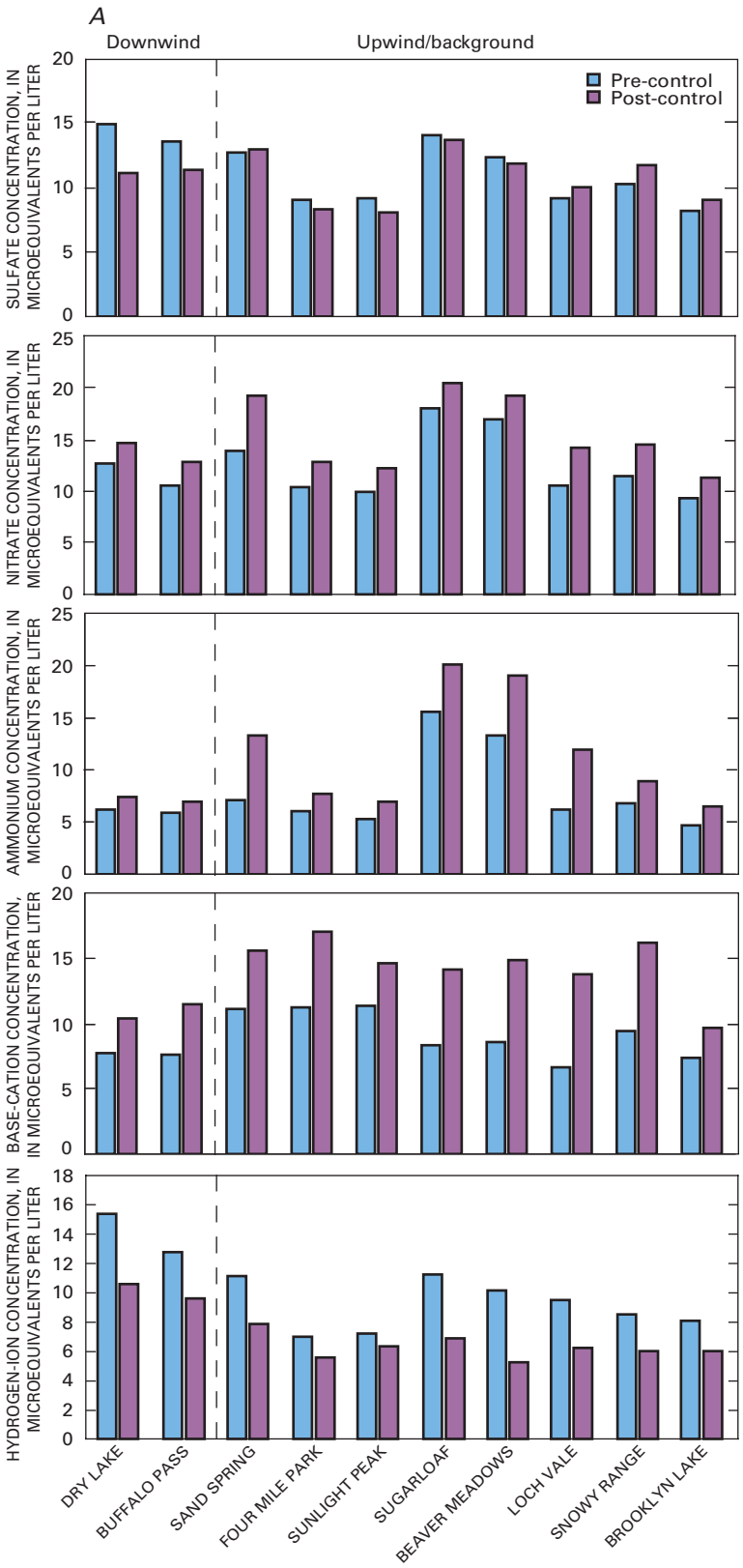


Figure 4. Average annual (*A*) concentrations and (*B*) deposition rates of selected chemical constituents at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

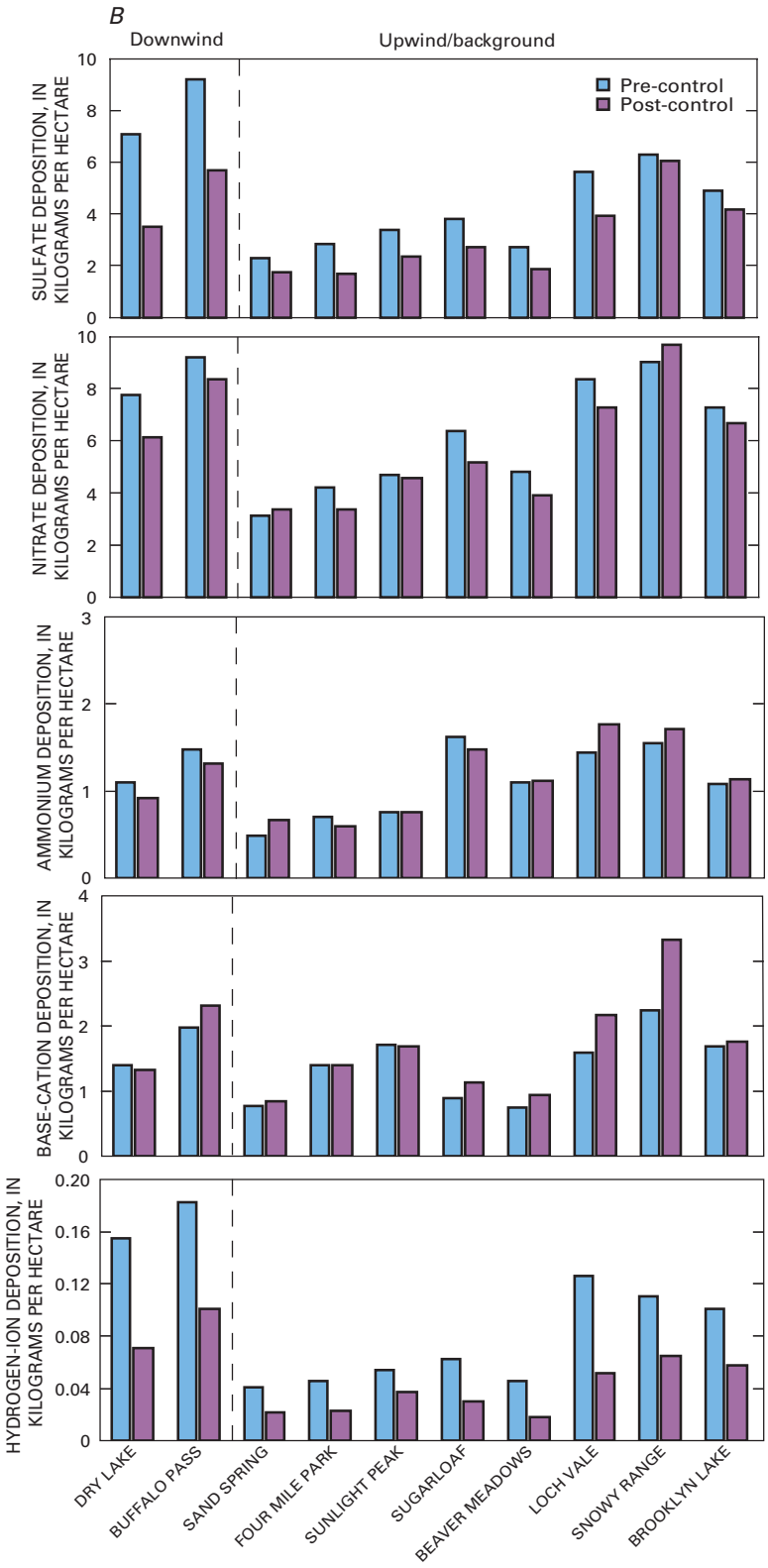


Figure 4. Average annual (*A*) concentrations and (*B*) deposition rates of selected chemical constituents at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.—Continued

of the difference is likely attributable to emission reductions at the Hayden powerplant. The cause of the small decreases in sulfate concentrations at Four Mile Park and Sunlight Peak is not clear, although it is unlikely to be related to emission reductions at the powerplant, considering the prevailing wind direction (fig. 1) and large topographic barrier (The Flat Tops) between the southern NADP sites and the powerplant.

Seasonal comparison of sulfate concentrations shows a consistent pattern among the 10 stations with the highest concentrations during summer and the lowest during winter (fig. 5). The highest concentration was at Sand Spring (22.6 μeq/L) during summer, and the lowest was at Four Mile Park (4.4 μeq/L) during winter. Comparison of concentrations between the pre- and post-control periods did not reveal any seasonal patterns that were consistent among stations. For example, sulfate concentrations in the post-control period during summer decreased at three stations, increased at six stations, and remained unchanged at one station. During winter, sulfate decreased at six stations and increased at four stations. These differences in seasonal patterns among stations indicate that sulfate concentrations may be controlled by different sources or processes during different times of the year. The downwind stations, Dry Lake and Buffalo Pass, exhibited similar seasonal patterns and were the only two stations that showed decreases in sulfate concentrations during all four seasons of the year (fig. 5). In addition, these two stations showed the largest decreases in concentrations among the 10 stations in each season, which is consistent with the hypothesis that emission reductions affected precipitation chemistry downwind from the powerplant. Both stations also showed larger relative decreases in sulfate concentration during the fall and summer compared to the winter. At Dry Lake, for example, sulfate concentrations decreased by 4.2 μeq/L (20.3 percent) during summer, but only 0.8 μeq/L (8.2 percent) during winter. At Buffalo Pass, concentrations decreased by 4.6 μeq/L (26.2 percent) during summer, but only 1.2 μeq/L (9.9 percent) during winter. One possible explanation for the smaller declines in winter compared to summer is that the conversion of sulfur dioxide to sulfate in the atmosphere may be more oxidant limited during the colder and darker winter months (Kleinman and Daum, 1991). This could result in little change in sulfate concentrations in precipitation, particularly during winter, even though atmospheric sulfur dioxide concentrations decreased due to emission reductions at the Hayden powerplant.

Annual sulfate deposition rates, which are the product of concentration and precipitation amount, are compared for each NADP station in figure 4*B*. In the pre-control period, sulfate deposition ranged from 2.7 to 9.1 kg/ha, with the highest deposition rates measured at Dry Lake (7.0 kg/ha) and Buffalo Pass (9.1 kg/ha). In the post-control period, sulfate deposition was lower, ranging from 1.7 to 6.1 kg/ha, with the highest rates measured at Snowy Range (6.1 kg/ha) and Buffalo Pass (5.8 kg/ha). All stations showed a decrease in deposition rate between the pre- and post-control periods, which primarily reflects the effect of less precipitation in the post-control period. The two downwind stations showed the greatest change in deposition rates between periods, decreasing by 3.4 kg/ha at Dry Lake and by 3.3 kg/ha at Buffalo Pass. This change in deposition reflects a combination of lower precipitation in the post-control period with lower sulfate concentrations that were likely caused by emission reductions at the powerplant.

Nitrate.—In contrast to sulfate, annual nitrate concentrations showed statistically significant (p=0.002) increases in concentrations between the pre- and post-control periods at all 10 stations (fig. 4*A*). The largest increase in concentration was at Sand Spring (5.4 μeq/L) just upwind from the Hayden powerplant, and the smallest increase was at Brooklyn Lake (1.9 μeq/L) in southeastern Wyoming. The similar response at all 10 stations indicates the pattern may reflect drought conditions in the post-control period, which would tend to have a concentrating effect on precipitation chemistry. Regional increases in nitrogen oxide emissions related to growing urban and agricultural areas in the Rocky Mountains also could have contributed to the increases in nitrate concentrations. However, data from the USEPA Clean Air Markets Program (*http://cfpub.epa.gov/gdm/*) indicate nitrogen oxide emissions from powerplants and other large stationary sources in Colorado actually declined by about 5 percent statewide between 1995 and 2003, indicating the drought likely was an important factor in the concentration increases. Despite reductions in nitrogen oxide emissions at the Hayden powerplant, nitrate concentrations increased at both Dry Lake and Buffalo Pass, indicating any response to local emission reductions probably were masked by more regional factors such as the drought.

Seasonal comparison of average nitrate concentrations shows a consistent pattern among the 10 stations with higher concentrations during summer compared to fall, winter, and spring (fig. 6). The highest concentration was at Sand Spring (30.7 μeq/L) during summer and the lowest was at Brooklyn Lake (7.3 μeq/L) during winter. Comparison between the pre- and post-control periods showed that nitrate increased at most stations during most seasons of the year, with the exception of a few sites during fall and winter. The largest seasonal increases in nitrate were during the summer season, which ranged from 3.4 to 12.7 μeq/L. The two smallest increases during summer were at Dry Lake (3.4 μeq/L) and Buffalo Pass (4.4 μeq/L) and the largest was at Sand Spring (12.7 μeq/L). Interestingly, the pattern was opposite during winter. The largest increases in nitrate during winter were observed at Dry Lake (3.7 μeq/L) and Buffalo Pass (3.9 μeq/L), and Sand Spring showed a small decrease in concentration of 1.3 μeq/L.

Annual nitrate deposition rates, which are the product of concentration and precipitation amount, are compared for the 10 stations in figure 4*B*. In the pre-control period, nitrate deposition ranged from 3.1 to 9.2 kg/ha, with the highest deposition rates measured at Buffalo Pass. In the post-control period, nitrate deposition was similar ranging from 3.4 to 9.8 kg/ha, with the highest rate measured at Snowy Range. Eight of the 10 stations showed a small decrease in nitrate deposition between the pre- and post-control periods, primarily due to lower precipitation in the post-control period. Nitrate deposition decreased by 1.6 kg/ha at Dry Lake and 0.8 kg/ha

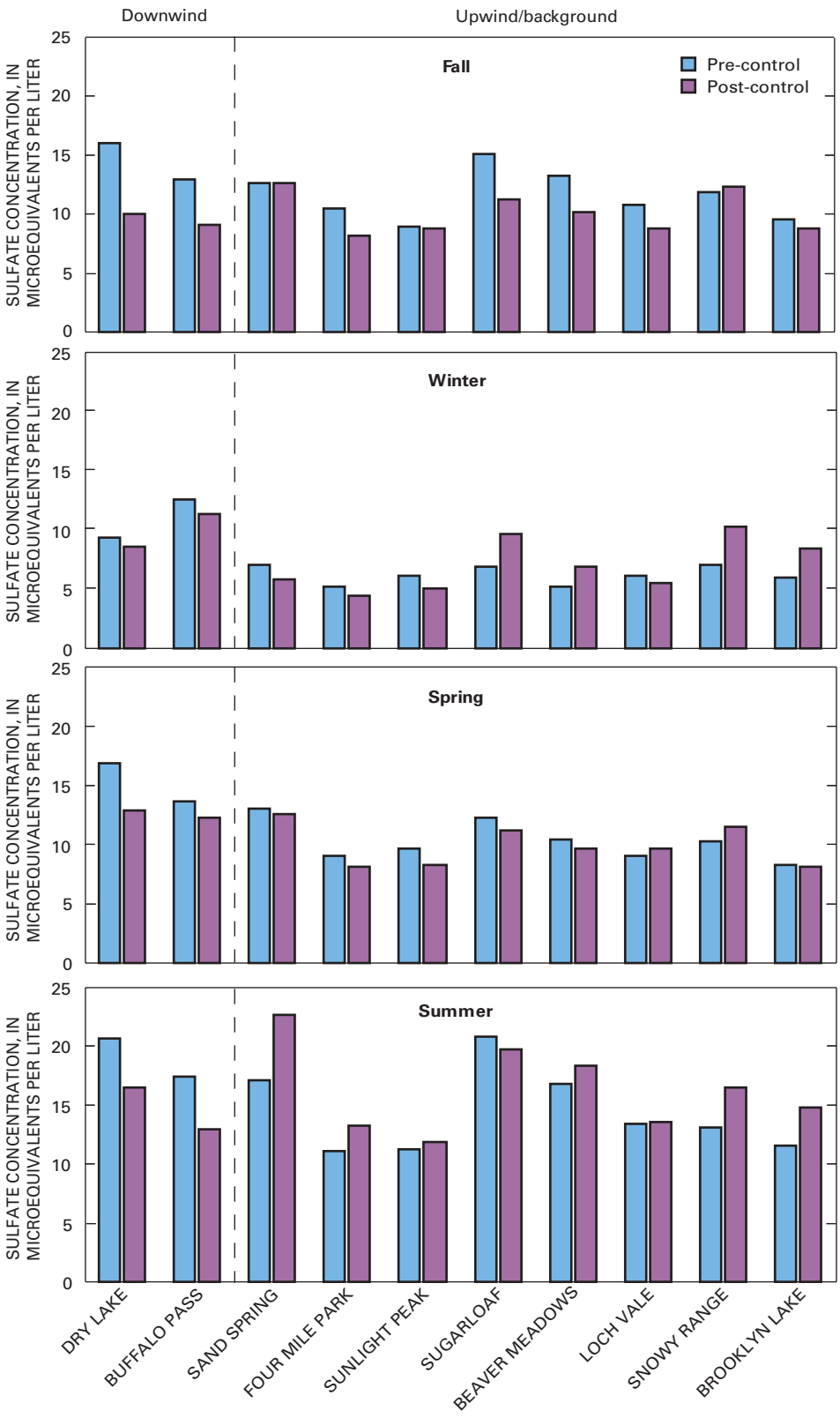


Figure 5. Average seasonal sulfate concentrations at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

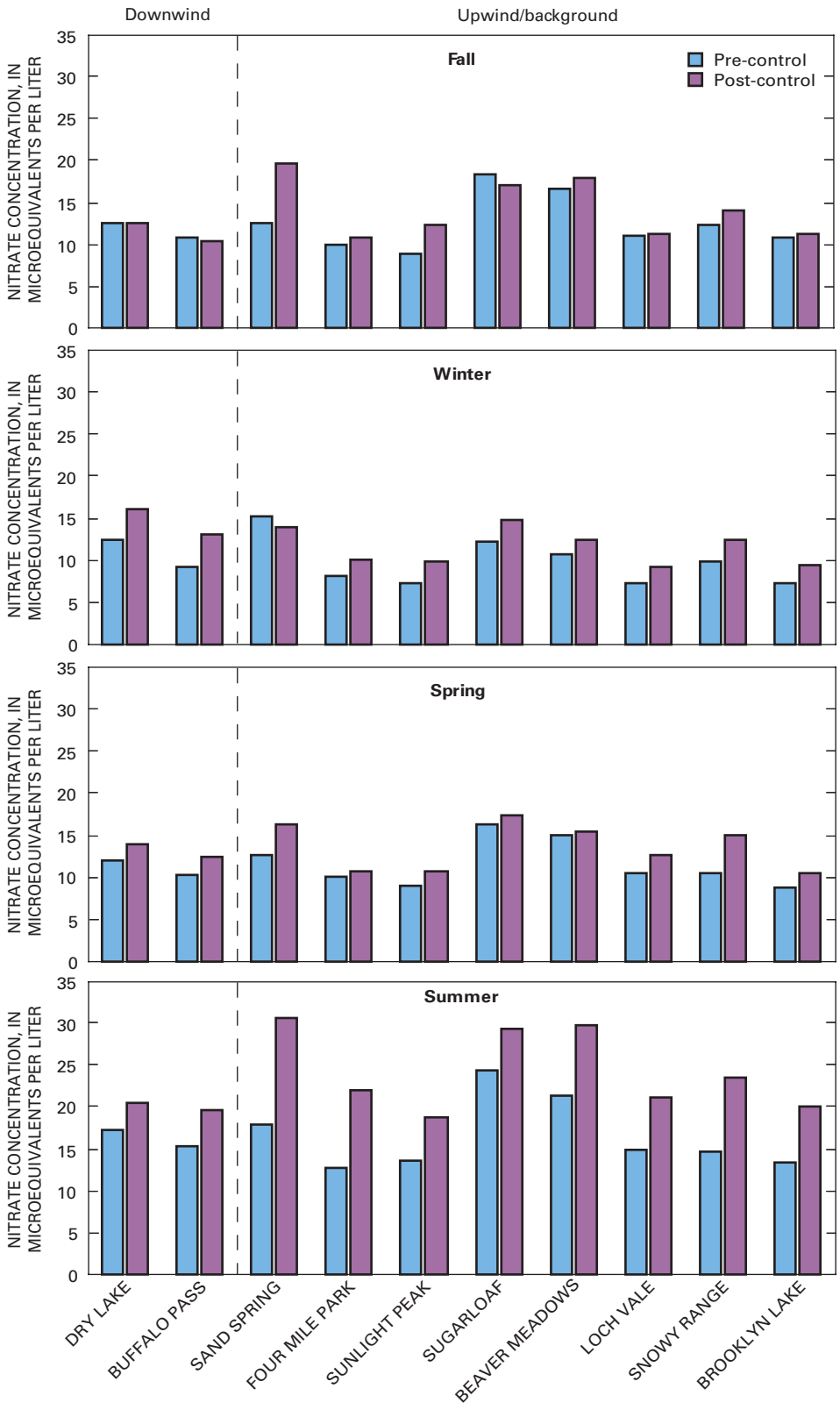


Figure 6. Average seasonal nitrate concentrations at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

at Buffalo Pass. Because nitrate concentrations increased at the two downwind stations, the decrease in deposition was likely caused by the drought rather than by reductions in nitrogen oxide emissions at the Hayden powerplant.

Ammonium.—Annual ammonium concentrations also showed statistically significant (p=0.002) increases in concentration between the pre- and post-control periods at all 10 stations (fig. 4*A*). The largest increase in concentration was at Sand Spring (6.1 µeq/L), and the two smallest increases were at Dry Lake (1.3 µeq/L) and Buffalo Pass (1.1 µeq/L). Similar to nitrate, the pattern may reflect drought conditions in the post-control period, which would tend to have a concentrating effect on precipitation chemistry. Some of the increase also may have been related to regional ammonia emissions, which have increased throughout the United States during the 1990s (Nilles and Conley, 2001). Clow and others (2003) found that ammonium concentrations increased at 12 of 19 NADP stations in Colorado and Wyoming from 1985 to 1999, which they suggested was driven by regional increases in ammonia emissions in the Western United States.

Seasonal comparison of nitrate concentrations showed a consistent pattern among the 10 stations with the highest concentrations during summer and lowest during winter (fig. 7). The highest concentration was at Beaver Meadows (31.6 µeq/L) during summer and the lowest was at Brooklyn Lake (2.6 µeq/L) during winter. Comparison between the pre- and post-control periods revealed that ammonium increased at most stations during all four seasonal periods. Similar to nitrate, the largest seasonal increases in ammonium occurred during the summer season, ranging from 5.2 µeq/L at Sunlight Peak to 16.7 µeq/L at Sand Spring. At the two downwind stations, ammonium increased in summer by 8.7 µeq/L at Dry Lake and 7.8 µeq/L at Buffalo Pass. In winter, ammonium increased by only 0.2 µeq/L at Dry Lake and by 1.0 µeq/L at Buffalo Pass.

Annual ammonium deposition rates, which are the product of concentration and precipitation amount, are compared for the pre- and post-control periods in figure 4*B*. Ammonium deposition in the pre-control period ranged from 0.5 to 1.6 kg/ha, with the highest rate at Sugarloaf. Ammonium deposition in the post-control period ranged from 0.6 to 1.8 kg/ha, with the highest rate at Loch Vale. Three of the 10 stations showed decreases in deposition between the pre- and post-control periods, four stations showed increases, and three stations showed little or no change (<0.1 kg/ha) between periods. At the downwind stations, ammonium deposition decreased in the post-control period by 0.18 kg/ha at Dry Lake and 0.15 kg/ha at Buffalo Pass.

Base cations.—Annual base-cation concentrations showed statistically significant (p=0.002) increases in concentrations between the pre- and post-control periods at all 10 stations (fig. 4*A*). The largest increase in concentration was at Loch Vale (7.2 µeq/L) and the smallest increase was at Brooklyn Lake (2.4 µeq/L). Base-cation concentrations increased at Dry Lake by 2.7 µeq/L and at Buffalo Pass by 3.9 µeq/L, which were in the middle of the range observed at the other eight stations. In general, the increase in base-cation concentrations was greater than increases in nitrate and ammonium, indicating it may be caused by more than just a simple concentrating effect (that is, less precipitation to dilute constituents scrubbed from the atmosphere). For example, base-cation concentrations increased by an average of 5.7 percent at all the stations compared to an average of 2.3 percent for nitrate and 4.1 percent for ammonium. The excess calcium and magnesium in precipitation in the post-control period may reflect higher levels of carbonate-rich dust in the atmosphere due to drier soils and less vegetation and snow cover during the drought.

Seasonal comparison of base-cation concentrations showed a consistent pattern among the 10 stations with the highest concentrations during spring and lowest during winter (fig. 8). The highest concentration was at Snowy Range (31.3 µeq/L) during fall and the lowest was at Snowy Range (2.8 µeq/L) during winter. Comparison between the pre- and post-control periods revealed that base-cation concentrations increased at all stations during all seasons of the year except at Sand Spring and Beaver Meadows during winter and Four Mile Park during fall. The largest seasonal increases in base cations were during spring, which ranged from 1.9 to 14.4 µeq/L. Base cations increased at 8 of the 10 stations during winter, but the increases were small compared to spring. The large increases in base cations at Snowy Range and Sand Spring during fall were caused by very high concentrations in samples collected during 2003. At Dry Lake and Buffalo Pass, base cations increased during spring by 7.3 and 10.6 µeq/L, respectively, but only by 1.7 and 0.8 µeq/L, respectively, during winter.

Annual base-cation deposition rates, which are the product of concentration and precipitation amount, are compared for the pre- and post-control periods in figure 4*B*. Base-cation deposition in the pre-control period ranged from 0.7 to 2.3 kg/ha, with the highest at Snowy Range. In the post-control period, deposition rates ranged from 0.8 to 3.3 kg/ha, with the highest also at Snowy Range. Nine of the 10 stations showed increases in base-cation deposition between the pre- and post-control periods, although the increase was quite small a several stations. At the downwind stations, base-cation deposition decreased slightly at Dry Lake (0.08 kg/ha) but increased by 0.31 kg/ha at Buffalo Pass.

Hydrogen ion.—Annual hydrogen-ion concentrations showed statistically significant (p=0.002) decreases in concentration between the pre- and post-control periods at all 10 stations (fig. 4*A*), opposite to that observed for nitrate, ammonium, and base cations. The largest decrease in concentration was at Beaver Meadows (4.9 µeq/L), and the smallest decrease was at Sunlight Peak (0.9 µeq/L). At the downwind sites, hydrogen-ion concentrations decreased by 4.8 µeq/L at Dry Lake and by 3.2 µeq/L at Buffalo Pass. The decrease in hydrogen ion in the drier post-control period most likely reflects higher levels of alkaline dust in the atmosphere, which neutralizes the acidity associated with nitrate and sulfate.

Seasonal comparison of hydrogen-ion concentrations shows a consistent pattern among the 10 stations (fig. 9). At most stations, hydrogen-ion concentrations were higher (more acidic) during summer and lower (less acidic) during spring. The highest concentration was at Dry Lake (21.2 µeq/L) during summer, and the lowest was at Beaver Meadows

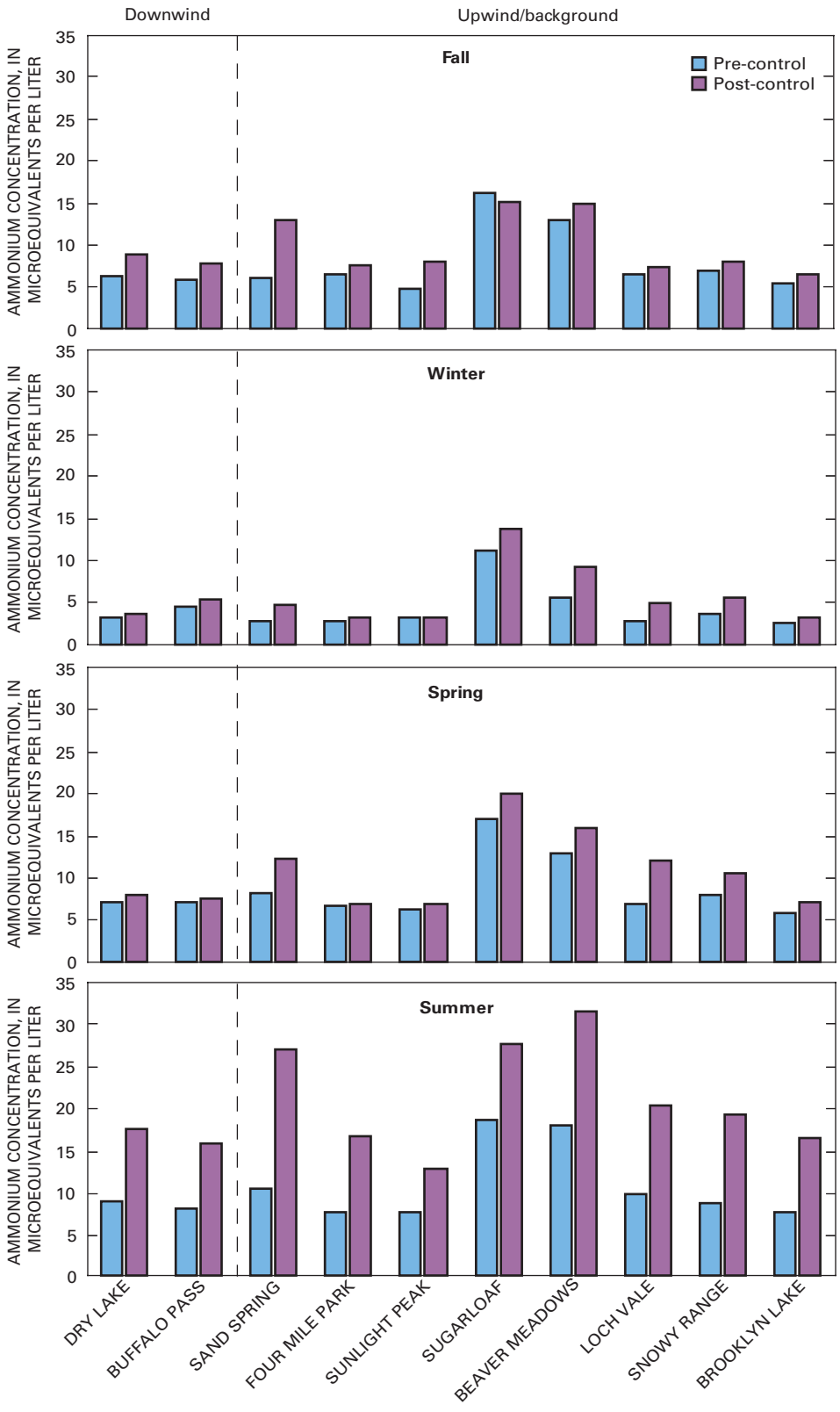


Figure 7. Average seasonal ammonium concentrations at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

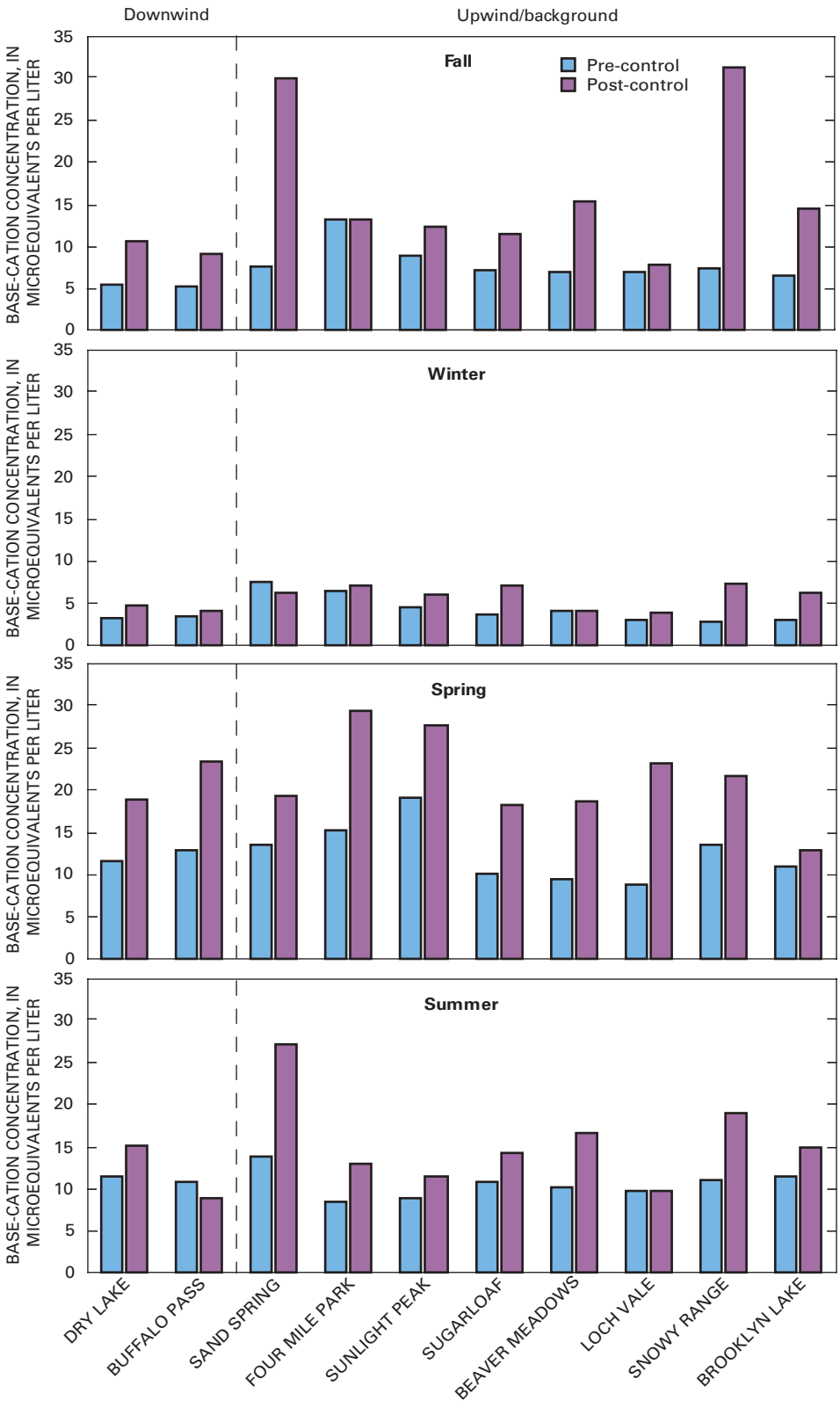


Figure 8. Average seasonal base-cation concentrations at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

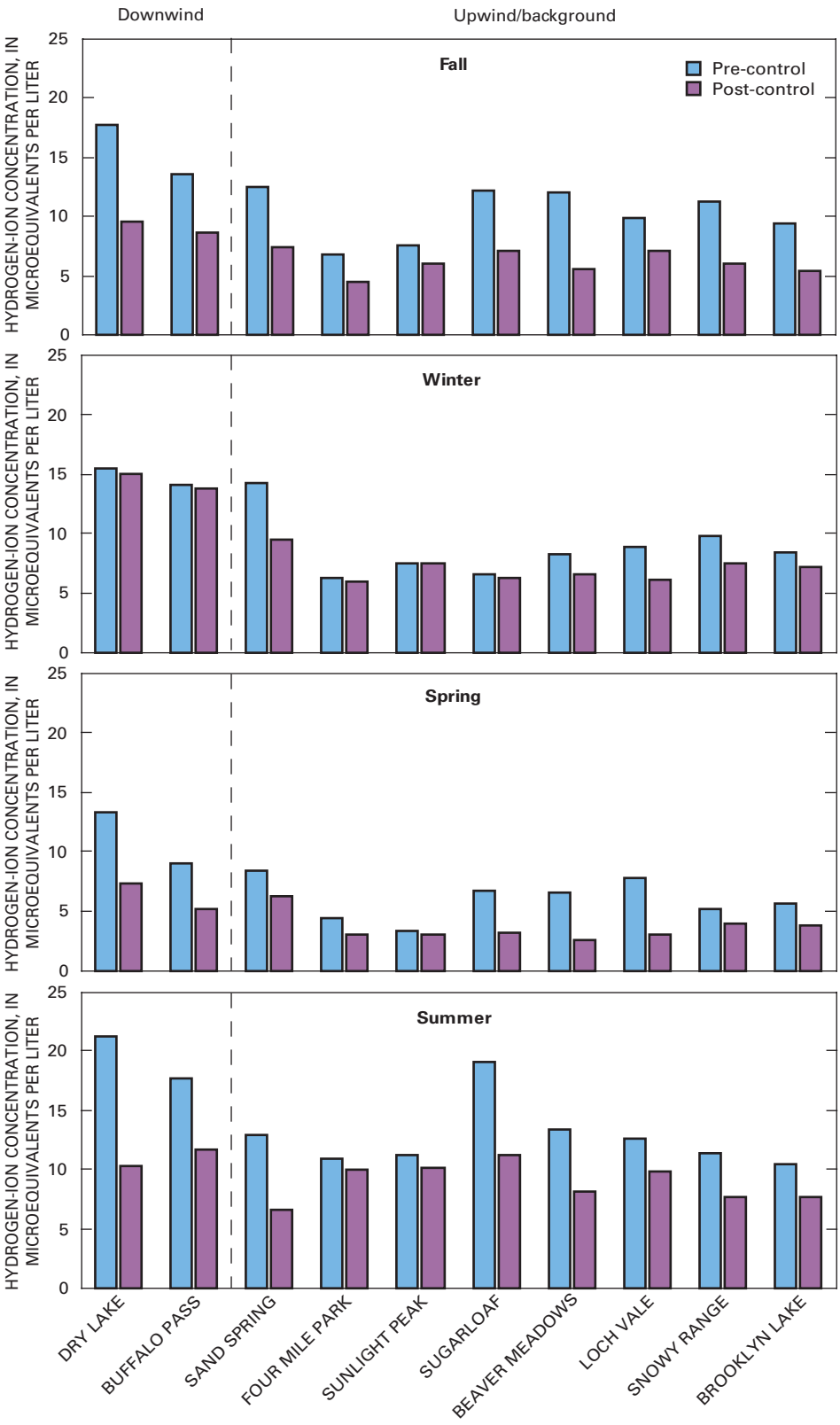


Figure 9. Average seasonal hydrogen-ion concentrations at precipitation stations before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

(2.6 μeq/L) during spring. Comparison between the pre- and post-control period revealed that hydrogen-ion concentrations decreased at every station in all seasons except for Sunlight Peak during winter, which remained unchanged. The largest seasonal decreases in hydrogen ion were during summer and spring. The largest decreases in hydrogen ion at all the stations were observed at Dry Lake during fall (8.0 μeq/L), spring (5.8 μeq/L), and summer (11.0 μeq/L).

Annual hydrogen-ion deposition rates, which are the product of concentration and precipitation amount, are compared for the pre- and post-control periods in figure 4*B*. Hydrogen-ion deposition in the pre-control period ranged from 0.04 to 0.18 kg/ha, with the highest rate at Buffalo Pass. In the post-control period, deposition ranged from 0.02 to 0.10 kg/ha, with the highest rate also at Buffalo Pass. Hydrogen-ion deposition rates decreased between the pre- and post-control periods at all 10 stations, and the decreases were greater than the other constituents. This is due to the combination of both lower precipitation and lower concentrations during the post-control period. At the downwind sites, hydrogen-ion deposition decreased by 0.07 kg/ha at Dry Lake and by 0.08 kg/ha at Buffalo Pass.

Snowpack Chemistry

This section compares snowpack chemistry at RMS sites before (1995–98) and after (2000–2003) emission reductions at the Hayden powerplant. Chemical data were analyzed for 22 RMS sites in northwestern Colorado and southeastern Wyoming located within 175 km of the Hayden powerplant (fig. 1 and table 1). Four of the RMS sites, Buffalo Pass, Dry Lake, Rabbit Ears 1, and Rabbit Ears 2, were selected to represent downwind effects from the Hayden powerplant. Flow directions of surface winds in the Rocky Mountains are variable, but prevailing westerly winds dominate in this region (fig. 1), especially during winter snow accumulation (Banta and Cotton, 1981; Barry, 1992). The remaining 18 sites are upwind or distant from the Hayden powerplant and should be minimally affected by the powerplant emissions. These 18 were selected as background stations to evaluate regional changes in snowpack chemistry during the study period. Snow telemetry (SNOTEL) sites operated by the Natural Resources Conservation Service, which measure snow-water equivalent (SWE), are located near all four downwind sites. The Brooklyn Lake, Buffalo Pass, Dry Lake, Loch Vale, and Sunlight Peak sites also are collocated with NADP stations (fig. 1) discussed in the "Precipitation Chemistry" section of this report.

Data Collection and Analysis

Snow samples were collected during March or April of each year around the time of maximum snow accumulation but prior to snowmelt. Depth-integrated composite samples were collected from the entire face of a snowpit dug to the ground surface (Ingersoll and others, 2002). Snow samples were placed in 8-liter Teflon bags that were sealed; the samples were frozen until analyzed at USGS laboratories in Boulder and Denver, Colorado. Samples were analyzed for pH, alkalinity, major ions, and nutrients. Analytical methods, detection limits, and quality-assurance procedures used by the RMS network are described in Ingersoll and others (2002).

Average annual concentrations in microequivalents per liter and annual deposition rates in kilograms per hectare were calculated for the pre-control and post-control periods and compared graphically. Deposition rates were calculated for the four downwind sites (Buffalo Pass, Dry Lake, Rabbit Ears 1, and Rabbit Ears 2) and for only two of the upwind sites (Sunlight Peak and Dunckley Pass); herein, these six sites are referred to as the "local sites." Deposition rates were calculated by multiplying the constituent concentration by the SWE of the snowpack and a factor to convert the results to units of kilograms per hectare. At most sites, SWE measurements were made using a density cutter along the face of the snowpit that was excavated at the time of sample collection. In cases when SWE was not directly measured, it was estimated from SWE measurements at nearby SNOTEL stations (National Resources Conservation Service, 2004a) or from a linear regression between SWE and snow depth developed for each site.

Statistical comparisons of annual concentrations between pre- and post-control periods for the five chemical constituents for two groups of sites were made. One group included the 4 downwind sites and the other group included the 18 upwind/distant sites, considered to represent background. Because the data were not normally distributed and sample numbers were small, the nonparametric Wilcoxon rank-sum test (Helsel and Hirsch, 1992) was used.

Water Content of the Snowpack

The pre-control period includes years when above-average snow depths and water content of the snowpack or SWE were common as compared to 30-year averages (1971–2000) at collocated SNOTEL sites. The post-control period includes years of below-average snowpack depths and SWE because drought affected many western river basins. For example, in the Yampa and White River Basins, maximum annual SWE ranged from 68 to 101 percent of the 30-year (1971–2000) average in the post-control period compared to 91–133 percent of average in the pre-control period (National Resources Conservation Service, 2004b) (fig. 10). Of the four downwind sites, Buffalo Pass received the greatest amount of snowfall during the study period and showed the largest difference in SWE between the pre- and post-control periods (fig. 11). Average SWE at Buffalo Pass was 126 cm for the pre-control period and 104 cm for the post-control period, which represents a 17-percent decrease in SWE in the post-control period. The difference in SWE between periods at the other three downwind sites was slightly smaller, ranging from 6 percent at Rabbit Ears 2, 7 percent at Dry Lake, and 11 percent at Rabbit Ears 1.

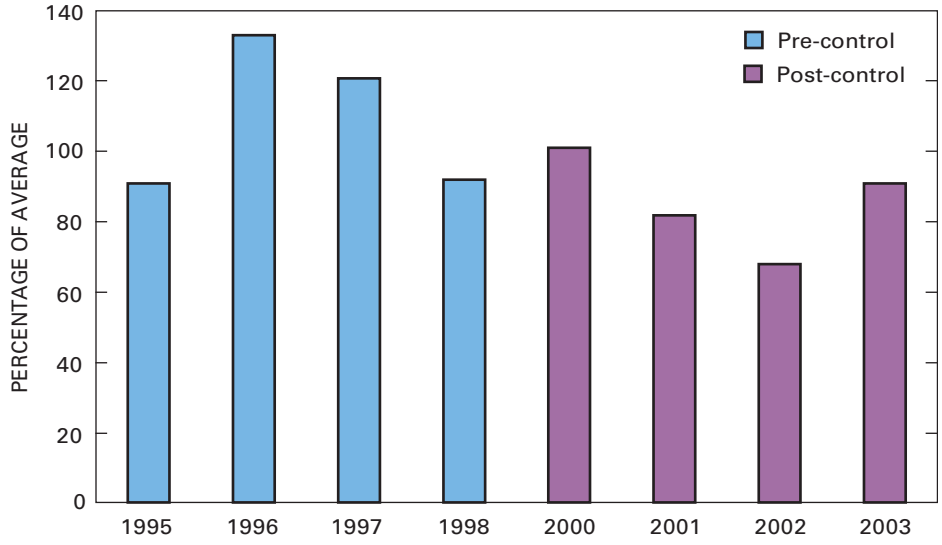


Figure 10. Percentage of 30-year (1971–2000) average snow-water equivalent at snow telemetry (SNOTEL) sites in the Yampa and White River Basins during the study period.

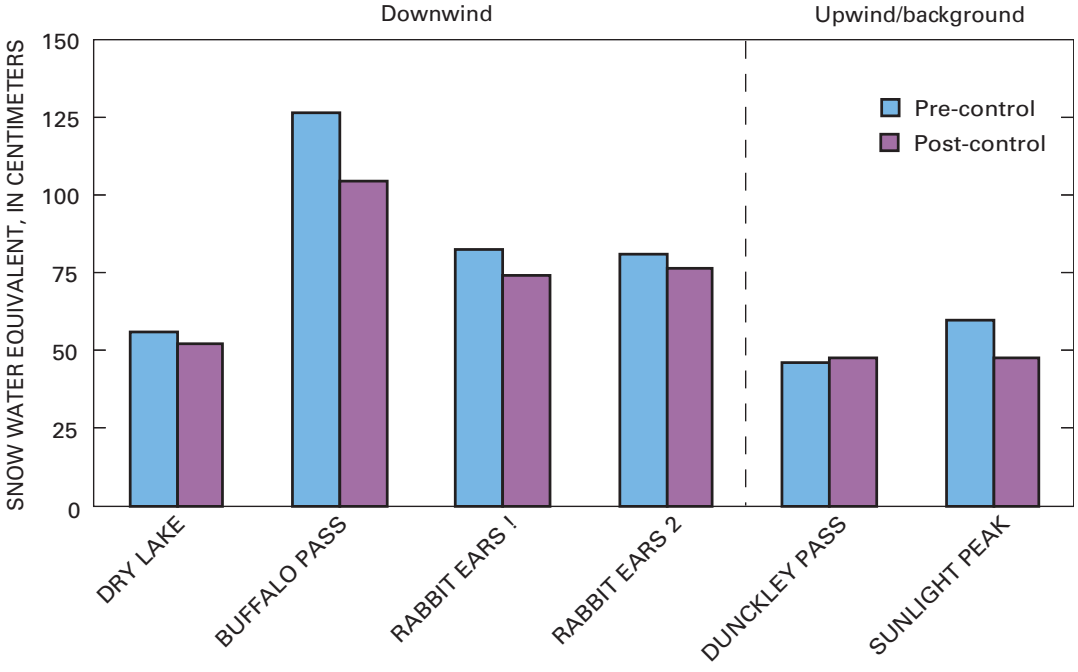


Figure 11. Average annual snow-water equivalent at six local snow-sampling sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

Chemical Constituent Concentrations and Deposition Rates

Sulfate.—There were no statistically significant changes ($p<0.05$, table 2) in average annual sulfate concentrations among the two groups compared (4 sites downwind at Dry Lake, Buffalo Pass, Rabbit Ears 1 and Rabbit Ears 2, and 18 upwind/distant sites). However, average annual snowpack sulfate concentrations increased between the pre- and post-control periods at 11 of the 22 RMS sites (fig. 12). All 11 sites that showed increases were distant from the powerplant. Average annual sulfate concentrations decreased at five of six local sites.

Average annual deposition rates for each of five constituents for each of the six local sites are shown in figure 13. The four downwind sites are shown on the left side of the figure, and the upwind sites (Dunckley Pass and Sunlight Peak) are shown on the right side. No significant differences in sulfate deposition were found among the six sites. However, sulfate deposition in snowpacks decreased at five of six sites by 13 to 21 percent in the post-control period compared to the pre-control period (fig. 13); no change in deposition was observed at the Dunckley Pass site. The observed decrease in sulfate deposition at five of the six sites, although not statistically significant, is consistent with sulfur dioxide emissions reductions at the Hayden powerplant and with the national trend in decreasing sulfur dioxide emissions (Nilles and Conley, 2001). Buffalo Pass had the highest annual deposition of 6.2 kg/ha (pre-control) and 5.2 kg/ha (post-control), partly because of the greater amount of snowfall at this site. Other downwind sites (Dry Lake and Rabbit Ears 1 and 2) had sulfate deposition amounts of 2.7 to 3.8 kg/ha (pre-control) and 2.5 to 3.2 kg/ha (post-control). The two upwind sites at Dunckley Pass and Sunlight Peak had substantially lower values of 1.6 to 1.9 kg/ha (pre-control) and 1.5 to 1.6 kg/ha (post-control). Similar sulfate deposition rates were measured at the three collocated NADP stations (Buffalo Pass, Dry Lake, and Sunlight Peak) during the pre- and post-control periods as shown in the "Precipitation Chemistry" section of this report. The agreement in decreased rates of sulfate deposition at downwind snowpack and NADP sites during the post-control period indicates that emission reductions at the Hayden powerplant may have been a factor in lower deposition rates; however, part of the decrease in deposition also is attributable to the decrease in SWE during the post-control period.

Nitrate.—Comparisons of annual snowpack nitrate concentrations between the pre- and post-control periods showed increases at each of 22 RMS sites (fig. 14) that were significantly different ($p\leq0.003$) in both the downwind and upwind/distant groups (table 2). Increases in nitrate concentrations occurring at every site examined within about 200 km of the Hayden powerplant indicate the possibility that factors other than the Hayden powerplant are affecting nitrate concentrations.

Average nitrate deposition increased 4 to 26 percent between the pre- and post-control period at all six local sites (fig. 13). The largest rates of nitrate deposition were measured at Buffalo Pass with 7.5 kg/ha (pre-control) and 8.4 kg/ha (post-control). The remaining five local sites had nitrate deposition ranging from 2.8 to 5.0 kg/ha (pre-control) and 3.4 to 6.0 kg/ha (post-control). Dunckley Pass had the lowest nitrate deposition rates at 2.8 kg/ha (pre-control) and 3.4 kg/ha (post-control). This increase at all the local sites occurred while nitrogen oxide emissions at the Hayden powerplant decreased, indicating other factors such as the drought or other regional emissions sources were affecting nitrate deposition during the study period. By contrast, nitrate deposition rates noted in the "Precipitation Chemistry" section of this report decreased at Buffalo Pass and Dry Lake NADP sites (fig. 4*B*). Dry deposition, not captured by NADP wetfall collectors, may account for part of the increased nitrate deposition to snowpacks. Although Turk and others (2001) found little evidence that there was significant dry deposition of nitrate to snowpacks in the Rocky Mountains, those findings are based on annual snowpacks sampled before the drier years of the post-control period.

Ammonium.—Patterns of average annual ammonium concentrations were similar to nitrate concentrations between the pre- and post-control periods with increases at each of 22 RMS sites (fig. 15), and significant concentration differences ($p\leq0.002$) exist for the two groups of sites compared (table 2). Increases in ammonium occurring at each of 22 sites sampled support the possibility of regional emissions or drought affecting ammonium concentrations.

Table 2. Results of Wilcoxon rank-sum test comparing annual snowpack concentrations at 4 downwind and 18 upwind/distant snowpack sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

[n, total number of samples in each group; p-value is significance of 2-sided test; µeq/L, microequivalents per liter; base cations, sum of calcium and magnesium; concentrations shown in bold are for $p<0.05$; pre- and post-control are median concentrations in each period; four samples per site compared in each period; <, less than]

	Downwind (n=16)			Upwind or distant (n=72)		
	p-value	Pre-control	Post-control	p-value	Pre-control	Post-control
Sulfate (µeq/L)	0.309	9.6	9.4	0.250	6.9	7.4
Nitrate (µeq/L)	0.003	**10.6**	**13.4**	<0.001	**9.3**	**12.3**
Ammonium (µeq/L)	0.002	**4.0**	**6.0**	<0.001	**3.3**	**5.5**
Base cations (µeq/L)	<0.001	**6.2**	**9.3**	<0.001	**7.0**	**12.0**
Hydrogen ion (µeq/L)	0.044	**12.8**	**10.0**	<0.001	**7.4**	**6.2**

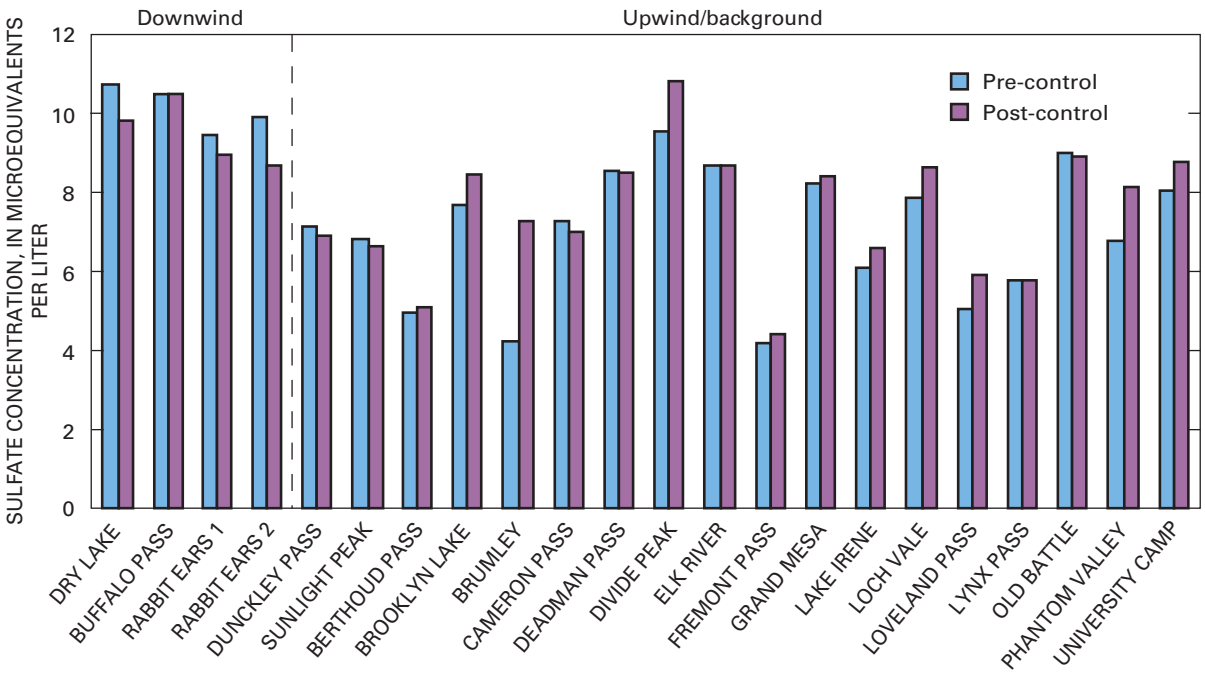


Figure 12. Average annual sulfate concentrations at snow-sampling sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

Average annual ammonium deposition increased 15 to 40 percent at the six local sites between the pre- and post-control periods (fig. 13). The largest annual deposition rates of ammonium were observed at Buffalo Pass with 0.9 kg/ha (pre-control) and 1.2 kg/ha (post-control). The remaining five sites had ammonium deposition rates ranging from 0.3 to 0.6 kg/ha (pre-control) and 0.5 to 0.8 kg/ha (post-control). Dunckley Pass had the lowest ammonium deposition rate at 0.3 kg/ha (pre-control). As with nitrate deposition in wet-fall precipitation noted above, ammonium deposition rates at the Buffalo Pass and Dry Lake NADP sites decreased in the post-control period (fig. 4*B*), whereas increases in snowpack deposition were observed. These increases may be attributable to added dry deposition captured in annual snowpacks.

Base cations.—Concentrations of base cations (calcium plus magnesium) in snow samples were higher at all 22 sites during the post-control period (fig. 16) and were significantly different ($p<0.001$) for both groups as compared to the pre-control period (table 2). The elevated base-cation concentrations during the post-control period were probably due, in part, to increased mobility of dust, particularly from lower elevation areas (Clow and Ingersoll, 1994). With less snow cover observed during the below-average snowfall years (2000–2003), more soil material would have been available for wind transport from areas upwind from the study sites during winter. Expanses of arid land in western Colorado and eastern Utah have sparse vegetation and an abundance of weathered, fine dust particles potentially containing carbonate minerals. Snowpit profile data collected at the snow-sampling sites at Grand Mesa and Sunlight Peak in 2002 and at Buffalo Pass in 2003 noted the presence of red dust layers near the top of the sampled snowpack.

Average annual base-cation deposition increased by 32 to 98 percent at the four downwind sites and two background sites between the pre- and post-control periods (fig. 13). Deposition to snowpacks nearly doubled at Buffalo Pass and Sunlight Peak, while relatively smaller differences occurred in NADP wetfall samples from two collocated stations at Buffalo Pass and Sunlight Peak (fig. 4*B*). While deposition at Buffalo Pass was the highest of the six local sites (1.4 kg/ha, pre-control; 2.8 kg/ha, post-control), deposition to upwind sites at Dunckley Pass (1.0 kg/ha, pre-control; 1.6 kg/ha, post-control) and Sunlight Peak (1.0 kg/ha, pre-control; 1.9 kg/ha, post-control) during both periods was greater than at the other three downwind sites; Rabbit Ears 1 (0.9 kg/ha, pre-control; 1.2 kg/ha, post-control), Rabbit Ears 2 (0.6 kg/ha, pre-control; 1.2 kg/ha, post-control), and Dry Lake (0.7 kg/ha, pre-control; 1.0 kg/ha, post-control). Higher deposition rates of base cations to the two upwind sites are in contrast to the pattern of lower or only moderately higher deposition rates for the other four chemical constituents. This pattern supports the possibility mentioned above that proximity to sources upwind from the Hayden powerplant, like the arid lands to the west, more likely affected base-cation deposition at the six local sites.

Hydrogen ion.—Average annual hydrogen-ion concentrations (fig. 17) decreased significantly between the pre- and post-control periods for both groups of sites compared ($p<0.05$). Carbonate associated with the elevated calcium and magnesium concentrations during the post-control period probably neutralized much of the available acidity and lowered hydrogen-ion concentrations.

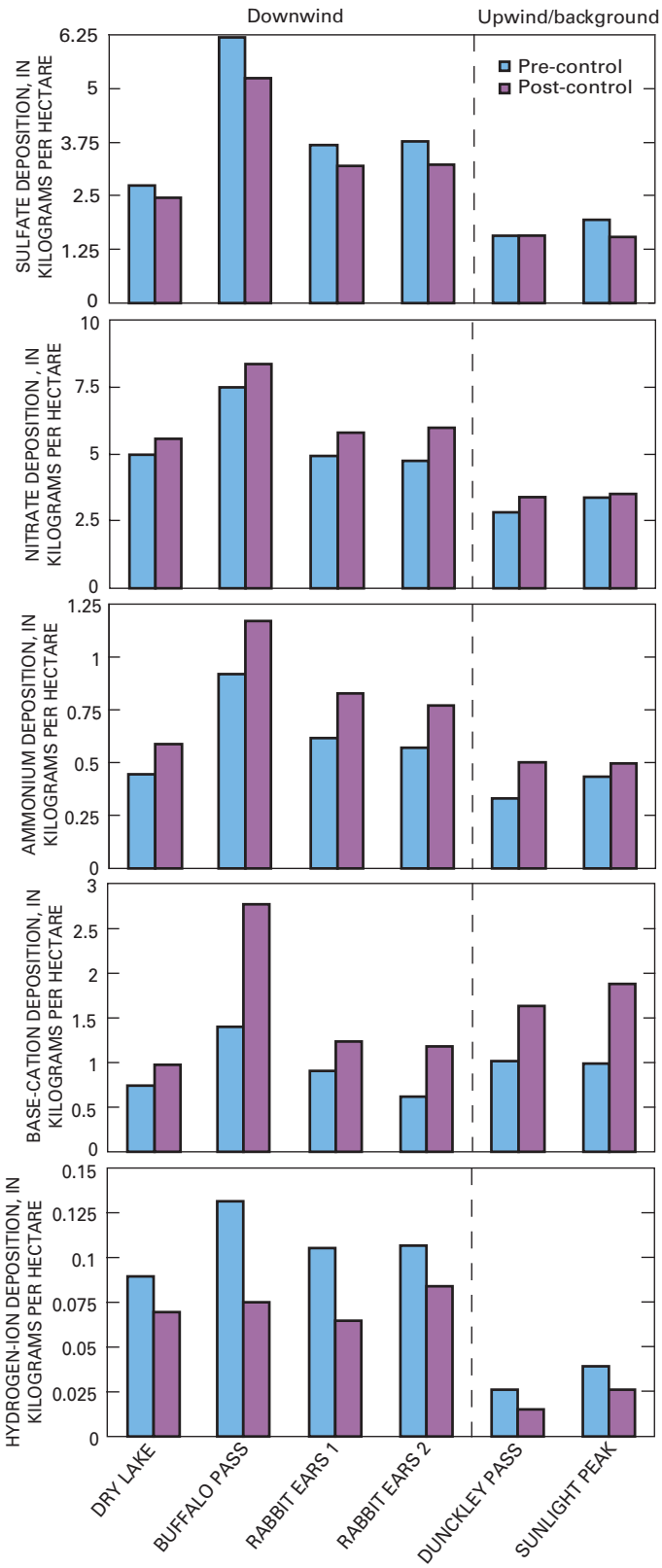


Figure 13. Average annual deposition rate of selected constituents at six local snow-sampling sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

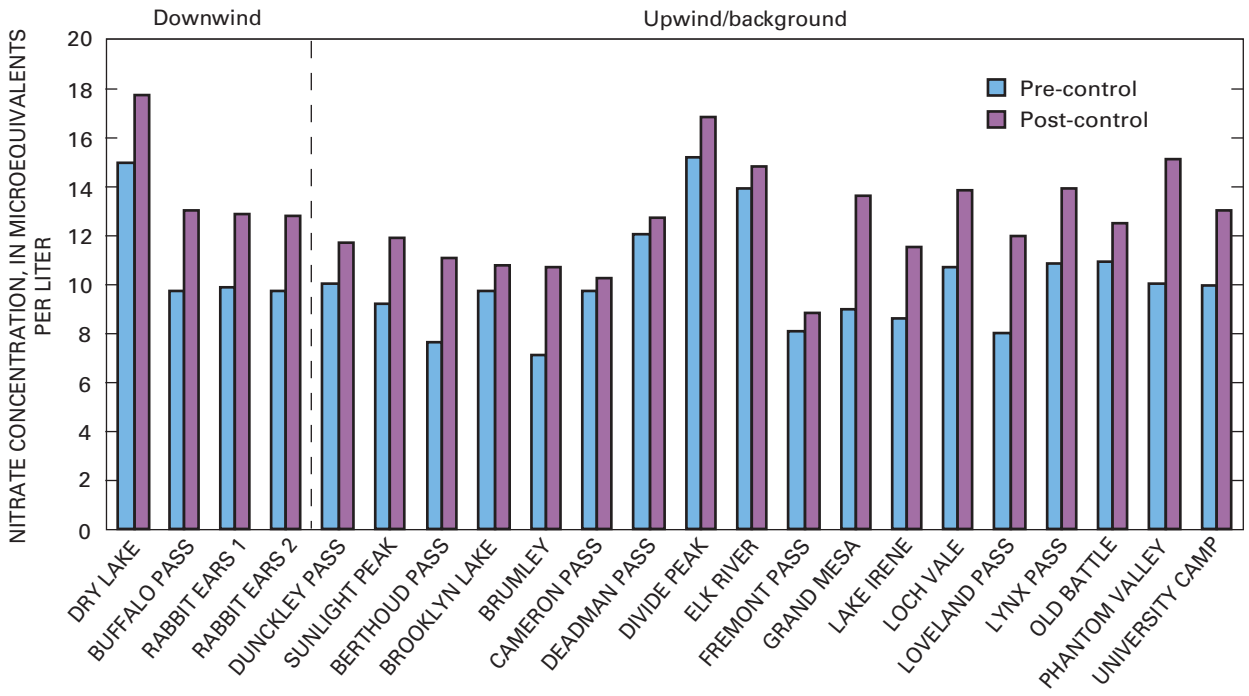


Figure 14. Average annual nitrate concentrations at snow-sampling sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

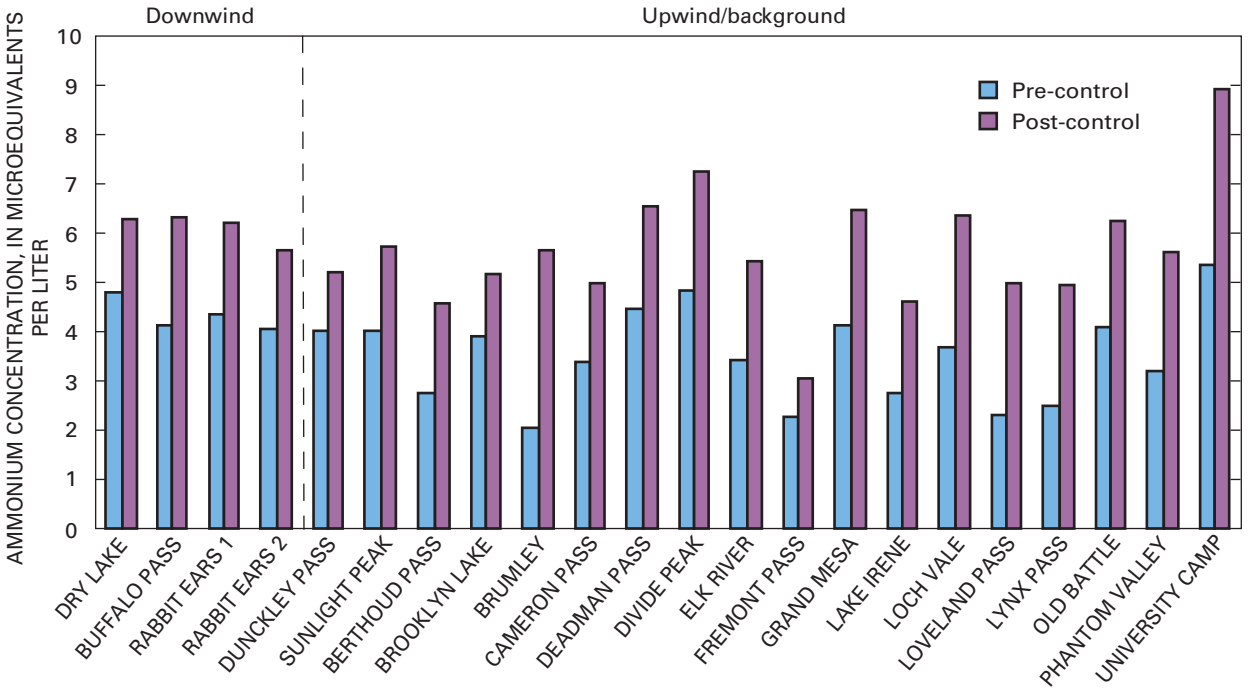


Figure 15. Average annual ammonium concentrations at snow-sampling sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

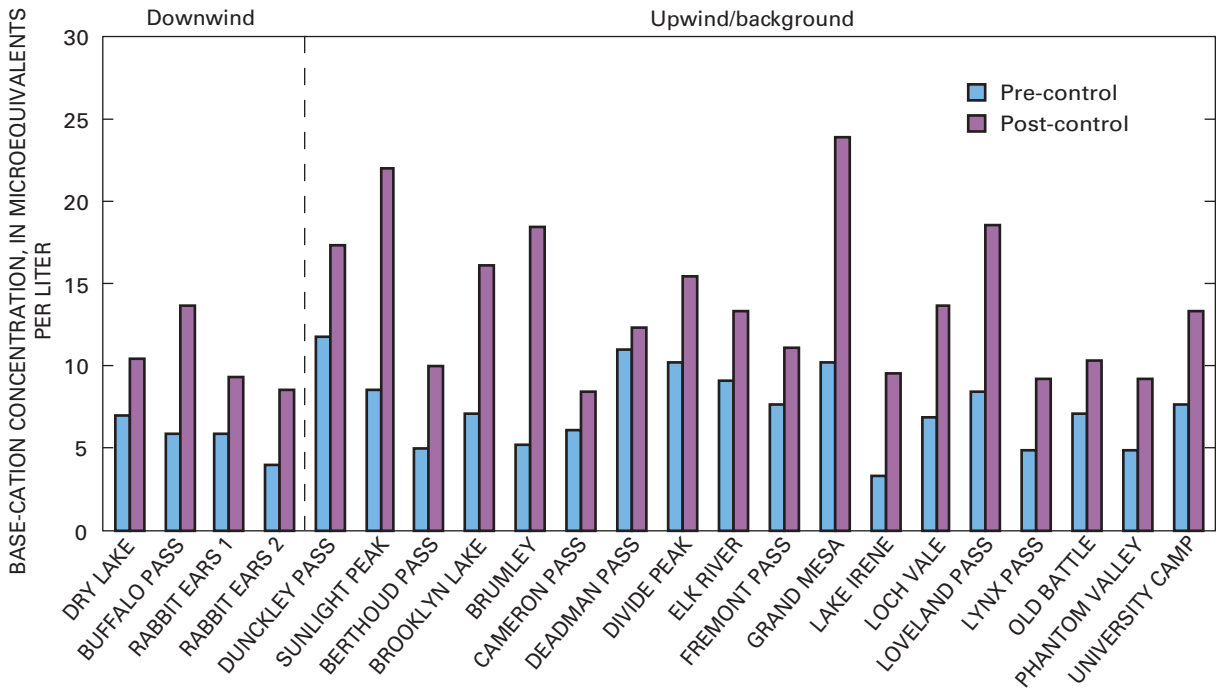


Figure 16. Average annual calcium plus magnesium concentrations at snow-sampling sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

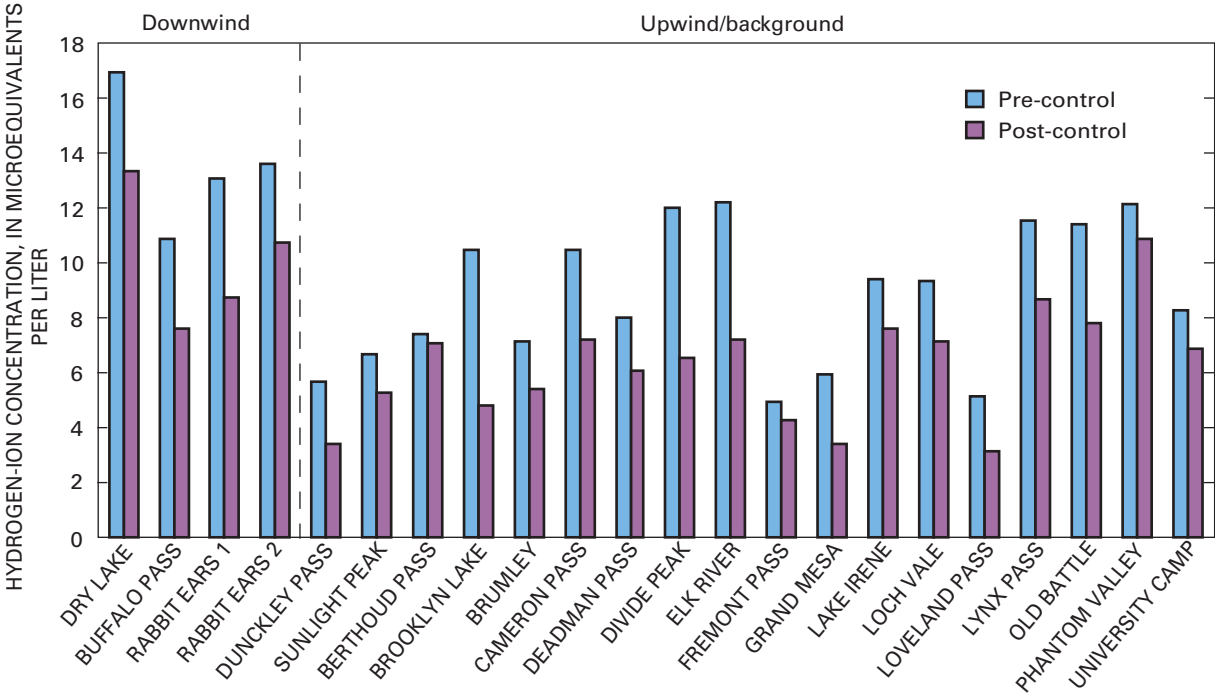


Figure 17. Average annual hydrogen-ion concentrations at snow-sampling sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

Average annual hydrogen-ion deposition also decreased at all six local sites in the pre- and post-control periods by 21 to 43 percent (fig. 13). The most substantial decrease in deposition of 43 percent occurred at Buffalo Pass, where observed deposition was 0.13 kg/ha in the pre-control period and 0.075 kg/ha in the post-control period. Average annual deposition at remaining sites ranged from 0.02 to 0.11 kg/ha, with the lowest values observed at Dunckley Pass (0.03 kg/ha, pre-control; 0.02 kg/ha, post-control) and Sunlight Peak (0.04 kg/ha, pre-control; 0.03 kg/ha, post-control). Similar decreases in hydrogen deposition were noted at all NADP stations mentioned in the "Precipitation Chemistry" section of this report (fig. 4*B*). The decrease in deposition could be the result of acid-neutralizing potential of dust and wind-transported material.

Surface-Water Chemistry

A survey of lake chemistry in 1983 demonstrated that many lakes in and near the MZWA are sensitive to acidic deposition; since 1983, a number of the lakes and their inflows have been part of a USGS long-term lakes-monitoring program for acid deposition (Turk and Campbell, 1987; Turk and others, 1993). Six lakes and lake inlets in and near the MZWA were examined to determine whether their chemistry had responded to the decrease in sulfate deposition associated with emission reductions at the Hayden powerplant (table 1 and fig. 1). From south to north: Long Lake Reservoir has moderately higher concentrations of most chemical constituents than most other lakes due to a shallow ground-water system in glacial deposits underlying the lake watershed. Summit Lake lies just south of the wilderness boundary on the Continental Divide, Lake Elbert is farther north in the heart of the MZWA, and Seven Lakes is near the northern boundary of the wilderness. All of the lakes support sport fisheries of stocked trout. The inlets of Lake Elbert and Seven Lakes consist of small streams draining alpine meadow, tundra, and exposed soil and rock.

Lake and pond chemistry also has been monitored in the Flat Tops Wilderness Area (FTWA), a nearby area that also is sensitive to acidic deposition (Turk and Adams, 1983). These lakes and ponds are more than 60 km south of the Yampa Valley and are unlikely to be affected by local emission sources at Hayden or Craig. Five lakes and ponds in the FTWA are examined in this section as control sites believed to be unaffected by emission reductions at the Hayden powerplant (table 1 and fig. 1). Upper Ned Wilson Lake, Upper Packtrail Pothole, and Lower Packtrail Pothole are small ponds 1–3 m deep; some are occupied by salamanders and none support fish. Ned Wilson Lake is approximately 5 m deep and supports a fishery of stocked trout. Ned Wilson Spring is a spring in an alpine meadow. Based on earlier studies of sulfate concentrations and isotopic composition, hydrologic residence times and response to changes in sulfate deposition are on the order of months in the ponds, 1–3 years in the lake, and many years in the spring (Campbell and others, 1991; Michel and others, 2002).

In this section, differences in the chemistry of each lake and inflow before and after emission reductions at the Hayden powerplant are compared, and the results are evaluated with respect to changes in atmospheric deposition and climatic variability.

Data Collection and Analysis

The lakes, ponds, and inflows have been sampled 2–5 times per year during the open-water season (July–October) since 1984. Grab samples of lake water were collected manually from outlets and inlets, when flowing, or from a point on the shore with little or no vegetation. Samples were chilled within 5 hours and filtered within 48 hours of collection. Acid-neutralizing capacity (ANC) was measured in the laboratory on unfiltered, unpreserved, air-equilibrated samples. Gran titration for ANC was performed to pH 3.5 on an automatic titrator. Filtered (0.45-μm), refrigerated aliquots were used to analyze ammonium, chloride, nitrate, and sulfate by ion chromatography. Filtered aliquots preserved with nitric acid (pH less than 2) were used to analyze calcium, magnesium, and silica by inductively coupled plasma spectroscopy. Detection limits were less than 1 μeq/L for all constituents. Samples were analyzed in a USGS laboratory in Lakewood, Colorado.

Five chemical constituents and indicators were chosen for this analysis: sulfate, sulfate:chloride ratio, nitrate, ANC, and sum of base cations (SBC, or the sum of calcium and magnesium). Concentrations are expressed in units of microequivalents per liter, and the sulfate:chloride ratio is unitless. The primary source of sulfate and nitrate in these alpine/subalpine ecosystems is atmospheric deposition, but concentrations in the lakes also are affected by biogeochemical cycling in the watershed and the lake itself. The sulfate:chloride ratio provides a means of removing variability in sulfate concentrations caused by climatic variables. ANC is a measure of the net acid/base chemistry of the water—it has less diurnal variation than pH and thus is more useful to determine long-term trends in water chemistry. Base cations in lakes primarily come from soils and geologic weathering and are indications of how these watershed processes affect the acid/base status of the lakes. Base-cation concentrations respond to changes in ground-water residence times and hydrologic flow paths related to climatic variability.

Discharge Adjustment to Concentration Data

Seasonality strongly affects chemical concentrations in most alpine lakes. Snowmelt begins around early May, flushing water that has been stored in soils over the winter. Initial concentrations may be high; then as snowmelt progresses, lake water is diluted by snowmelt. Later in the summer, concentrations typically increase again as snow is depleted and ground-water discharge has a stronger influence on surface-water chemistry. The seasonal patterns of lake chemical

concentrations differ from year to year, depending on the amounts of snowfall and summer rainfall as well as other climate variables, such as temperature.

A robust statistical test to analyze long-term monotonic trends in surface-water chemistry is the discharge-adjusted seasonal Kendall test (Helsel and Hirsch, 1992). This test models the concentration in relation to instantaneous or daily discharge, then determines seasonal trends in the model residuals. However, the test is not designed for step-function changes such as a change in local emissions. The discharge adjustment also is not particularly effective in alpine systems; concentration/discharge relations exhibit strong hysteresis because concentrations for a given discharge are higher on the rising limb of the hydrograph than they are on the falling limb (Campbell and others, 1995). Therefore, an alternate approach to account for both seasonality and climate variability was used.

Discharge of lake inlets and outlets is not measured in these lakes because of wilderness restrictions and the difficulty of access during winter and spring. For this analysis, we used discharge data from two nearby streamflow-gaging stations (fig. 1) with long-term records: Encampment River above Hog Park Creek near Encampment, Wyoming (USGS station 06623800), which drains the northern part of the MZWA; and White River above Coal Creek near Meeker, Colorado (USGS station 09304200), which drains the northwestern part of the FTWA (data available at *http://waterdata.usgs.gov/nwis/sw*). Although these sites are at lower elevations than the surface-water sites used in this study, their seasonal hydrographs are dominated by high-elevation snowmelt, and they provide a good indication of the interannual variability in timing and magnitude of runoff in the alpine lake watersheds.

In this discharge-adjusted analysis, seasonality and climatic variability are accounted for by modeling the relation between concentration of a chemical constituent and cumulative discharge for the water year at a given site. This cumulative discharge reflects the degree to which the current year's snowmelt runoff has flushed shallow soil and ground-water reservoirs. The period of record for water-quality samples (approximately 1984–2003) was used to develop a locally weighted scatterplot smoothing (LOWESS) fit with a smoothing factor of 0.6 for each constituent at each sampling site. LOWESS smoothing is a nonparametric technique that requires no assumptions about the data distribution and does not force the data to the shape of a specific function (Helsel and Hirsch, 1992). The concentration-cumulative discharge models removed a substantial amount of the variability from the data. However, because the latter part of the long-term record, including the post-control period, spanned a regional drought (discussed in "Precipitation Chemistry" section), it is possible that the model did not fully capture all of the climatic effect on surface-water concentrations.

Residuals of the concentration-cumulative discharge model were compared using the Wilcoxon rank-sum test (also nonparametric) for the periods before and after emission reductions at the Hayden powerplant. The results of the Wilcoxon test are presented in table 3, with statistically significant results ($p<0.05$) shown in bold type.

Chemical Constituent Concentrations

Sulfate.—The analysis of precipitation and snowpack concentration data indicated that sulfate concentrations decreased in the post-control period compared to the pre-control period and that the decrease was of greater magnitude at the downwind MZWA sites than at the control sites. Raw (unadjusted for discharge) mean sulfate concentrations in the surface water (fig. 18) did not follow this pattern. In fact, slight increases were observed at most of the MZWA sites, consistent with the effects of drought, whereas concentrations were unchanged or decreased slightly in all of the FTWA sites. The exception was Long Lake Reservoir, a site with much higher sulfate concentration and sulfate:chloride ratio than the other sites, reflecting differences in hydrology and biogeochemistry that may complicate interpretation of changes resulting from atmospheric deposition (Turk and others, 1993).

In addition to analyzing sulfate concentrations alone, the sulfate:chloride ratio in the lakes was analyzed as an alternate approach to account for variations in sulfate caused by seasonality or climate. For both raw and discharge-adjusted data, results for sulfate:chloride ratio was similar to those for sulfate concentration: statistically significant changes were present at more sites in the FTWA than the MZWA (fig. 18 and table 3).

Discharge-adjusted sulfate concentrations in the MZWA and FTWA either decreased slightly or were not significantly different during the post-control period compared to the pre-control period (table 3). The largest decrease was in Long Lake Reservoir, the Mount Zirkel lake with the greatest influence of ground water and the one expected to be least responsive to changes in atmospheric deposition. Because sulfate concentrations in Long Lake were higher than in the other sites, the percent decrease was relatively small. Changes in surface-water sulfate concentrations were similar between the MZWA and FTWA, indicating that decreased emissions from the Hayden powerplant did not have a substantial effect on surface-water chemistry in the MZWA. Detection of a response to changes in emissions and deposition in the lake-chemistry data may have been confounded by drought conditions during the period after emissions reductions occurred. It also is possible that a lag time between changes in deposition and response in surface water may delay detection of the response. A previous study of FTWA lakes indicated that lake concentrations of sulfate responded to changes in deposition on timescales that varied depending on their position along hydrologic flow paths (Campbell and others, 1991). The magnitude of reduced sulfate in atmospheric deposition indicates that at some time in the future, a reduction in lake sulfate attributable to Yampa Valley emission reduction should be detectable. The trend of decreasing sulfur dioxide emissions throughout western North America over the past 20 years is reflected in reduced concentrations of sulfate in lakes that were part of this study, as well as other lakes in the Rocky Mountains. However, detection of the surface-water response

Table 3. Results of Wilcoxon rank-sum test comparing discharge-adjusted concentrations at surface-water sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

[MZWA, Mount Zirkel Wilderness Area; FTWA, Flat Tops Wilderness Area; p-value, significance of difference using 2-sided test; Diff., discharge-adjusted average concentration for post-control period minus discharge-adjusted average concentration for pre-control period; concentrations in microequivalents per liter; Sulfate:chloride, ratio of sulfate to chloride; ANC, acid-neutralizing capacity; Base cations, sum of calcium and magnesium; <, less than; number of samples in pre- and post-control periods; values in bold statistically significant at p<0.05]

Wilderness	Site	Sulfate		Sulfate:chloride		Nitrate		ANC		Base cations		Number of samples	
		p-value	Diff.	p-value	Diff.	p-value	Diff.	p-value	Diff.	p-value	Diff.	Pre	Post
MZWA	Lake Elbert	0.177	–0.7	0.678	–1.0	.001	**0.0**	.640	2.6	.835	2.2	11	15
MZWA	Lake Elbert Inflow	.362	–1.2	.543	–0.4	.095	–0.6	.879	1.8	.879	–3.6	11	9
MZWA	Long Lake Reservoir	**.037**	**–3.8**	.838	0.4	**.004**	**0.0**	**.046**	**31.8**	**.025**	**35.0**	10	9
MZWA	Seven Lakes	.954	0.0	.562	–0.7	.118	–0.3	.105	–3.0	.105	–1.7	11	13
MZWA	Seven Lakes Inflow	.479	0.1	.230	–0.9	.518	0.8	.829	8.5	.782	12.0	11	12
MZWA	Summit Lake	**.032**	**–1.4**	**.008**	**–1.4**	**<.001**	–0.5	**<.001**	**12.4**	**.002**	**8.1**	22	29
FTWA	Lower Packtrail Pothole	.083	–1.1	**.047**	**–0.8**	.302	–0.2	**.043**	**5.3**	.213	4.5	27	23
FTWA	Ned Wilson Lake	**<.001**	**–1.4**	**<.001**	**–0.9**	**<.001**	–0.9	**<.001**	**10.1**	**<.001**	**12.6**	29	35
FTWA	Ned Wilson Spring	**.022**	**–0.9**	.071	0.0	**<.001**	**–1.5**	.705	13.1	.188	73.9	27	19
FTWA	Upper Ned Wilson Lake	**.004**	**–1.4**	.135	–1.3	.223	–0.6	**<.001**	**10.1**	**<.001**	**13.1**	29	21
FTWA	Upper Packtrail Pothole	.493	–0.5	.519	0.0	**.001**	**–0.1**	.114	4.1	.135	4.1	27	21

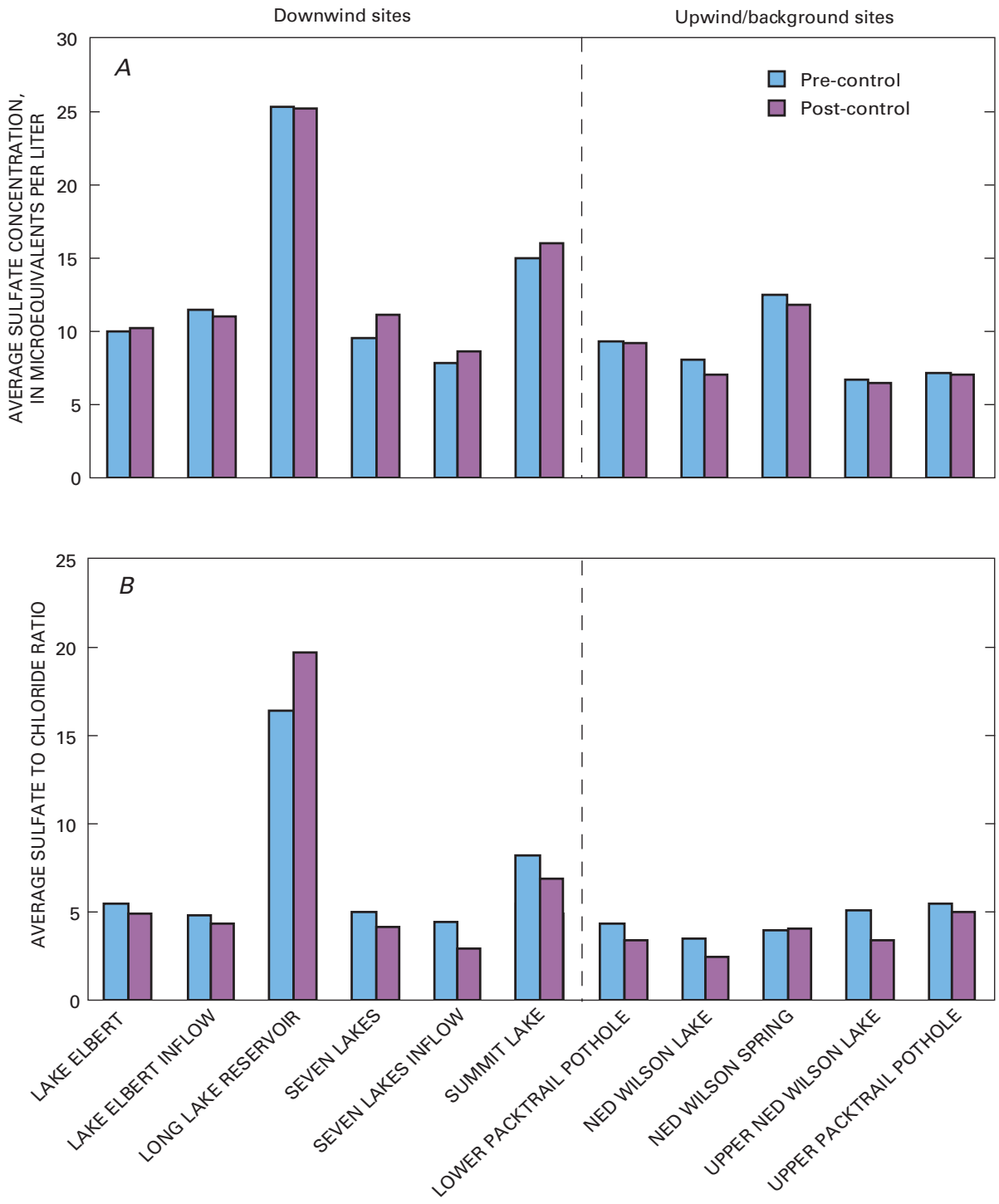


Figure 18. Average (*A*) sulfate concentrations and (*B*) sulfate to chloride ratio at surface-water sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

to changes in deposition requires a sufficiently long record to minimize effects of climate variability and to allow for lag time as sulfate moves through storage in soil, ground water, and lake reservoirs.

Nitrate.—Ecosystems in the FTWA and MZWA are not as sensitive to nitrogen deposition as those in the Front Range, probably because they contain more soil and vegetation with nitrogen assimilation capacity. As a result, most values for nitrate concentrations in lakes in the MZWA and FTWA were below the detection limit of 0.7 µeq/L. Figure 19 shows mean nitrate concentrations (unadjusted for discharge) calculated with all nondetect values set to the detection limit. Discharge-adjusted calculations were made with all nondetect values set to one-half the detection limit, or 0.35 µeq/L (table 3). Some significant decreases in the discharge-adjusted nitrate were found in both the FTWA and the MZWA data, but the magnitude of the decreases was small and reflected the influence of a few values during the pre-control period that were only slightly above the detection limit.

Because nitrogen concentrations in precipitation did not decrease significantly at NADP or RMS sites in the MZWA as a result of the emission reductions, no effect was expected in the surface-water sites. In the MZWA, the combination of a high rate of nitrogen deposition and little export of nitrogen to surface waters indicates accumulation of nitrogen in the terrestrial ecosystem. Soil nitrogen could eventually reach threshold levels where nitrogen begins to leach from soils, based on nitrogen saturation studies from other parts of the world.

Acid-neutralizing capacity (ANC) and sum of base cations.—Both the unadjusted and discharge-adjusted ANC increased substantially in some of the lakes between the pre- and post-control periods (fig. 20). Because increases in ANC were 5–10 times greater than decreases in sulfate, decreased deposition of sulfate is not likely the cause for much of the increase in ANC. Increases in ANC were generally accompanied by increases in sum of base cations (SBC) of comparable magnitude. The most likely explanation for these increases is a combination of drought-related effects such as increased influence of concentration by evapotranspiration and increased influence of ground-water inputs, as there was less flushing by snowmelt during the post-control period drought. Again, this indicates that the concentration-cumulative discharge model did not completely account for the effect of the multiyear drought on concentrations of weathering products in the lakes. Low-flow conditions persisting over extended periods likely have a stronger effect than can be accounted for by using existing models and datasets of 20 years or less.

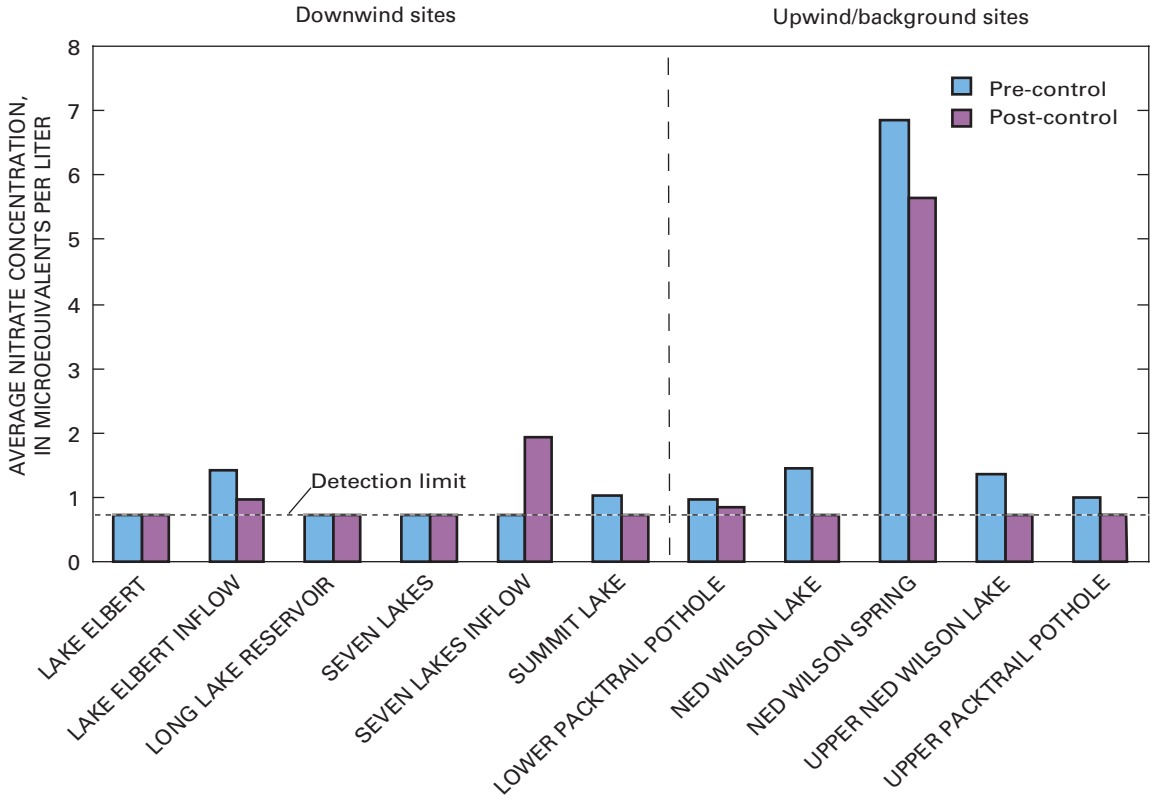


Figure 19. Average nitrate concentrations at surface-water sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

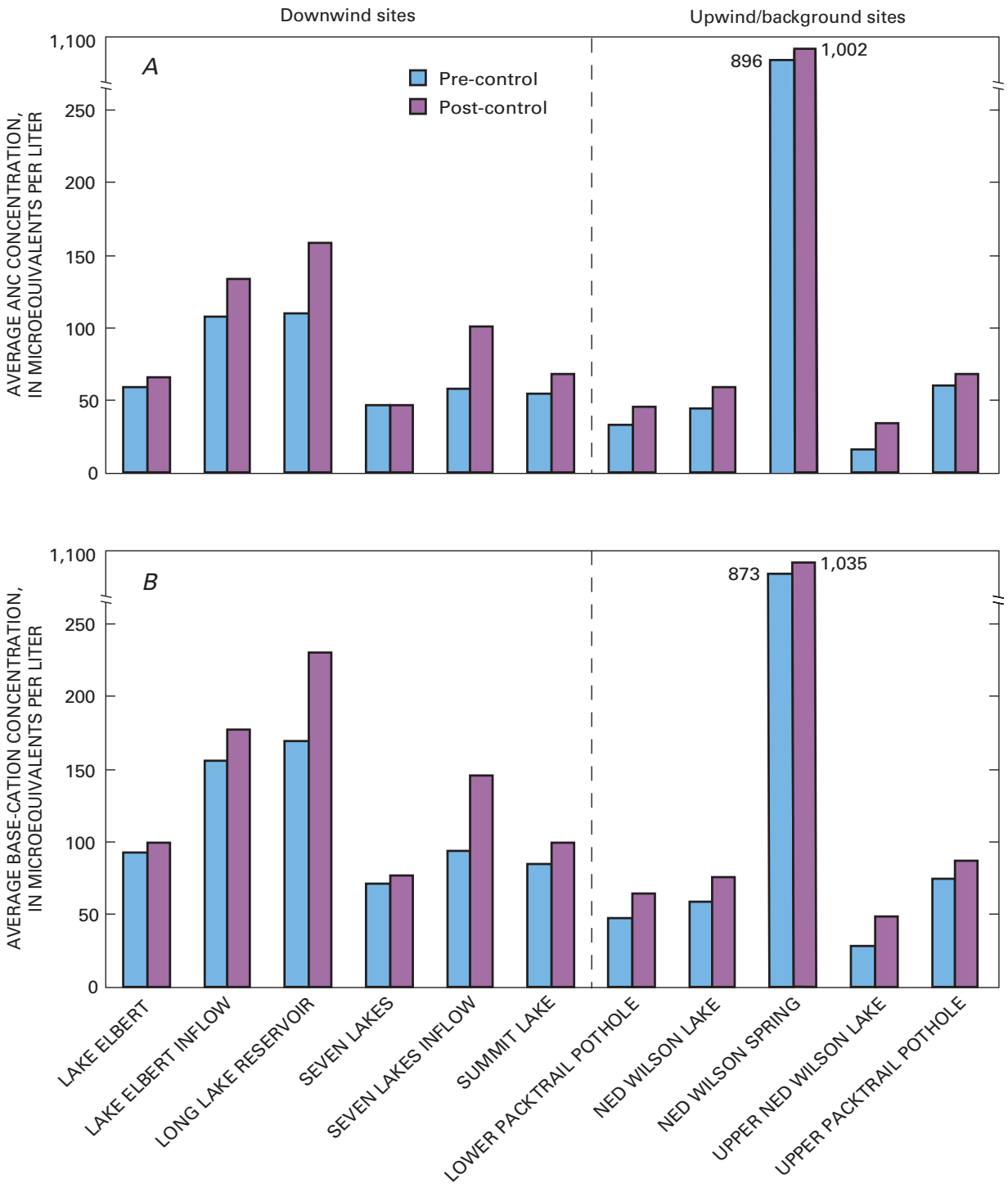


Figure 20. Average (*A*) acid-neutralizing capacity and (*B*) base-cation concentrations at surface-water sites before (pre-control, 1995–98) and after (post-control, 2000–2003) installation of emission controls at the Hayden powerplant in Colorado.

Summary and Conclusions

Precipitation, snowpack, and surface-water samples collected during 1995–2003 were analyzed to evaluate the environmental effects of emission reductions at the Hayden powerplant on the Mount Zirkel Wilderness Area (MZWA) in Colorado. The Hayden powerplant is one of two large coal-fired powerplants in the Yampa Valley that are situated directly upwind from the wilderness area. Due to concerns about impairment of air-quality-related values in the wilderness, the Hayden powerplant was retrofitted with control systems in 1999 to reduce sulfur dioxide and nitrogen oxide emissions—the primary precursors of haze and acidic precipitation. The U.S. Geological Survey, in cooperation with the Colorado Department of Public Health and Environment, evaluated data from three monitoring networks including wet-only precipitation collected at 10 stations in the National Atmospheric Deposition Program (NADP), bulk snowpack collected at 22 sites in the Rocky Mountain Snowpack (RMS) network, and surface water collected at 11 sites in a USGS long-term lakes-monitoring program. Chemical constituent concentrations and deposition rates were compared for periods before and after emission reductions at the Hayden powerplant. Data collected during 1995–98 were used to represent the pre-control period and data collected during 2000–2003 were used to represent the post-control period.

Precipitation chemistry.—Comparison of the NADP data between the pre- and post-control periods indicates that regional and local factors may have influenced precipitation amount and chemistry during the study period. At all 10 NADP stations, average annual precipitation amount was lower in the post-control period than the pre-control period. This pattern in precipitation is clearly caused by drought conditions that persisted in the region during the post-control period. The effect of the drought was widespread, as evidenced by the decrease in precipitation amount at all 10 stations, but also was persistent throughout the year, based on the seasonal patterns in precipitation amount. Because concentrations in precipitation commonly are inversely correlated with amount, climatic patterns may complicate the ability to detect changes in precipitation chemistry caused by the emission reductions at the powerplant.

In contrast to precipitation amount, there was no consistent pattern of change in sulfate concentrations between the pre- and post-control periods, indicating sulfate was not strongly influenced by the regional drought or that the drought effect was masked by regional declines in sulfur dioxide emissions. Among the 10 stations evaluated in this study, 3 showed slight increases in sulfate concentrations, 3 showed little or no change, and 4 showed decreases between the pre- and post-control periods. The largest decrease in sulfate concentrations occurred at the two NADP stations downwind from the Hayden powerplant, decreasing by 3.3 μeq/L at Dry Lake and by 2.2 μeq/L at Buffalo Pass. In addition, Dry Lake and Buffalo Pass were the only two stations that showed decreases in sulfate concentrations during all four seasons of the year. Moreover, declines in sulfate deposition were greater at Dry Lake (3.4 kg/ha) and Buffalo Pass (3.3 kg/ha) than at the eight background stations. These results indicate emission reductions at the Hayden powerplant appear to have been a factor in declines in atmospheric deposition of sulfate in areas directly downwind from the station.

In contrast to sulfate, regionally consistent patterns were observed in the concentrations of the other chemical constituents. Nitrate, ammonium, and base-cation concentrations at all 10 NADP stations were higher in the post-control period compared to the pre-control period. Because the concentration patterns corresponded to the decrease in precipitation amount, the results indicate that the drought had a concentrating effect on precipitation chemistry. The drought also may explain the patterns in hydrogen-ion concentrations, which were lower in the post-control period than the pre-control period at all 10 stations. During drought conditions, higher levels of alkaline dust may be present in the atmosphere, which could neutralize acidity associated with nitrate and sulfate. Carbonate-rich dust also is a potential source of excess calcium and magnesium in precipitation, which may explain the larger relative increase in base-cation concentrations between periods compared to nitrate and ammonium. Another factor that might have contributed to the increase in nitrate and ammonium concentrations was a regional increase in nitrogen emissions related to growing urban and agricultural areas in the Rocky Mountains. Although ammonium emissions have increased steadily in the Western United States over the past decade, nitrogen oxide emissions from powerplants and other large stationary sources in Colorado actually declined by about 5 percent statewide between 1995 and 2003.

Snowpack chemistry.—The post-control period was influenced by the regional drought. Annual snow-water equivalent (SWE) values reported April 1 of each year of the study (at SNOTEL sites in the area near the six local snow-sampling sites) were as much as 133 percent of average during the pre-control period and declined to as little as 68 percent in the post-control period. Decreasing SWE at five of six local sites in the study did not effect a reduction in deposition in many cases for three of the five constituents. Thus, the effect of the recent drought on atmospheric deposition to the six local sites in this study possibly is less than that of snowpack chemical concentration.

No statistically significant changes were detected in average annual snowpack sulfate concentrations among the two groups comparing the pre- and post-control periods. Nonetheless, small increases in snowpack sulfate concentrations were observed during the post-control period in Colorado

and Wyoming at 11 of the 22 RMS snow-sampling sites. Modest decreases in sulfate deposition to snowpack samples occurred at five of six local sites near the Hayden powerplant, which is consistent with decreasing SWE in the snowpack and with sulfur dioxide emission reductions at the Hayden powerplant.

Higher average annual nitrate concentrations were measured at all 22 RMS sites in the study during the drought years of the post-control period. Increases in nitrate deposition occurred at all six local sites, while nitrogen oxide emissions at the Hayden powerplant decreased, and nitrate decreased in wetfall at two collocated NADP stations. This suggests that other factors such as the drought or other regional emission sources were affecting nitrate concentrations and deposition during the study period. Dry deposition, not captured by NADP wetfall collectors, may account for part of the increased nitrate deposition to snowpacks.

Average annual concentrations of ammonium and base cations increased, while hydrogen-ion concentrations decreased at all 22 RMS sites observed. Ammonium deposition increased at all six local sites in the post-control period despite decreasing precipitation at five of six sites in the study and decreases observed in wetfall at NADP stations. Average annual base-cation-concentration increases probably were due, in part, to increased mobility of dust in lower elevations with less snow cover. Base-cation deposition increased at all six sites in the study and nearly doubled at Buffalo Pass and Sunlight Peak, while deposition values at two collocated NADP stations at Buffalo Pass and Sunlight Peak showed relatively little change. In contrast to increased ammonium and base cations, hydrogen-ion deposition decreased at all sites, as seen at NADP stations, and could be the result of acid-neutralizing potential of dust and wind-transported material.

Surface-water chemistry.—The chemistry at six surface-water sites in and near the MZWA and five control sites in the Flat Tops Wilderness Area (FTWA) was examined. No response to emission reductions was detectable in chemistry of the surface water in the MZWA. Detection of a response to changes in emissions and deposition in the lake chemistry data may have been confounded by drought conditions during the period after emission reductions occurred. The magnitude of reduced sulfate in atmospheric deposition indicates that at some time in the future, a reduction in lake sulfate attributable to Yampa Valley emission reduction should be detectable. The trend of decreasing sulfur dioxide emissions throughout western North America over the past 20 years is reflected in reduced concentrations of sulfate in lakes that were part of this study, as well as other lakes in the Rocky Mountains. However, detection of the surface-water response to changes in deposition requires a sufficiently long record to minimize the effects of climate variability and to allow for lag time as sulfate moves through storage in soil, ground water, and lake reservoirs.

References Cited

Banta, R., and Cotton, W.R., 1981, An analysis of the structure of local wind systems in a broad mountain basin: Journal of Applied Meteorology, v. 20, p. 1255–1266.

Barry, R.G., 1992, Mountain weather and climate, 2d ed.: London, Routledge, p. 226–259.

Burns, D.A., 2002, The effects of atmospheric nitrogen deposition in the Rocky Mountains of Colorado and southern Wyoming—A synthesis and critical assessment of published results: U.S. Geological Survey Water-Resources Investigations Report 02–4066, 41 p.

Campbell, D.H., Clow, D.W., Ingersoll, G.P., Mast, M.A., Spahr, N.E., and Turk, J.T., 1995, Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains: Water Resources Research, v. 31, no. 11, p. 2811–2821.

Campbell, D.H., Turk, J.T., and Spahr, N.E., 1991, Response of Ned Wilson Lake watershed, Colorado, to changes in atmospheric deposition of sulfate: Water Resources Research, v. 27, no. 8, p. 2047–2060.

Clow, D.W., and Ingersoll, G.P., 1994, Particulate carbonate matter in snow from selected sites in the south-central Rocky Mountains: Atmospheric Environment, v. 28, p. 575–584.

Clow, D.W., Sickman, J.O., Striegl, R.G., Krabbenhoft, D.P., Elliot, J.G., Dornblaser, M., Roth, D.A., and Campbell, D.H., 2003, Changes in chemistry of lakes and precipitation in high-elevation national parks in the western United States, 1985–99: Water Resources Research, v. 39, no. 6, 13 p.

Colorado Department Public Health and Environment, 2004, Long-term strategy review and revision of Colorado's State implementation plan for Class I Area visibility protection—Part 1, Review of the long-term strategy: Prepared by Colorado Air Pollution Control Division Technical Services Program, Visibility, Fire, and Quality Assurance Unit, November 18, 2004.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., and Weathers, K.C., 2001, Acid rain revisited—Advances in scientific understanding since the passage of the 1970 and 1990 Clean Air Act Amendments: Hubbard Brook Research Foundation, Science Link Publication, v. 1, no. 1, 24 p.

Helsel, D.R., and Hirsch, R.M., 1992, Statistical methods in water resources: Amsterdam, The Netherlands, Elsevier Science B.V., 529 p.

Ingersoll, G.P., 1995, Maximum-accumulation snowpack chemistry at selected sites in northwestern Colorado during spring 1994: U.S. Geological Survey Open-File Report 95–139, 14 p.

Kleinman, L.I., and Daum, P.H., 1991, Oxidant limitation to the formation of H_2SO_4 near a SO_2 source region: Atmospheric Environment, v. 25, p. 2023–2028.

Michel, R.L, Turk, J.T., Campbell, D.H., and Mast, M.A., 2002, Use of natural ^{35}S to trace sulphate cycling in a small lake in the Flat Tops Wilderness Area, Colorado, USA: Water, Air, and Soil Pollution Focus, v. 2, p. 5–18.

Nilles, M.A., and Conley, B.E., 2001, Changes in chemistry of the precipitation in the United States, 1981–1998: Water, Air, and Soil Pollution, v. 130, p. 409–414.

Turk, J.T., and Adams, D.B., 1983, Sensitivity to acidification of lakes in the Flat Tops Wilderness Area, Colorado: Water Resources Research v. 19, no. 2, p. 346–350.

Turk, J.T., and Campbell, D.H., 1987, Estimates of acidification of lakes in the Mount Zirkel Wilderness Area, Colorado: Water Resources Research, v. 23, no. 9, p. 1757–1761.

Turk, J.T., and 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?: U.S. Geological Survey Fact Sheet FS–043–97, 4 p.

Turk, J.T., Campbell, D.H., Ingersoll, G.P., and Clow, D.W., 1992, Initial findings of synoptic snowpack sampling in the Colorado Rocky Mountains: U.S. Geological Survey Open-File Report 92–645, 6 p.

Turk, J.T., Campbell, D.H., and Spahr, N.E., 1993, Use of chemistry and stable sulfur isotopes to determine sources of trends in sulfate of Colorado lakes: Water, Air, and Soil Pollution, v. 67, p. 415–431.

Turk, J.T., Taylor, H.E., Ingersoll, G.P., Tonnessen, K.A., Clow, D.W., Mast, M.A., Campbell, D.H., and Melack, J.M., 2001, Major-ion chemistry of the Rocky Mountain snowpack, USA: Atmospheric Environment, v. 35, no. 23, p. 3957–3966.

Watson, J.G., Blumenthal, D., Chow, J., Cahill, C., Richards, L.W., Dietrich, D., Morris, R., Houck, J., Dickson, R.J., and Andersen, S., 1996, Mt. Zirkel Wilderness Area reasonable attribution study of visibility impairment—Volume II, Results of data analysis and modeling final report, July 1, 1996: Prepared for the Technical Steering Committee, Colorado Department of Public Health and Environment Air Pollution Control Division, Denver, Colo.

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