

# Effect of power plant emission reductions on a nearby wilderness area: a case study in northwestern Colorado

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**Abstract** This study evaluates the effect of emission reductions at two coal-fired power plants in northwestern Colorado on a nearby wilderness area. Control equipment was installed at both plants during 1999–2004 to reduce SO<sub>2</sub> and NO<sub>x</sub> emissions. One challenge was separating the effects of local from regional emissions, which also declined during the study period. The long-term datasets examined confirm that emission reductions had a beneficial effect on air and water quality in the wilderness. Despite a 75 % reduction in SO<sub>2</sub> emissions, sulfate aerosols measured in the wilderness decreased by only 20 %. Because the site is relatively close to the power plants (<75 km), the slow rate of conversion of SO<sub>2</sub> to sulfate, particularly under conditions of low relative humidity, might account for this less than one-to-one response. On the clearest days, emissions controls appeared to improve visibility by about 1 deciview, which is a small but perceptible improvement. On the haziest days, however, there was little improvement perhaps reflecting the dominance of

regional haze and other components of visibility degradation particularly organic carbon and dust. Sulfate and acidity in atmospheric deposition decreased by 50 % near the southern end of the wilderness of which 60 % was attributed to power plant controls and the remainder to reductions in regional sources. Lake water sulfate responded rapidly to trends in deposition declining at 28 lakes monitored in and near the wilderness. Although no change in the acid–base status was observed, few of the lakes appear to be at risk from chronic or episodic acidification.

**Keywords** Mount Zirkel Wilderness · SO<sub>2</sub> emissions · NO<sub>x</sub> emissions · Visibility · Aerosols · Atmospheric deposition · Lake chemistry

## Introduction

The Mount Zirkel Wilderness Area (MZWA) located in northwestern Colorado encompasses 600 km<sup>2</sup> of mountainous terrain along the Continental Divide. Because MZWA is one of 156 class I wilderness areas in the USA, visibility is protected by law under the Federal Clean Air Act. Although the wilderness is in a remote part of the state, its western boundary is within 30 km of the Hayden power plant and 60 km of the Craig power plant, two of the largest coal-fired facilities in Colorado (Fig. 1). In 1993, the U.S. Department of Agriculture Forest Service certified to

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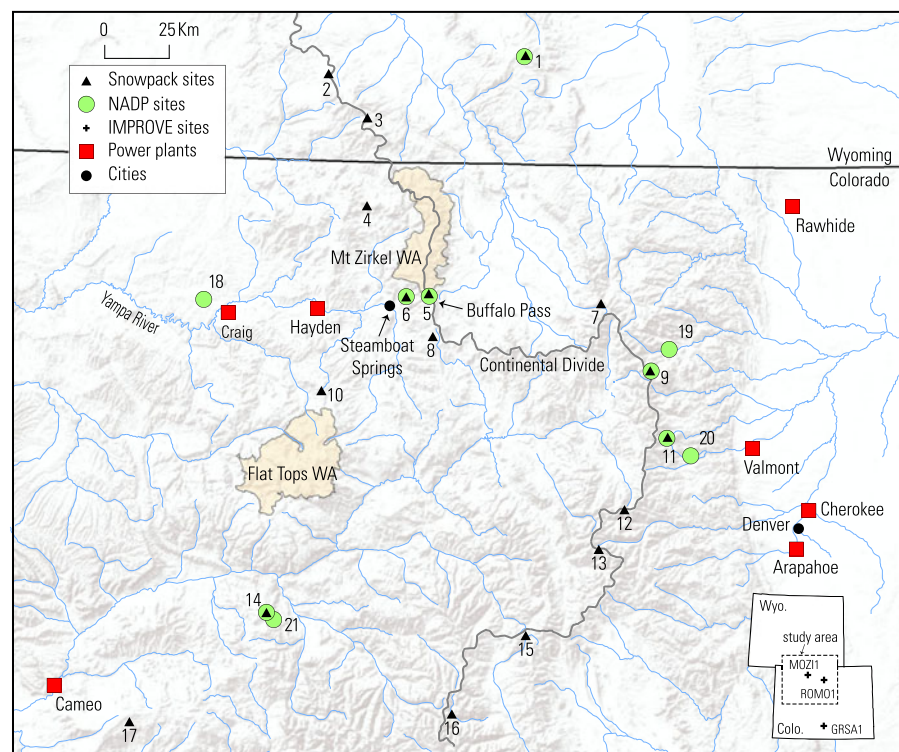
the State of Colorado that sulfur dioxide (SO<sub>2</sub>) and nitrogen oxide (NO<sub>x</sub>) emissions from Hayden and Craig were contributing to visibility impairment in the wilderness (Colorado Department of Public Health and Environment 2007). Sulfate aerosols formed in the atmosphere from gaseous SO<sub>2</sub> often are the largest single contributor to visibility impairment (Malm et al. 2004). In 1994, the Mount Zirkel Visibility Study was commissioned to determine the cause of visibility impairment in the MZWA (Watson et al. 1996). The study concluded that the 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 that could be hundreds of kilometers distant from the MZWA. The study also concluded that sulfate haze from Hayden and Craig occasionally entered the MZWA and, together with regional haze, contributed to visibility impairment.

There also were concerns that Hayden/Craig emissions might be causing acidic precipitation, which could damage aquatic ecosystem in the MZWA. Oxidation of

gaseous SO<sub>2</sub> and NO<sub>x</sub> in the atmosphere forms sulfuric and nitric acids, which are the primary components of acidic precipitation (Driscoll et al. 2001). Regional surveys conducted in the early 1990s showed that snowpacks in the MZWA were the most acidic in the western USA (Turk and Campbell 1997; Turk et al. 2001). Lakes and streams in the MZWA are especially sensitive to acidic precipitation because they drain bedrock and soils that have little capacity to buffer acidic inputs (Turk and Campbell 1987). In addition, snowmelt-dominated ecosystems are subject to periods of episodic acidification during the early stages of snowmelt, when elevated concentrations of acidity can be released from the snowpack (Campbell et al. 2004; Turk and Campbell 1997). Some studies suggested that the tiger salamander is sensitive to acidity at levels that might be found in snowmelt and rainfall in the MZWA (Harte and Hoffman 1989; Kiesecker 1996; Turk and Campbell 1997).

Due to concerns about air and water quality impairment in the MZWA, an agreement was made between the owners of the power plants and the Forest Service, State of Colorado, Sierra Club, and U.S. Environmental Protection Agency to install emission control equipment including SO<sub>2</sub> scrubbers, overfire air boiler modifications for control of NO<sub>x</sub>, and baghouses to capture

**Fig. 1** Study area and deposition sites in northwestern Colorado



particulates (Colorado Department of Public Health and Environment 2007). At Hayden, the upgrades occurred between September 1998 and November 1999, and at Craig between September 2003 and April 2004. The installation of pollution controls at the power plants resulted in a decline in SO<sub>2</sub> emissions of 75 % in just over 5 years (1999–2004).

This large reduction provides a unique opportunity to investigate source–receptor relationships between SO<sub>2</sub> emissions and air and water quality in a sensitive mountain environment directly downwind of the power plants. In this analysis, changes in environmental data collected by several long-term monitoring networks in and near the MZWA during the periods before and after installation of emission controls were examined. The datasets evaluated included chemically speciated aerosol concentrations, optical data (particle scattering), deposition (rain and snow) chemistry, and lake chemistry. Because SO<sub>2</sub> emissions have been declining across Colorado as well as the greater Rocky Mountain region over the past 15 years, one of the major challenges of the study was separating out the effects of local (Hayden/Craig) from regional emission sources.

## Methods

### Study area description

The MZWA straddles the Continental Divide in the Park Range of northwestern Colorado and lies at the headwaters of the west-flowing Yampa River (Fig. 1). The wilderness area includes 650 km<sup>2</sup> of mountainous terrain covered by subalpine spruce/fir forests and alpine tundra with over 70 lakes. Situated directly west and predominantly upwind of the wilderness are the Hayden and Craig coal-fired power plants, two of the largest electricity producers in Colorado. The Hayden power plant, which is 30 km to the west, consists of one 184-MW and one 262-MW generating unit, and the Craig power plant, which is 60 km to the west, consists of three 450-MW generating units. Other anthropogenic activities in the Yampa River Valley are tourism, ranching and coal mining, and the total population is around 27,000 (Mast et al. 2005) including the towns of Steamboat Springs, Hayden, and Craig (Fig. 1).

Climate of the area is characterized by long cold winters and short cool summers. Winter precipitation is associated with both large-scale storms and orographic

uplift as air masses move over the Continental Divide. Summer precipitation is dominated by localized convective thunderstorms. Mean annual precipitation is 145 cm per year (1979–2009) of which 70 % accumulates in a snowpack between November and April. Mean annual precipitation was 10 % above average in the 5 years prior to emission controls (1994–1998) and 2 % below average in the 5 years after (2005–2009). Precipitation in 2002 was 33 % below average reflecting drought conditions that prevailed across the state in the early 2000s (<http://www.wcc.nrcs.usda.gov/snotel/Colorado/colorado.html>). Upper-level winds (600 m above ground level) in the area are usually synoptically driven resulting in west–southwesterly to westerly flow during all times of the year (Watson et al. 1996). Local wind patterns are largely controlled by the topography of the Yampa River Valley. During the nights, surface winds are predominantly from the east as cold air drains downward from the surrounding mountains into the river valley (Watson et al. 1996). During daytime, vertical mixing causes air at all levels to move up the valley towards the southern end of the wilderness.

### Aerosol and visibility monitoring

An aerosol sampler and nephelometer were operated at Buffalo Pass by the IMPROVE monitoring program, which was established in 1985 to track visibility in class I areas (e.g., national parks and wilderness areas) (<http://vista.cira.colostate.edu/improve/>). The Buffalo Pass site (elevation, 3,200 m) was selected to represent high-elevation areas of the MZWA (Fig. 1). Moreover, its location near the southern end of the wilderness places it closest to the Yampa River Valley power plants and may provide an upper limit for emission exposure to the environment. Aerosol samples are collected every 3 days and analyzed for sulfate, nitrate, and other constituent concentrations (<http://vista.cira.colostate.edu/improve/Publications/OtherDocs/IMPROVEDataGuide/IMPROVEDataguide.htm>). The measurements are used to reconstruct a haze index expressed in deciview (dv) units (Pitchford and Malm 1994). The deciview is proportional to perceived changes in haze levels and increases as visibility decreases providing a convenient numerical method for presentation of visibility values. Summaries of mean annual aerosol concentrations and the haze index are available on the IMPROVE website at [http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary\\_data.htm](http://vista.cira.colostate.edu/improve/Data/IMPROVE/summary_data.htm).

The nephelometer at Buffalo Pass measures particle light scattering which is caused by both fine and coarse aerosol species and is the largest contributor to haze in most locations (Malm et al. 2004). Data are available from the IMPROVE website as an hourly average aerosol scattering coefficient ( $B_{sp}$ ) reported in megameter. The hourly  $B_{sp}$  values were screened for possible weather influence using the standard criteria relative humidity (RH) > 90 %,  $B_{sp} > 5000 \text{ Mm}^{-1}$ , and hourly change in  $B_{sp} > 50 \text{ Mm}^{-1}$  (Gebhart et al. 2001). Weather filtering of the data removes measurements that are likely to have been influenced by precipitation, fog, and clouds (Gebhart et al. 2001).

Deposition monitoring

Snowpack chemistry data were obtained from the Rocky Mountain Snowpack Network (RMSN), a network of sites in the Rocky Mountain Region where full depth (annual) snowpack samples are collected each spring and analyzed for major ions and nutrients. Collection methods and analytical techniques used by RMSN are described in Ingersoll et al. (2002). Annual chemistry data for 1993–2010 were retrieved from the RMSN website at [http://co.water.usgs.gov/projects/RM\\_snowpack/](http://co.water.usgs.gov/projects/RM_snowpack/) for 17 snowpack sites in northern Colorado and southern Wyoming (Fig. 1 and Table 1).

**Table 1** Temporal trends in sulfate, nitrate, and hydrogen ion concentrations for 1993–2010 at snowpack and NADP sites

Number	Site name	Elevation	Sulfate	Nitrate	Hydrogen
Snowpack sites					
1	Brooklyn Lake	3,231	-0.16	-0.08	<b>-0.38</b>
2	Divide Peak	2,634	-0.12	0.06	<b>-0.47</b>
3	Old Battle	3,024	<b>-0.19</b>	-0.01	-0.39
4	Elk River	2,636	<b>-0.15</b>	-0.03	<b>-0.52</b>
5	Buffalo Pass	3,139	<b>-0.38</b>	-0.13	<b>-0.54</b>
6	Dry Lake	2,526	<b>-0.45</b>	0.01	<b>-0.53</b>
7	Cameron Pass	3,132	<b>-0.21</b>	-0.02	-0.19
8	Rabbit Ears	2,986	<b>-0.27</b>	-0.02	<b>-0.56</b>
9	Loch Vale	3,216	<b>-0.22</b>	-0.06	<b>-0.45</b>
10	Dunckley Pass	2,987	<b>-0.14</b>	-0.03	-0.20
11	University Camp	3,149	-0.07	0.08	<b>-0.44</b>
12	Berthoud Pass	3,466	-0.01	0.14	<b>-0.28</b>
13	Loveland Pass	3,615	-0.07	-0.01	-0.23
14	Sunlight Peak	3,226	<b>-0.11</b>	0.05	<b>-0.33</b>
15	Fremont Pass	3,440	-0.02	0.01	-0.15
16	Brumley	3,231	-0.04	0.11	-0.08
17	Grand Mesa	3,158	<b>-0.17</b>	0.06	<b>-0.28</b>
NADP sites					
1	Snowy Range (WY00) <sup>a</sup>	3,286	<b>-0.19</b>	-0.15	<b>-0.32</b>
5	Buffalo Pass (CO97) <sup>a</sup>	3,234	<b>-0.48</b>	-0.12	<b>-0.48</b>
6	Dry Lake (CO93) <sup>a</sup>	2,538	<b>-0.53</b>	-0.15	<b>-0.68</b>
18	Sand Springs (CO15)	1,998	<b>-0.39</b>	-0.02	<b>-0.45</b>
19	Beaver Meadows (CO19)	2,490	<b>-0.30</b>	-0.19	<b>-0.36</b>
9	Loch Vale (CO98) <sup>a</sup>	3,159	<b>-0.19</b>	-0.05	<b>-0.33</b>
11	Niwot Saddle (CO02) <sup>a</sup>	3,520	<b>-0.25</b>	-0.12	<b>-0.25</b>
20	Sugarloaf (CO94)	2,524	<b>-0.47</b>	-0.27	<b>-0.46</b>
14	Sunlight Peak (CO92) <sup>a</sup>	3,218	<b>-0.21</b>	-0.08	<b>-0.28</b>
21	Four Mile Park (CO08)	2,502	<b>-0.19</b>	-0.05	<b>-0.28</b>

Statistically significant trends shown in bold ( $p < 0.05$ ). Trend slopes in units of microequivalents per liter per year and elevation in meters. Site number shown on Fig. 1

<sup>a</sup>Co-located snowpack and NADP site

Wet deposition chemistry was obtained from the National Atmospheric Deposition Program (NADP), which collects weekly composite samples year round at 250 stations nationwide for major ions and nutrients. Sample collection protocols, analytical methods, and quality-assurance procedures used by NADP are documented at <http://nadp.sws.uiuc.edu/>. Annual precipitation-weighted mean concentrations were retrieved from the NADP website for 10 high-elevation sites in Colorado and Wyoming (Fig. 1 and Table 1). Mean concentrations are computed using only samples with complete and valid laboratory analyses and valid measurements of precipitation amount (<https://nadp.isws.illinois.edu/documentation/notes-AvMg.html>).

### Surface-water monitoring

Surface-water chemistry for 28 lakes and ponds in and adjacent to the southern part of the Mount Zirkel Wilderness were analyzed as part of this study. These sites were sampled once each summer beginning in 1993 as part of a long-term U.S. Geological Survey (USGS) monitoring program (Mast et al. 2011). At one of the 28 sites, Summit Lake, sampling was more frequent (3 to 5 times per summer) and chemistry records go back to the mid-1980s. Chemistry data for lakes in the nearby Flat Tops Wilderness Area (Fig. 1) also were included in this analysis and were used as regional background sites for comparison to lakes downwind of the power plants. At all the surface-water sites, grab samples were collected from the lake outlets or shoreline and analyzed for major ions, nutrients, pH, and acid neutralizing capacity (ANC). Details of collection and analytical methods can be found in Mast et al. (2011) and data are available through the USGS National Water Information System (NWIS) database at <http://waterdata.usgs.gov/nwis>.

### Data analysis

Due to the variable nature of the aerosol and visibility measurements, changes were evaluated by comparing data before and after installation of emission controls. Data collected during 1994–98 were used to represent the before period and data collected during the 2005–09 were used to represent the after period. Annual mean aerosol concentrations and the haze index were computed for the before and after periods for the 20 % clearest and 20 % haziest visibility days in each year

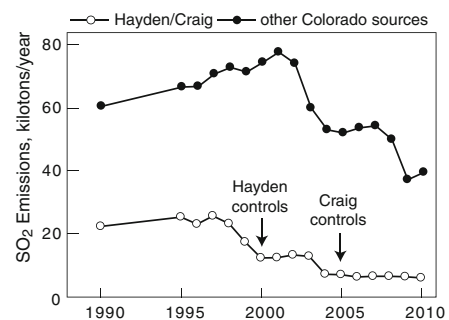
as well as for all the days in each year. The percent change in aerosol concentration was computed as the mean of the before period minus the mean of the after period divided by the mean of the before period. For the visibility data, mean daily  $B_{sp}$  was computed using the filtered dataset then separated according to the before and after periods and binned into 4 relative humidity (RH) groups (20–40 %, 40–60 %, 60–80 %, 80–100 %). The 0–20 % RH bin was not used because it contained less than 1 % of the total measurements. The means of the four RH groups were compared in the before and after periods using a *t* test.

To describe changes in precipitation (NADP and snowpack) and lake chemistry during the study period, long-term temporal trends were determined for the period 1993–2010. Trends were computed with mean annual or seasonal concentrations using the nonparametric Mann–Kendall, which tests for the presence of monotonic upward or downward trends (Helsel and Hirsch 1992). A *p* value of <0.05 was used to indicate statistical significance. The slope of each trend was determined with Sen's slope estimator (Helsel and Hirsch 1992).

## Results

### Emissions

Emission data used in this study were obtained from the EPA Clean Air Markets Division at <http://ampd.epa.gov/ampd/>. Combined SO<sub>2</sub> emissions from Hayden/Craig peaked at over 25,000 tons in 1997 at which time they accounted for 27 % of total SO<sub>2</sub> emissions in Colorado (Fig. 2). SO<sub>2</sub> emissions declined by 50 % following installation of controls at



**Fig. 2** Trends in annual SO<sub>2</sub> emissions from the Hayden/Craig power plants and from other stationary sources in Colorado. Arrows indicate the first year after installation of emission controls

Hayden and by another 40 % following controls at Craig. Combined Hayden/Craig emissions were less than 6,500 tons by 2006 representing a total reduction of nearly 75 % since the mid-1990s. SO<sub>2</sub> emissions from other stationary sources in Colorado also showed substantial changes over the last decade, but the timing was slightly different. Emissions from other facilities in Colorado increased steadily until 2002 then declined by over 50 % reaching a minimum in 2009. The same pattern of declining SO<sub>2</sub> emissions also occurred on a regional scale with emissions declining by 55 % between 1995 and 2010 in the five state area including Colorado, Wyoming, Utah, New Mexico, and Arizona (<http://ampd.epa.gov/ampd/>).

Reductions in NO<sub>x</sub> emissions following installation of controls at Hayden/Craig were more modest and gradual than for SO<sub>2</sub>. Emission reductions at Hayden were close to 50 %, but at Craig, the reduction was closer to 25 %. Combined emissions peaked in 1997 at 30,585 tons then declined by 30 % to a minimum of 21,050 tons in 2009. Over the same period, NO<sub>x</sub> emissions from other stationary sources in Colorado declined by about 45 % from a maximum of 59,015 in 1996 to a minimum of 32,425 tons in 2009. These estimates, however, do not include NO<sub>x</sub> emissions from mobile and non-point sources such as vehicle emissions, oil and gas exploration and production, and agricultural activities, which in Colorado account for over 60 % of annual NO<sub>x</sub> emissions (<http://www.epa.gov/ttnchie1/trends/>).

## IMPROVE aerosol and nephelometer data

IMPROVE aerosol data were examined at a site on Buffalo Pass (MOZII) and compared to two more distant sites in Colorado (ROMO1 and GRSA1) (Fig. 1), which were assumed to be minimally influenced by Hayden/Craig. The composition of fine aerosols at MOZII is dominated by sulfates, organic carbon, and soil components, which make up on average 30 %, 38 %, and 22 %, respectively, of the fine particle mass. In western USA, sulfates largely are a product of power plant SO<sub>2</sub> emissions, organic aerosols are associated with wildfire activity, and the soil component reflects wind-blown dust (Malm et al. 2004). Table 2 shows annual average aerosol concentrations for sulfate and nitrate and the haze index (deciview) in the before and after periods for the 20 % clearest, 20 % haziest days, and for all days. Aerosol sulfate concentrations were similar among the three sites and were highest on the haziest days and lowest on the clearest days. On the clearest days, sulfate concentrations at MOZII decreased 42 % between the before and after periods, whereas the decrease was 19 % and 13 % at the control sites (ROMO1 and GRSA1). On the haziest days, the decrease at MOZII was 20 %, which was just slightly higher than at the control sites. Aerosol nitrate concentrations at ROMO1 were highest of the three sites particularly on the haziest days likely reflecting its

**Table 2** Comparison of annual average aerosol concentrations and haze index at three Colorado IMPROVE sites for periods before and after installation of emission controls

	Before (1994–1998)			After (2005–2009)					
	MOZII	ROMO1	GRSA1	MOZII	ROMO1	GRSA1	MOZII	ROMO1	GRSA1
Sulfate aerosol (µg/m <sup>3</sup> )							% Change		
20 % Clearest	0.40	0.32	0.40	0.23	0.26	0.35	-42 %	-19 %	-13 %
20 % Haziest	1.38	1.60	1.48	1.11	1.36	1.29	-20 %	-15 %	-13 %
All data	0.87	0.92	0.89	0.69	0.80	0.79	-20 %	-12 %	-11 %
Nitrate aerosol (µg/m <sup>3</sup> )							% Change		
20 % Clearest	0.07	0.05	0.08	0.08	0.05	0.08	11 %	13 %	-3 %
20 % Haziest	0.20	0.54	0.28	0.26	0.70	0.28	26 %	30 %	-2 %
All data	0.15	0.26	0.17	0.17	0.31	0.18	17 %	19 %	10 %
Haze index (deciview)							Difference		
20 % Clearest	2.95	3.56	4.26	0.68	2.03	3.56	-2.27	-1.53	-0.69
20 % Haziest	10.34	12.77	11.93	9.72	12.62	11.44	-0.63	-0.15	-0.48
All data	6.64	8.13	7.84	5.15	7.17	7.41	-1.49	-0.96	-0.43

proximity to the Denver metropolitan area (Fig. 1). In contrast to sulfate, nitrate concentrations at MOZI1 showed increases between the before and after periods ranging from 11 % on the clearest days to 26 % on the haziest days. Because NO<sub>x</sub> emissions were actually declining at Hayden/Craig, the increase in aerosol concentrations suggests that emissions from mobile and nonpoint sources might be offsetting improvements at large stationary sources. The magnitude of the haze index was fairly similar among the sites although visibility overall was better at MOZI1 than the two more distant sites. Similar to sulfate, the greatest improvement in visibility occurred on the clearest days. On the haziest days, there was little change in the haze index at MOZI1 and the two control sites.

The *t* test for the filtered nephelometer measurements was statistically significant for each RH grouping indicating the light scattering coefficient ( $B_{sp}$ ) is higher in the after period than the before period (Table 3). Annual averages also were computed for  $B_{sp}$  using only data collected at noon and for RH in the 20–80 % range to help minimize the effects of daily variations in RH and for weather influences. A linear regression with time yielded a statistically significant increase of 0.33 Mm<sup>-1</sup>/year ( $r^2=0.43$ ,  $p=0.006$ ) during 1994–2009. Conversely, a regression of annual reconstructed particle scattering coefficient ( $B_{ext}$ ) from the IMPROVE network over time showed the opposite trend, with a decrease of 0.21 Mm<sup>-1</sup>/year ( $r^2=0.34$ ,  $p=0.009$ ). The  $B_{ext}$  is an estimate of the particle light scattering coefficient reconstructed from the IMPROVE bulk aerosol measurements (Pitchford and Malm 1994). Because the nephelometer measures total light scattering, it is possible that overall regional haze worsened during the after period although this is not supported by the aerosol concentrations at MOZI1. Another possibility could be measurement errors, while

the IMPROVE aerosol data undergo extensive and regular quality assurance reviews, the nephelometer data are not subject to the same level of review and documentation ([http://vista.cira.colostate.edu/improve/Data/QA\\_QC/qa\\_qc\\_Branch.htm](http://vista.cira.colostate.edu/improve/Data/QA_QC/qa_qc_Branch.htm)). A recent study reported statistically significant downward trends in  $B_{sp}$  at most IMPROVE sites across the USA, with the exception of a few desert sites and MOZI1, which showed upward trends (Collaud Coen et al. 2012). Similar to our results, the authors noted that the positive trend at MOZI1 was contradicted by aerosol measurements made at the site and thus were not able to provide an explanation for the observed upward trends (Collaud Coen et al. 2012).

Snowpack chemistry

Snowpack sites analyzed in this study were selected over a broad geographic area (40,000 km<sup>2</sup>). The Buffalo Pass and Dry Lake sites are immediately downwind of Hayden/Craig (sites 5 and 6; Fig. 1), whereas the more distant sites were selected to evaluate regional sources over the same period of record. Snow chemistry was extremely dilute and slightly acidic. In 2010, for example, the median pH for all sites was 5.23, sulfate was 5.6 µeq/L, and nitrate was 9.5 µeq/L. Downward trends in sulfate concentrations were observed at all 17 sites from 1993 to 2010 although the trends were statistically significant at only ten sites (Table 1). Downward trends in sulfate ranged from -0.01 to -0.45 µeq/L/year with the largest observed at the two downwind sites Dry Lake (-0.45 µeq/L/year) and Buffalo Pass (-0.38 µeq/L/year). Sites in the southeast part of the study area (Brumley, Fremont Pass, Loveland Pass, and Berthoud Pass) showed very small sulfate trends, none of which were statistically significant. Significant trends in nitrate concentrations were not detected at any of the snowpack sites despite substantial declines in NO<sub>x</sub> emissions from major stationary sources. Hydrogen ion concentrations showed statistically significant downward trends at 11 of the sites. However, the slope of the hydrogen trend typically was two to three times greater than the slope of the sulfate trend indicating that reductions in SO<sub>2</sub> are not the only explanation for declining snowpack acidity. The greater than anticipated declines correspond to increased calcium and alkalinity in the snowpack, particularly since 2006. These trends in snow chemistry are consistent with observations of recent dust storms that have deposited large amounts of dust on the snowpack in many areas of Colorado (Painter et al. 2007).

**Table 3** Average daily particle scattering ( $B_{sp}$ ) and relative humidity (RH) at MOZI1 for periods before and after emission controls and *t* test results for  $B_{sp}$

RH bin	Before		After		<i>t</i> Test <i>p</i> value
	$B_{sp}$	RH	$B_{sp}$	RH	
20–40	8.8	32.4	12.6	33.5	<0.001
40–60	8.9	49.9	10.7	50.2	<0.001
60–80	11.3	70.3	16.5	70.8	<0.001
80–100	30.5	84.8	42.2	84.3	<0.001

## NADP chemistry

Although there are fewer NADP than snowpack sites, precipitation is collected year round so these sites provide a more complete record of annual deposition chemistry. Statistically significant downward trends in sulfate concentrations over the period 1993–2010 were observed at all ten NADP sites (Table 1). Similar to snowpack sites, the largest trends were observed at the two downwind sites, Dry Lake ( $-0.53 \mu\text{eq/L/year}$ ) and Buffalo Pass ( $-0.48 \mu\text{eq/L/year}$ ), which amounts to a 50 % decrease in sulfate concentrations during 1993–2010. The Sand Springs site, which is only 11 km northwest of Craig, had a slightly lower trend of  $-0.39 \mu\text{eq/L/year}$ . This site is upwind of the power plants with respect to the prevailing wind direction and receives much less precipitation than the two downwind sites due to its lower elevation (1,998 m). A large downward trend in sulfate concentration ( $-0.47 \mu\text{eq/L/year}$ ) also was measured at the Sugarloaf site, which is on the east slope of the Front Range. Due to its location and lower elevation, Sugarloaf is influenced by different weather patterns than higher elevation Front Range sites and experiences a greater frequency of easterly upslope winds that transport pollutants from urban areas in the Front Range (Losleben et al. 2000). In fact,  $\text{SO}_2$  emissions from the Valmont power plant just 25 km east of Sugarloaf were reduced by 85 % in 2003 (<http://camd.dataandmaps.epa.gov/gdm/>), which may have had a strong localized effect on chemistry at this site. Downward trends at the remaining NADP sites (Snowy Range, Beaver Meadows, Loch Vale, Niwot Saddle, Sunlight Peak, Four Mile Park) were smaller ranging from 0.19 to  $0.30 \mu\text{eq/L/year}$ . These six sites should be minimally influenced by Hayden/Craig and in this study were selected as the control group. Hydrogen ion concentrations showed strong downward trends at all ten sites, which were of similar magnitude ( $-0.25$  to  $-0.68 \mu\text{eq/L}$ ) to the declines in sulfate. This suggests reductions in wetfall acidity have largely resulted from declines in  $\text{SO}_2$  emissions in contrast to snowpack acidity, which was partially neutralized by increasing dust deposition. Trends in nitrate concentrations were not statistically significant at any NADP sites tested.

## Lake water chemistry

The 28 MZWA lakes and ponds analyzed in this study are located within a 15-km radius of Buffalo Pass and range

in elevation from 2,957 to 3,578 m (Table 4). Although none of the lakes are acidic, they are considered acid sensitive with 40 % having ANCs below  $50 \mu\text{eq/L}$  and 70 % having ANCs below  $100 \mu\text{eq/L}$ . Average sulfate concentrations range from 5.1 to  $31.8 \mu\text{eq/L}$ , and isotopic data indicate dissolved sulfate largely is derived from atmospheric sources and contributions from geologic sources are negligible (Mast et al. 2011). Since 1993, trends in lake water sulfate concentrations in late summer have decreased at all 28 lakes at rates ranging from  $-0.16$  to  $-0.92 \mu\text{eq/L/year}$  (Table 4). The average rate of decrease for all lakes was  $-0.51 \mu\text{eq/L/year}$ , which is remarkably similar to the decrease in sulfate concentration

**Table 4** Lake elevation, average sulfate concentrations, and trend slopes for 1993–2010 at 28 lakes in the MZWA

Lake name	Elevation (m)	Concentration ( $\mu\text{eq/L}$ )	Trend ( $\mu\text{eq/L/yr}$ )
Fish Hawk Lake	2,957	18.2	<b>-0.85</b>
Snow Storm Lake	2,971	17.7	<b>-0.80</b>
Fish Hook Lake	3,011	24.6	<b>-0.51</b>
Lost Lake	3,018	27.9	<b>-0.67</b>
Rosa Lake	3,042	14.8	<b>-0.67</b>
Margaret Lake	3,044	17.7	<b>-0.69</b>
Mirror Lake	3,054	14.7	<b>-0.63</b>
Whale Lake	3,054	17.5	<b>-0.53</b>
Little Lost Lake	3,065	22.8	<b>-0.65</b>
Round Lake	3,066	31.8	<b>-0.87</b>
Dos Equis Pothole	3,075	18.3	<b>-0.92</b>
Jonah Lake	3,098	18.4	<b>-0.55</b>
Dinosaur Lake	3,103	20.0	<b>-0.66</b>
Pothole B-14	3,106	19.4	<b>-0.79</b>
Martha Lake	3,140	17.6	<b>-0.47</b>
Summit Lake	3,144	14.4	<b>-0.45</b>
George Lake	3,168	10.5	<b>-0.60</b>
Porcupine Lake	3,193	13.1	<b>-0.38</b>
Luna Lake	3,195	11.1	<b>-0.34</b>
Slide Lake	3,209	9.6	<b>-0.38</b>
Pothole B-6	3,228	10.1	<b>-0.48</b>
Pothole B-5	3,280	8.8	<b>-0.41</b>
Lake Elbert	3,292	10.0	<b>-0.34</b>
Lake of the Craggs	3,310	9.7	<b>-0.30</b>
Pothole A-7	3,380	5.2	<b>-0.20</b>
Pothole A-8	3,383	5.1	<b>-0.16</b>
Pothole A-3	3,487	9.4	<b>-0.30</b>
Upper Slide Lake	3,273	5.8	<b>-0.27</b>

Statistically significant trends ( $p < 0.05$ ) shown in bold



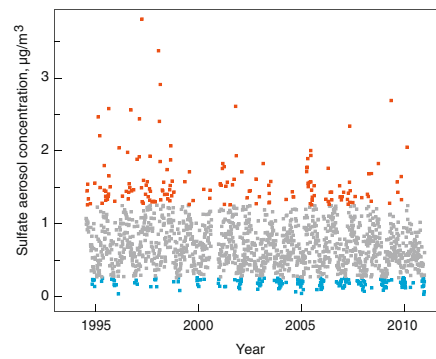
in wet deposition of  $-0.48 \mu\text{eq/L/year}$  at the Buffalo Pass NADP station. The trend slopes for the lakes showed a strong inverse correlation with elevation ( $r^2=0.66$ ) as did the average lake water sulfate concentrations ( $r^2=0.59$ ). When expressed as a percent change in sulfate per year (average= $-3.6 \%$ ), the relation between trend and elevation is no longer apparent ( $r^2=0.01$ ), indicating that the response of lake chemistry was fairly uniform across the southern end of the wilderness. Most of the study lakes had non-detectable nitrate concentrations during summer base-flow conditions indicating biological uptake is sufficient to remove nitrate from surface waters at current rates of deposition.

**Discussion**

**Aerosols and visibility**

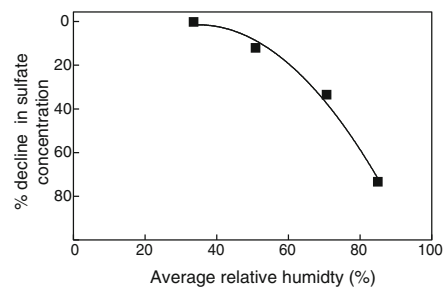
Sulfate aerosols decreased at MOZI1 as well as the two control sites during 1994–2009 consistent with reductions in both local and regional  $\text{SO}_2$  emissions. On the clearest days, the sulfate decrease at MOZI1 was about twice that of the closest control site (ROMO1) suggesting that Hayden/Craig controls accounted for about half of the decline and the remainder was due to regional improvements in air quality. In contrast, on the haziest days, sulfate declines at MOZI1 were similar in magnitude to the control sites suggesting declines in sulfate largely reflected regional air quality. Because sulfate concentrations were much higher on hazy days, this could simply indicate that the power plant signal was masked by higher sulfate concentrations from regional sources under these conditions. Looking at all the daily concentrations together better illustrates how sulfate aerosols changed over time. Following emission controls, fewer high concentration days and more numerous low concentration days are evident (Fig. 3). For example, the percent of days with concentrations  $>1.25 \mu\text{g/m}^3$  decreased from 17 % in the before period to 9 % in the after period. On the low end, the percent of days with sulfate concentrations  $<0.25 \mu\text{g/m}^3$  increased from 5 % in the before period to 13 % in the after period.

The overall reduction in sulfate aerosols of 20 % at MOZI1 was over three times lower than the decline in local power plant emissions of 75 %. A possible reason emission controls did not have more of an effect on aerosol concentrations might be the proximity of the power plants to the wilderness and the rate at which



**Fig. 3** Daily sulfate aerosol concentrations at the MOZI1 IMPROVE station during 1994–2010. Blue symbols indicate samples with concentrations  $<0.25 \mu\text{g/m}^3$  and orange symbols indicate concentrations  $>1.25 \mu\text{g/cm}^3$

$\text{SO}_2$  is converted to sulfate, which can be quite slow particularly in dry, cloud-free environments (Green et al. 2005). Watson et al. (1996) found that although plumes from Hayden/Craig regularly arrived in the wilderness, there was minimal conversion of  $\text{SO}_2$  to sulfate if RH was below 80 %. Model results and measured RH at the wilderness boundary suggested that conditions promoting rapid conversion of  $\text{SO}_2$  to sulfate occurred on only 3 % to 8 % of the daylight hours during the year (Watson et al. 1996). In a study of plume chemistry in Arizona, secondary aerosol formation was found to be minimal for distances up to 100 km (Richards et al. 1981), which is twice the distance between Buffalo Pass and Hayden. To look at this possible effect, the daily aerosol sulfate concentrations were grouped into four RH classes (20–40, 40–60, 60–80, 80–100), and average concentrations for each class were compared for the before and after periods. The percent change in sulfate concentrations clearly decreased with increasing RH reaching over 70 % for RH  $>80 \%$  (Fig. 4), which is similar to the



**Fig. 4** Percent decline in sulfate aerosol concentrations at MOZI1 between the before and after periods as a function of relative humidity

total reduction in SO<sub>2</sub> emissions of 75 %. This result suggests that aerosol production was rate limited under some conditions, which provides a possible explanation for why a one-to-one relationship between SO<sub>2</sub> emissions and sulfate aerosol concentrations was not observed in the Yampa River Valley.

Visibility improvements as inferred from the reconstructed haze index showed the same pattern as for sulfate suggesting that emission controls improved visibility most on the clearest days. The haze index at MOZI1 decreased by 2.3 dv on the clearest days compared to decreases of 0.7 to 1.5 dv at the control sites. Assuming the control sites mainly reflect regional haze, it seems unlikely that the Hayden/Craig controls resulted in improvements of more than 1 dv, which represents a small but perceptible improvement in visibility. On the haziest days, emission controls appeared to have only a minor effect on visibility impairment. A similar pattern of little change in visibility on the haziest days with improvements on the clearest days has been observed at IMPROVE sites throughout the Rocky Mountain region during a period of reducing SO<sub>2</sub> emissions (National Park Service 2009). This likely reflects the importance of other particulate components particularly organic material from wildfire and wind-blown dust, which often are responsible for the haziest days particularly in the western USA (Hand et al. 2011). Despite the lack of improvement on the haziest days, the annual haze index of 9.72 dv in the after period at MOZI1 was the third lowest out of 156 federal class I areas in the USA. Similarly, on the clearest days, MOZI1 ranked second out of 156 sites indicating current visibility conditions in the wilderness are good.

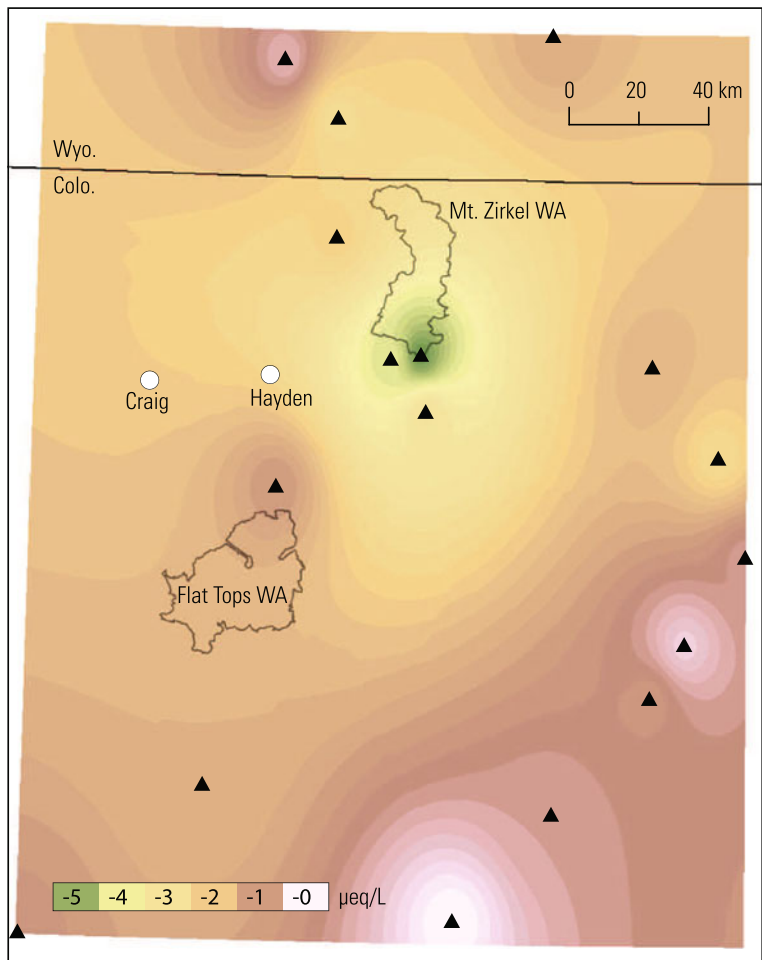
### Deposition chemistry

Decreasing sulfate deposition was observed across northwestern Colorado, which is consistent with reductions in both local and regional SO<sub>2</sub> emissions since the mid-1990s (Mast et al. 2011). All NADP sites showed statistically significant downward trends in sulfate concentrations (Table 1); however, the largest declines were at the Dry Lake and Buffalo Pass sites. Given the proximity of these sites to the Yampa River Valley and the path of prevailing air masses, the trends suggest that deposition chemistry in the southern part of the wilderness has responded to reductions in emissions from Hayden/Craig. Although the Sand

Springs site is only 11 km west of Craig, the sulfate decline was considerably smaller compared to sites near the wilderness. While local airflow often is to the west (down valley) at night, precipitation events are predominantly associated with storm systems from the west, which likely transport pollutants from more distant sources. The snowpack chemistry data confirms the same geographic patterns in sulfate reductions as shown by an isopleth map of concentration difference between the before and after period at the 17 snowpack sites (Fig. 5). Sulfate declines in snowpack at two nearby stations, Rabbit Ears Pass (site 8) and Elk River (site 4), were not markedly elevated over regional background. This could indicate that Yampa River Valley emission sources have a rather limited geographic influence perhaps reflecting topographic controls on local wind and weather patterns. In contrast to sulfate, there was no evidence that reductions in NO<sub>x</sub> emissions from Hayden/Craig resulted in improvements in nitrate deposition in the wilderness. This may indicate that increases from mobile sources and other nonpoint emissions have offset improvements from major stationary sources both locally and across the state.

Temporal patterns in NADP chemistry also support the premise that Hayden/Craig emissions have had a substantial influence on sulfate deposition near the southern end of the wilderness. At the Dry Lake NADP site (Fig. 6a), sulfate concentrations tracked SO<sub>2</sub> emissions at Hayden/Craig much closer than other Colorado sources, which were actually increasing during the period when sulfate at Dry Lake was declining most rapidly (1999–2001). By contrast, the average annual sulfate concentrations for the NADP control group remained fairly constant while emissions were falling dramatically in the Yampa River Valley (Fig. 6b). Control group concentrations began to decline steadily after 2000 roughly paralleling trends in SO<sub>2</sub> emissions from other Colorado sources indicating that the control group primarily was responding to regional SO<sub>2</sub> sources. Sulfate concentrations at the Dry Lake NADP site leveled out after the initial round of controls (Hayden) but did not show a similar drop after installation of controls at Craig (Fig. 6a). Additionally, sulfate concentrations at Dry Lake were more strongly correlated with emissions from Hayden ( $r^2=0.88$ ) than either Craig ( $r^2=0.27$ ) or other Colorado sources ( $r^2=0.21$ ) suggesting that Hayden was the major factor in reducing sulfate

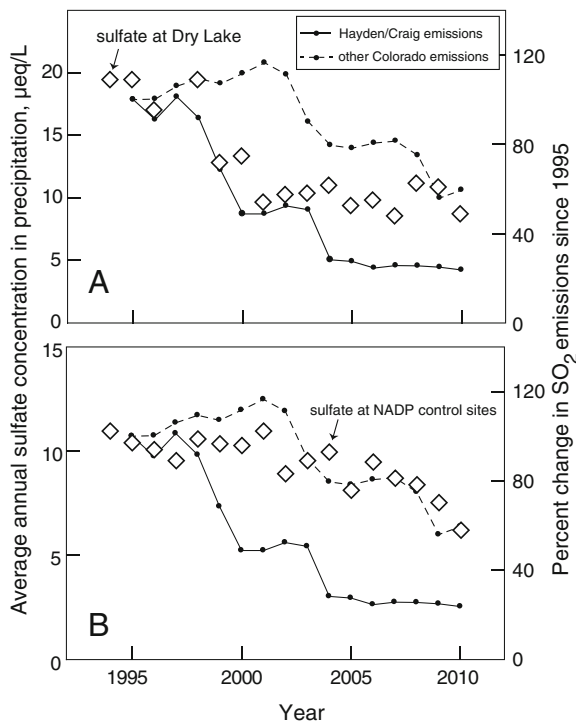
**Fig. 5** Isoleth map showing the change in sulfate concentrations in microequivalents per liter between before and after periods for 17 snowpack sites in northwestern Colorado



deposition to the wilderness. Possible explanations for this are lower emissions at Craig compared to Hayden and more importantly the greater distance of Craig from the wilderness boundary, which results in larger dispersion and dilution of its plumes (Watson et al. 1996). This is supported by simulations of plume transport and dispersion, which showed that Hayden contributed between 75 % and 85 % of the calculated SO<sub>2</sub> concentrations at Buffalo Pass (Watson et al. 1996).

One objective of this study was to apportion the changes in precipitation chemistry to local (Hayden/Craig) and regional air pollution sources. The sulfate decline due to regional sources was estimated as the average sulfate trend for the control group or -0.22 µeq/L/year. Removing this influence at the downwind sites (Buffalo Pass and Dry Lake) indicates that nearly 60 % of the improvement in sulfate deposition near the wilderness was attributable to the Hayden/Craig

controls (Fig. 7). Dry Lake showed a slightly greater power plant influence than Buffalo Pass perhaps because it is closer to Hayden and is lower in elevation. Despite being only 11 km from Craig, less than half the sulfate decrease at Sand Springs was attributable to Hayden/Craig emission reductions. This may reflect the location of Sand Springs, which is upwind of the power plants. Also, because SO<sub>2</sub> is oxidized very slowly, the relationship between emissions and concentrations depends on distance from emission sources (Dutkiewicz et al. 2000). A similar analysis for the snowpack sites yields a regional trend of -0.18 µeq/L/year based on background sites where trends were statistically significant. When subtracted from the downwind sites, improvements apportioned to Hayden/Craig emission reductions were nearly identical to those based on the NADP data (Fig. 7). This is not unexpected considering the sites are collocated and suggests that annual sampling of the snowpack provides a cost-effective and reliable

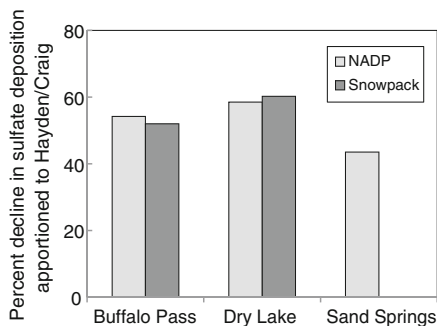


**Fig. 6** Temporal patterns in annual average sulfate concentrations at **a** the Dry Lake NADP station and **b** NADP control sites compared to annual SO<sub>2</sub> emission trends at Hayden/Craig and other stationary sources in Colorado

means of tracking deposition changes in remote ecosystems where snowpacks persist through the winter.

Lake water chemistry

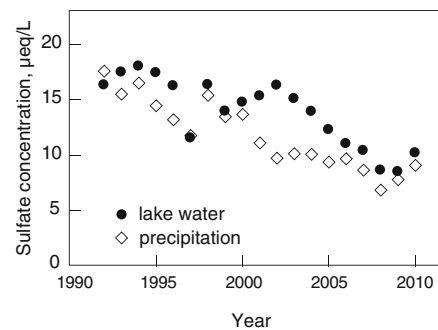
As expected with decreases in sulfate deposition, all the study lakes in and adjacent to the MZWA showed downward trends in sulfate concentrations following



**Fig. 7** Percent decline in sulfate deposition attributed to emissions controls at Hayden/Craig at three deposition sites in the Yampa River Valley

installation of emission controls. Trend slopes ranged from  $-0.16$  to  $-0.92$   $\mu\text{eq/L/year}$ , which were relatively small compared to sulfate trends reported for lakes in the northeast and midwest ( $-1.8$  to  $-3.4$   $\mu\text{eq/L/year}$ ), where emissions are higher and reductions have been more dramatic as a result of the Acid Rain Program (Waller et al. 2011; Stoddard et al. 2003). Average annual sulfate concentrations in precipitation and lake water in the MZWA were strongly correlated ( $r^2=0.75$ ,  $p<.001$ ) providing convincing evidence that lake sulfate is responding to declines in sulfate deposition driven by reductions in SO<sub>2</sub> emissions. The link between lake chemistry and deposition is further supported by sulfur isotopic data published by Mast et al. (2011), which indicate lake sulfate in the MZWA is dominantly derived from atmospheric sources. The average sulfate trend of  $-0.51$   $\mu\text{eq/L/year}$  in lake water was remarkably similar to the sulfate trend in wet deposition of  $-0.48$   $\mu\text{eq/L/year}$  at Buffalo Pass, although dry deposition and evapotranspiration can complicate direct comparison of the slope magnitudes between precipitation and surface water (Stoddard et al. 2003). Expressed as a percent change in sulfate, the percent decline in lake sulfate concentrations ranged from  $-2.1\%$  to  $-5.7\%$ , which bracketed the deposition trend of  $-4.3\%$  per year at Buffalo Pass. The similarity in slopes suggests that lakes in the wilderness have responded rapidly to changes in deposition, reflecting the sparse soil coverage and short hydrologic residence times, which are characteristic of alpine watersheds (Turk and Campbell 1987).

Although the overall trend in lake sulfate was downward, most lakes exhibited short-term increases in sulfate in the early 2000s (Fig. 8) in response to a regional drought that peaked in severity in 2002 (Mast

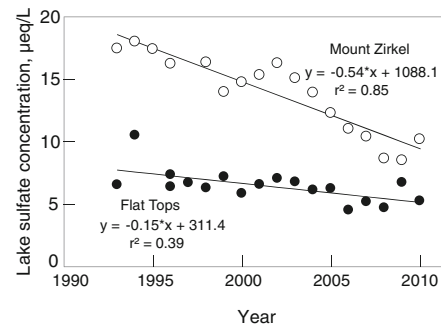


**Fig. 8** Temporal trends in the average annual sulfate concentration of lake water and precipitation (NADP) in the Mount Zirkel Wilderness

et al. 2011). This pattern highlights the importance of climate in controlling lake water concentrations and the question arises as to how much of the sulfate trend might be attributed to climate variability. This was further investigated by comparing annual precipitation amount at Buffalo Pass to sulfate concentrations at Summit Lake, a site at the southern boundary of the MZWA where chemistry data extend back to 1985. Stream discharge would be preferable to precipitation in analyzing climate affects; however, discharge is not measured at the outlet of any study lake or at any nearby streams in the MZWA due to wilderness restrictions and accessibility during winter and spring. The concentration of sulfate in Summit Lake clearly is sensitive to precipitation with decreases during wet periods (1995) and increases during dry periods (1989 and 2002). However, the overall trend in precipitation amount during the study period (1993–2010) is weak ( $r^2=.04$ ,  $p=0.542$ ) compared to the trend for sulfate ( $r^2=0.50$ ,  $p<.001$ ), and in addition, the precipitation trend is slightly downward, which would tend to increase concentrations indicating that the downward trend in sulfate is not related to climate variability.

As was done for deposition, sulfate trends in MZWA lakes were compared to trends in background lakes to determine if the lake response to local emission reductions could be distinguished from the regional signal. Long-term lake chemistry is available for the Flat Tops Wilderness area, which is located 80 km southwest of the MZWA (Fig. 1). Because it is south of the Yampa River Valley, it is not directly impacted by the power plants. Similar to lakes in the MZWA, isotopic data indicate that dissolved sulfate in the Flat Tops is derived primarily from atmospheric sources (Mast et al. 2011), therefore, lake chemistry should be strongly linked to deposition. Average annual lake water sulfate was computed for each wilderness area, and the change in concentration during 1993–2010 was determined by linear regression. The average sulfate trend of the MZWA lakes ( $-0.54 \mu\text{eq/L/year}$ ) was substantially higher than the average trend for the Flat Tops lakes ( $-0.15 \mu\text{eq/L}$ ) (Fig. 9), providing evidence that MZWA lakes have responded to both local and regional  $\text{SO}_2$  emission reductions.

ANC should increase or base cations should decrease in response to decreases in surface water sulfate (Driscoll et al. 2001); however, upward trends in ANC were detected in only six of the 28 MZWA lakes, and



**Fig. 9** Comparison of trends in lake water sulfate concentrations in Mount Zirkel and Flat Tops Wilderness areas

none of the lakes showed trends in base cations. A possible explanation is that the precision of the base cation and ANC analyses is not as good as for sulfate and that coupled with the low sulfate concentrations, the trend is masked by analytical uncertainty. During summer, when concentrations are typically highest, all of the lakes had measureable ANC indicating none were chronically acidic even before emission controls were installed. However, some of the smaller ponds had ANCs as low as  $10 \mu\text{eq/L}$  and could be at risk from episodic acidification particularly during early snowmelt when acidity is highest. Campbell et al. (2004) studied ephemeral ponds in the MZWA during snowmelt and although minimum ANCs were  $<40 \mu\text{eq/L}$ , net acidity ( $\text{ANC}<0$ ) was not observed in any of the ponds. Decreases in surface water pH due to acidic deposition have been shown to reduce species diversity and abundance of aquatic life in acid-sensitive ecosystems (Driscoll et al. 2001). Some studies conducted in the MZWA have suggested that the tiger salamander is sensitive to acidity at levels that might be found in snowmelt and rainfall in the wilderness (Harte and Hoffman 1989; Kiesecker 1996; Turk and Campbell 1997); however, the acidity of precipitation has decreased substantially since these studies were published. In a study of ponds near the MZWA, it was found that weather and pond characteristics were likely more important than pond acidity in influencing hatching success in amphibian larvae at levels of acid deposition in the early 2000s (Muths et al. 2003).

## Conclusions

In this paper, we use different environmental datasets to evaluate the effect of emission reductions at the

Hayden and Craig power plants on air and water quality in the downwind MZWA. The datasets evaluated included aerosol concentrations and optical data (particle scattering), deposition (rain and snow) chemistry, and lake chemistry. Because SO<sub>2</sub> emissions have been declining across Colorado as well as the greater Rocky Mountain region over the past 15 years, one of the major challenges of the study was separating the effects of local from regional emission reductions.

Sulfate aerosol concentrations decreased on the clearest days and were reduced by a factor of approximately 2 compared to the closest control site suggesting emission controls accounted for about half of the decrease. On the haziest days, sulfate aerosol concentrations were similar in magnitude to the control sites suggesting declines in sulfate largely reflected regional air quality. A possible reason emission controls did not have more of an effect on aerosol concentrations might be the proximity of the power plants to the wilderness and the rate at which SO<sub>2</sub> is converted to sulfate, which can be slow compared to transport rate, particularly in dry, cloud-free environments. The haze index indicated that visibility improved most on the clearest days but changed relatively little on the haziest days perhaps due to the importance of other particulate components such as organic carbon and wind-blown dust. Despite the lack of improvement, the haze index at Buffalo Pass was among the lowest of 156 monitored sites in national parks and class I wilderness areas across the USA indicating visibility conditions in the wilderness are good.

The largest declines in precipitation sulfate were at sites immediately downwind of the power plants clearly showing a response of deposition chemistry to emission reductions at Hayden and Craig. Sulfate concentrations declined by 50 % in deposition of which nearly 60 % was attributable to the emission controls and the remainder to improvements in regional air quality. Sulfate in precipitation was more strongly correlated with emissions from Hayden than Craig suggesting that Hayden was the major player in reducing deposition in the wilderness perhaps due to the greater distance of Craig from the wilderness boundary, which results in larger dispersion and dilution of its plumes. There was no evidence that power plant reductions in NO<sub>x</sub> resulted in improvements in nitrate deposition in the wilderness perhaps indicating contributions from nonpoint sources may have offset improvements from stationary sources, although the

importance of atmospheric transport and transformation processes cannot be ruled out.

All 28 monitored lakes in and near the wilderness area showed statistically significant downward trends in sulfate concentrations. Consistent trends in average annual sulfate concentrations in precipitation and surface water indicate that MZWA lakes responded quickly to reductions in SO<sub>2</sub> emissions. Concomitant trends in ANC or base cations were not observed in most of the lakes perhaps due to uncertainty in the analytical measurements. During summer base-flow conditions, all of the lakes had measureable ANC and appeared to be at minimal risk from chronic or episodic acidification.

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