

Response of lake chemistry to changes in atmospheric deposition and climate in three high-elevation wilderness areas of Colorado

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Abstract Trends in precipitation chemistry and hydrologic and climatic data were examined as drivers of long-term changes in the chemical composition of high-elevation lakes in three wilderness areas in Colorado during 1985–2008. Sulfate concentrations in precipitation decreased at a rate of -0.15 to -0.55 $\mu\text{eq/l/year}$ at 10 high-elevation National Atmospheric Deposition Program stations in the state during 1987–2008 reflecting regional reductions in SO_2 emissions. In lakes where sulfate is primarily derived from atmospheric inputs, sulfate concentrations also decreased although the rates generally were less, ranging from -0.12 to -0.27 $\mu\text{eq/l/year}$. The similarity in timing and sulfur isotopic data support the hypothesis that decreases in atmospheric deposition are driving the response of high-elevation lakes in some areas of the state. By contrast, in lakes where sulfate is derived primarily from watershed weathering sources, sulfate concentrations showed sharp increases during 1985–2008. Analysis of long-term climate records indicates that

annual air temperatures have increased between 0.45 and 0.93°C per decade throughout most mountainous areas of Colorado, suggesting climate as a factor. Isotopic data reveal that sulfate in these lakes is largely derived from pyrite, which may indicate climate warming is preferentially affecting the rate of pyrite weathering.

Keywords Atmospheric deposition · Water chemistry · Lake · Climate · Trends · Weathering · Alpine

Introduction

High-mountain environments are sensitive to changes in atmospheric pollution and climate and may provide early-warning indicators for change in more resistant ecosystems of higher-order drainages (Williams and Tonnesen 2000). Despite their vulnerability to environmental disturbance, these ecosystems generally have received less monitoring efforts than other landscape types in the United States. In the Rocky Mountain region, high-elevation lakes and streams are particularly sensitive to acidic deposition owing to fast hydrologic flushing rates, slow-weathering bedrock, and a paucity of soil and vegetation (Campbell et al. 1995). Although deposition rates of acidity are much lower than in eastern North America, there is evidence that some streams in Colorado may undergo episodic acidification during the early stages of snowmelt when

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high concentrations of acidity can be released from the snowpack (Turk and Campbell 1997). Perhaps of more pressing concern in the Rocky Mountain region is the effect of atmospheric nitrogen deposition on alpine ecosystems (Williams et al. 1996; Baron et al. 2000). When nitrogen deposition exceeds uptake by plant and microbial communities, the ecosystem becomes nitrogen saturated, and nitrate is leached from soils into surface waters (Burns 2004). Studies in Colorado indicate some high-elevation catchments in the Front Range are at an advanced stage of nitrogen saturation and that harmful effects on aquatic and terrestrial ecosystems are already occurring (Wolfe et al. 2003; Baron 2006; Bowman et al. 2006).

During the past several decades, atmospheric pollution has declined throughout large regions of North America in response to reductions in anthropogenic emissions implemented by the Clean Air Act Amendments of 1990 (Stoddard et al. 2003). In eastern North America, reduced concentrations of certain chemical constituents in precipitation and recovery of streams in response to these reductions have been documented by numerous studies (Driscoll et al. 2003; Kahl et al. 2004; Burns et al. 2006). In mountainous regions of the western U.S., the response of surface-water chemistry to changes in atmospheric deposition has been more difficult to evaluate because of a scarcity of long-term monitoring networks.

Alpine ecosystems also are facing potentially dramatic changes as a consequence of global warming because increases in air temperatures and climate variability are expected to be most pronounced at high latitudes and high elevations (Bradley et al. 2004). Even small temperature changes can have large hydrologic, chemical, and biological effects in alpine and subalpine environments where the depth and duration of snow cover is a major control of watershed processes (Koinig et al. 1998). Notable increases in solute concentrations were reported for numerous alpine lakes in Europe (Sommaruga-Wögrath et al. 1997; Tait and Thaler 2000; Mosello et al. 2002; Rogora et al. 2003). These chemical changes have been attributed to enhanced weathering rates and increased biological activity caused by rising air temperatures (Sommaruga-Wögrath et al. 1997). More recent studies suggested the effect of climate warming on increasing chemical concentrations in surface water in alpine areas is related to enhanced melting of ice features such as permafrost, rock

glaciers, and glaciers (Thies et al. 2007; Hill 2008; Baron et al. 2009). In alpine lakes in Canada, climate shifts over the past decade were found to decrease nutrient concentrations and increase DOC, resulting in taxonomic shifts in the phytoplankton community (Parker et al. 2008). These studies illustrate that climate change may introduce a greater degree of variability in surface-water chemistry, which could mask trends resulting from improvements in atmospheric deposition of pollutants (Mosello et al. 2002).

In this paper we evaluate changes in the chemistry of high-elevation lakes in three wilderness areas in Colorado that have been monitored by the U.S. Geological Survey for over two decades. Trends in precipitation chemistry from the National Atmospheric Deposition Program (NADP) and climate variables from the National Resources Conservation Service Snowpack Telemetry (SNOTEL) network also were evaluated over a similar period of record. One objective was to determine if changes in atmospheric deposition of pollutants in the Rocky Mountain region have resulted in measurable changes in the chemistry of high-elevation lakes. A second objective was to investigate linkages between lake chemistry and climate variability to improve understanding of the sensitivity of mountain lakes to climate warming.

Materials and methods

Study area description

The study lakes are located in three Class I wilderness areas in Colorado, which include the Mount Zirkel and Flat Tops areas in northwestern Colorado and the Weminuche area in southwestern Colorado (Fig. 1). Sampling of selected lakes in these three areas was initiated in the mid-1980s as part of the USGS Acid Rain Program (Aulenbach et al. 1997) or the U.S. Environmental Protection Agency (EPA) Long-Term Monitoring Network (Ford et al. 1993) and eventually became part of a Colorado lake-monitoring program supported by the USGS and the U.S. Department of Agriculture Forest Service. The 13 study lakes, whose characteristics are listed in Table 1, were originally selected because of their sensitivity to acidic deposition and their location relative to existing and proposed energy development and emission sources (Turk and Adams 1983; Turk and Campbell 1987). The lakes

Fig. 1 Locations of sample lakes within Mount Zirkel, Flat Tops, and Weminuche wilderness areas and nearby NADP and SNOTEL stations

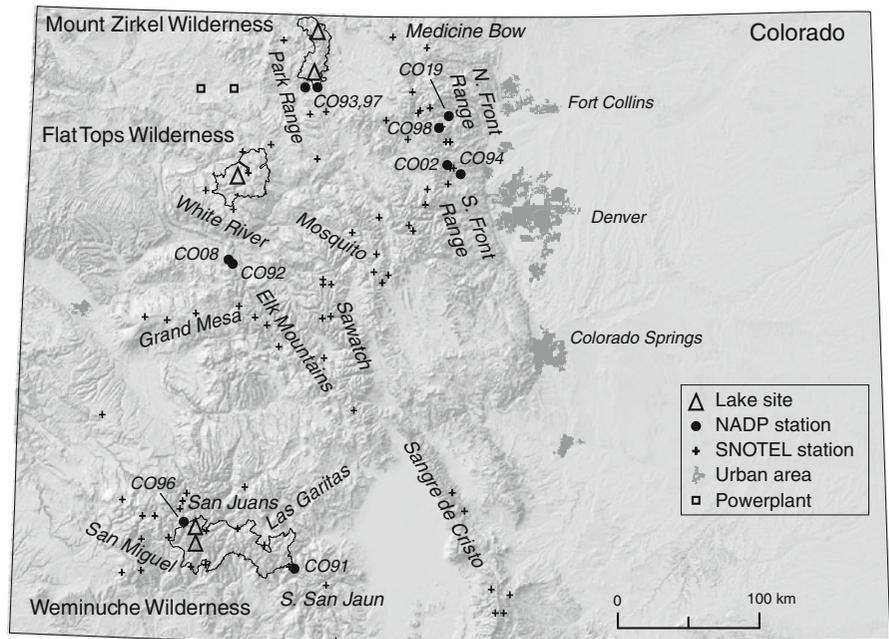


Table 1 Characteristics of study lakes in three Colorado wilderness areas

Lake name	USGS station no.	Elevation (m)	Max. lake depth (m)	Lake area (km ²)	Basin area (km ²)	Bedrock
Mount Zirkel Wilderness						
Seven Lakes	405344106405100	3,271	7.0	0.039	0.42	Granite
Lake Elbert	403803106422500	3,289	11.5	0.046	1.01	Granite
Summit Lake	403245106404900	3,144	6.0	0.018	0.10	Granite
Flat Tops Wilderness						
Ned Wilson Lake	395743107192500	3,383	4.5	0.009	0.48	Basalt
Upper Ned Wilson Lake	395746107192500	3,386	2.0	0.002	0.026	Basalt
Lower Packtrail Pothole	395805107192400	3,379	<2	0.005	0.13	Basalt
Upper Packtrail Pothole	395756107192300	3,380	<2	0.002	0.080	Basalt
Weminuche Wilderness						
Big Eldorado Lake	374248107323600	3,811	12.5	0.058	1.15	Quartzite
Little Eldorado Lake	374248107324500	3,812	7.5	0.010	0.47	Quartzite
White Dome Lake	374232107330900	3,822	–	0.022	0.38	Quartzite
Lower Sunlight Lake	373804107344300	3,668	–	0.070	1.06	Granite
Upper Sunlight Lake	373740107344700	3,824	–	0.059	0.80	Granite
Upper Grizzly Lake	373712107350100	3,993	–	0.028	0.30	Granite

drain areas within the alpine and high subalpine zones, and their watersheds are composed mainly of tundra, wet meadows, talus slopes, and bare rock. Scattered pockets of spruce and fir are present in the lower elevation watersheds. The lakes are oligotrophic and typically remain ice-covered for at least 6 months of

the year (November through April). Hydrologic inputs to the lakes are dominated by snowmelt runoff, although in the Weminuche Wilderness substantial runoff also can occur during the summer monsoon season. Bedrock in all three lake study areas is chemically resistant and, as a result, the surface water

has low dissolved solids. The Mount Zirkel Wilderness is underlain by Precambrian granite and gneiss, and the Flat Tops Wilderness is underlain by highly fractured Tertiary basalt flows. The Weminuche Wilderness is underlain by Precambrian quartzite, slate, and granite, with local hydrothermal alteration and mineralization in areas adjacent to Tertiary volcanic intrusions. Mineralization generally occurs in vein-type deposits which contain abundant quartz and pyrite and lesser amounts of metallic ore minerals, calcite, barite, fluorite, and clay (Steven et al. 1969).

Precipitation chemistry data

Precipitation chemistry was not measured as part of this study; however, it has been monitored routinely at several nearby stations by the NADP. The NADP is a national network that collects weekly composite samples of wet-only precipitation that are analyzed for major dissolved constituents and nutrients at a central laboratory located at the University of Illinois. Sample-collection protocols, analytical methods, and quality-assurance procedures used by NADP are documented at <http://nadp.sws.uiuc.edu/>. This study analyzed chemistry data from 10 high-elevation (2,490 to 3,520 m) NADP stations in Colorado (Fig. 1). The Summit Lake (CO97) and Dry Lake (CO93) stations are along the southern boundary of the Mount Zirkel Wilderness, and the Molas Lake (CO96) and Wolf Creek Pass (CO91) stations bound the Weminuche Wilderness. None of the NADP stations are immediately adjacent to the Flat Tops Wilderness, with the closest, Four Mile Park (CO08), being nearly 40 km to the south. Monthly precipitation-weighted mean concentrations and precipitation amounts were retrieved from the NADP web site. Mean concentrations provided by NADP are computed using only samples with complete and valid laboratory analyses and valid measurements of precipitation amount. Details of the sample screening process can be found at <https://nadp.isws.illinois.edu/documentation/notes-AvMg.html>. Trends in concentration and precipitation amount were calculated using the seasonal Kendall test, a non-parametric test that accommodates seasonality, outliers, missing data, and censored values (Helsel and Hirsch 1992). Trends were calculated for each NADP station for 1987 through 2008 with the exception of Wolf Creek Pass (CO91), for which trends were calculated for

1992 through 2008 because of a shorter period of record. Trends were not tested for hydrogen ion measured in the laboratory because of contamination from the bucket lid that occurred prior to 1994, which most strongly affected hydrogen-ion concentration at sites in the western U.S. (<http://nadp.sws.uiuc.edu/documentation/advisory.html>). Although dry deposition also is a source of atmospheric pollutants, it was not evaluated because it is difficult to measure and there are few sites in Colorado where dry deposition is routinely monitored (<http://www.epa.gov/castnet/>).

Lake-water chemistry data

Lakes in the three wilderness areas were sampled 2–5 times per year during the open-water season (July–October) starting in the mid-1980s. Sampling was conducted at 3 lakes in the Mount Zirkel Wilderness (Seven, Elbert, Summit), 4 lakes in the Flat Tops Wilderness (Ned Wilson, Upper Ned Wilson, Lower Packtrail Pothole, Upper Packtrail Pothole), and 6 lakes in the Weminuche Wilderness (Big Eldorado, Little Eldorado, White Dome, Lower Sunlight, Upper Sunlight, Grizzly). For the period of record through 1996, Seven Lakes, Lake Elbert, Summit Lake, Ned Wilson Lake, and Big and Little Eldorado Lakes were sampled from the epilimnion at the deepest part of the lake using an inflatable boat. The remaining lakes were sampled at the outlet or from a point on the shore with little or no vegetation. Beginning in 1996, sampling at all the lakes was conducted at the outlet or shore with the exception of Summit Lake, where a boat was used. Shore samples were assumed to not be significantly different from mid-lake samples because most of the study lakes are small and relatively shallow. Clow et al. (2003a) compared outflow and epilimnion samples at 14 high-elevation lakes and found no significant differences in chemistry, indicating bias from a change in sampling location is likely minimal.

Samples were collected in polyethylene bottles and generally were filtered in the field within 24 h using a peristaltic pump and a 0.45- μm plate or capsule filter. Specific conductance and pH were measured in the laboratory on unfiltered sample aliquots, and acid neutralizing capacity (ANC) was determined by Gran titration. Chloride, nitrate, and sulfate concentrations were determined by ion chromatography on filtered, chilled sample aliquots, and

calcium, magnesium, sodium, potassium, and silica were analyzed by ICP–AES on filtered, acidified (0.5% HNO₃) aliquots. Samples for stable sulfur isotopes were collected periodically at selected lakes in each of the three wilderness areas according to methods described by Turk et al. (1993) and Mast et al. (2001). All chemical analyses of lake water were conducted at USGS laboratories and data are stored in the USGS National Water Information System (NWIS) database available at <http://waterdata.usgs.gov/nwis>.

Trends in concentrations during the open-water season were calculated using the seasonal Kendall test. Concentrations could not be flow-adjusted, as normally is done with this test, because of a lack of discharge data for the study sites. Changes in analytical methods and laboratories that occurred during the study period were evaluated to ensure the comparability of the data over the study period. The evaluation determined that a step function in chloride concentrations results from a change in laboratories that occurred in 1988, so only chloride data after 1988 were retained for analysis. Laboratory pH measurements were considerably more variable in the first half of the record, perhaps reflecting changes in equipment or methods, and were not tested for trends.

Climate data

Air temperature and precipitation data were obtained from the National Resources Conservation Service SNOTEL network (<http://www.wcc.nrcs.usda.gov/snow/>), which is a network of automated snowpack and climate stations in mountain snowpack zones of the western U.S. Daily data were obtained for 77 SNOTEL stations in Colorado with 13 or more years of record (Fig. 1). Details of procedures used to screen SNOTEL records for outliers and anomalies are described in Clow (2010). Average annual air temperature and precipitation amount at each station were computed from the screened daily values, and the results were separated into 14 geographic groups corresponding to major mountain ranges in Colorado (Fig. 1). Trends for each group were calculated using the regional Kendall test, which is a modified form of the seasonal Kendall test that is used to test trends at numerous locations within a geographic region (Helsel and Frans 2006). Trends at individual stations

by year and by month also were calculated using the Mann-Kendall test (Helsel and Hirsch 1992).

Results

Chemical characteristics of precipitation and lake water

Chemical characteristics of precipitation at the 10 NADP stations and lake water in the three study areas are presented in Table 2. Precipitation chemistry is extremely dilute and slightly acidic with pH values ranging from 4.77 and 5.07. The dominant ions are sulfate, nitrate, ammonium, and hydrogen, indicating that precipitation solutes largely are derived from anthropogenic sources (Baron and Denning 1993). The composition of precipitation was fairly uniform across high-elevation areas of Colorado; however, some spatial patterns are notable for concentrations of sulfate and nitrogen species, which tend to be higher at stations farther to the north and east.

Lake water is a dilute calcium-bicarbonate type with pH ranging from 6.00 to 7.10 and specific conductance ranging from 5.2 to 19.7 $\mu\text{S}/\text{cm}$ (Table 2). Lakes in the Mount Zirkel and Flat Tops areas are fairly similar in chemical composition with the exception of sodium and silica, which are slightly higher in the Mount Zirkel area perhaps reflecting differences in geology. Lakes in the Weminuche area exhibited more variability in concentrations compared to the other two areas particularly for ANC, which ranged from 3.3 $\mu\text{eq}/\text{l}$ in Little Eldorado Lake to 100 $\mu\text{eq}/\text{l}$ in Lower Sunlight Lake. Median sulfate concentrations in the Weminuche lakes, which ranged from 30.7 to 83.2 $\mu\text{eq}/\text{l}$, were notably higher than lakes in the other two wilderness areas, which ranged from 6.9 to 15.8 $\mu\text{eq}/\text{l}$. During the summer growing season, nitrate concentrations were near or below detection levels in most of the lakes. Only in the Weminuche area did lakes have regularly detectable levels of nitrate, although the median concentrations were still quite low (<0.7 to 7.2 $\mu\text{eq}/\text{l}$).

Sources of lake-water sulfate

Comparison of ranges of concentrations and isotopic ratios of sulfate in precipitation and lake water illustrates a clear difference in the source of surface-

Table 2 Annual precipitation-weighted mean concentrations in precipitation and median concentrations in lake water at selected high-elevation sites in Colorado during 1985–2008

Station name (number)	SC	pH	ANC	Ca	Mg	Na	K	NH ₄	NO ₃	Cl	SO ₄	SiO ₂
Precipitation sites												
Dry Lake (CO93)	8.9	4.77	–	8.3	1.6	1.9	0.4	7.2	13.9	1.7	15.0	–
Summit Lake (CO97)	7.6	4.82	–	7.9	1.5	1.9	0.3	6.2	11.1	1.6	13.4	–
Beaver Meadows (CO19)	8.5	5.00	–	11.6	2.2	2.4	1.1	15.0	17.4	2.4	14.7	–
Loch Vale (CO98)	6.7	5.00	–	9.1	1.7	2.3	0.5	8.4	12.3	2.0	11.0	–
Sugarloaf (CO94)	9.0	4.91	–	10.0	1.7	1.9	0.6	17.6	19.3	1.8	15.1	–
Niwot Saddle (CO02)	7.5	4.92	–	10.1	2.0	2.8	0.7	8.2	15.2	2.3	11.4	–
Four Mile Park (CO08)	6.1	5.07	–	12.0	1.9	2.2	0.9	6.3	11.2	2.0	9.2	–
Sunlight Peak (CO92)	6.2	5.03	–	11.2	1.8	2.3	0.6	6.4	11.0	2.0	9.4	–
Molas Pass (CO96)	7.1	4.93	–	11.8	1.7	2.2	0.6	5.1	11.5	1.9	10.3	–
Wolf Creek Pass (CO91)	7.3	4.90	–	9.1	1.2	1.7	0.4	5.7	11.7	1.5	10.8	–
Mount Zirkel Wilderness Lakes												
Seven Lakes	8.4	6.60	42.3	35.4	13.0	18.3	4.1	–	<0.7	2.5	10.9	27.7
Lake Elbert	11.0	6.84	68.0	55.3	12.2	27.8	2.6	–	<0.7	2.3	10.6	47.4
Summit Lake	10.6	6.77	61.2	50.8	21.2	16.1	3.1	–	<0.7	2.7	15.8	11.1
Flat Tops Wilderness Lakes												
Ned Wilson Lake	7.9	6.86	50.8	41.9	15.6	6.5	4.0	–	<0.7	2.6	8.2	3.3
Upper Ned Wilson Lake	5.2	6.53	23.8	23.9	9.1	4.4	1.8	–	<0.7	1.9	7.1	4.7
Lower Packtrail Pothole	7.0	6.63	37.8	29.9	13.0	6.0	5.3	–	<0.7	2.2	9.5	3.8
Upper Packtrail Pothole	9.2	6.82	62.4	50.8	22.7	5.2	1.8	–	<0.7	1.4	6.9	9.5
Weminuche Wilderness Lakes												
Big Eldorado Lake	16.0	6.61	31.8	74.9	42.8	5.2	2.6	–	0.7	2.2	83.2	13.1
Little Eldorado Lake	9.2	6.00	3.3	45.4	10.9	3.5	2.5	–	5.1	2.1	47.8	17.2
White Dome Lake	8.9	6.13	6.6	41.3	12.2	3.9	2.6	–	7.2	2.5	39.8	13.6
Lower Sunlight Lake	19.7	7.10	100	134.5	21.4	13.5	4.1	–	<0.7	2.5	52.0	19.6
Upper Sunlight Lake	15.2	6.74	41.6	93.1	18.1	9.1	3.1	–	4.4	2.2	58.2	13.9
Upper Grizzly Lake	13.0	6.86	64.3	85.3	15.5	7.8	3.0	–	5.5	2.3	30.7	12.8

SC specific conductance in $\mu\text{S}/\text{cm}$, concentrations in $\mu\text{eq}/\text{l}$ except SiO_2 in $\mu\text{mol}/\text{l}$, – not measured

water sulfate among the three study areas (Fig. 2). For precipitation, the box plots show the range of annual sulfate concentrations at the 10 NADP stations over the period of record and the range of sulfur isotopic ratios ($\delta^{34}\text{S}$) for 176 bulk-snowpack samples collected at 26 high-elevation sites across Colorado (Mast et al. 2001). For lake water, the box plots show the range of concentrations for all lake samples collected throughout the period of record and the range of sulfur isotopic ratios for 18–20 lake samples collected in each of the 3 study areas. Lake water in the Mount Zirkel and Flat Tops areas is similar to precipitation in both concentration and sulfur isotopic ratio indicating that surface-water sulfate in these two areas is almost entirely derived from atmospheric

inputs. By contrast, concentrations and sulfur isotopic ratios in the Weminuche lakes are substantially different from those in precipitation, clearly indicating sulfate is derived from watershed weathering sources. The range of sulfur isotopic ratios for samples of vein pyrite collected from a mining district just north of the Weminuche Wilderness boundary are represented by the shaded box in Fig. 2 (Nordstrom et al. 2007). Although mineralization in the mining district is much more intense than in the wilderness, it is associated with the same Tertiary volcanic events (Bove et al. 2007). The isotopic ratios in pyrite bracket those in surface water providing strong evidence that pyrite oxidation is the dominant source of aqueous sulfate in the Weminuche lakes.

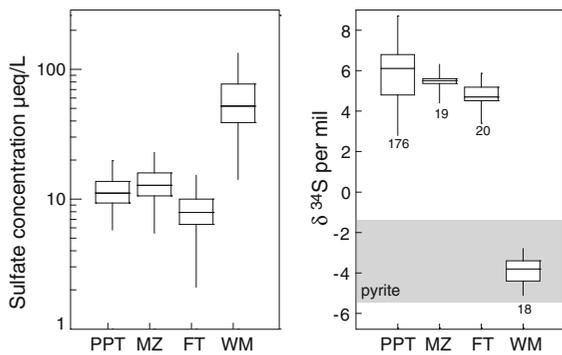


Fig. 2 Range of sulfate concentrations and $\delta^{34}\text{S}$ values in precipitation (PPT) and lake-water samples from the Mount Zirkel (MZ), Flat Tops (FT), and Weminuche (WM) wilderness areas. Shaded box represents the range of $\delta^{34}\text{S}$ values in pyrite samples from a mining district just north of the Weminuche Wilderness boundary

Gypsum dissolution also could be a source of sulfate to surface water; however, gypsum samples from the adjacent mining district have a much heavier (+15 to +18 per mil) isotopic signature (Nordstrom et al. 2007) indicating contributions from this source are minimal.

Trends in precipitation chemistry

Statistically significant trends in precipitation solute concentrations were detected for all 10 high-elevation NADP stations in Colorado (Table 3). Sulfate

concentrations exhibited strong downward trends at all stations and showed similar patterns in timing among sites (Fig. 3). Sulfate trends ranged from -0.15 to -0.55 $\mu\text{eq/l/year}$, which at many of the stations were largely balanced by decreases in hydrogen-ion concentrations. The trends in field hydrogen ion, however, only were detected at 7 stations compared to 10 for sulfate perhaps because the period of record was slightly shorter, ending in 2004 when field pH measurements were discontinued by NADP (Lehmann et al. 2004). For nitrogen species, upward trends in ammonium were detected at 4 of the 10 stations (range 0.17 to 0.24 $\mu\text{eq/l/year}$) and only 1 station, Dry Lake (CO93), showed a statistically significant upward trend in nitrate (0.23 $\mu\text{eq/l/year}$). For the base cations, small trends in calcium and magnesium were detected at a few stations although the direction was not always the same. By contrast, downward trends in sodium were observed at 9 of 10 stations and were quite uniform among sites, ranging from -0.08 to -0.11 $\mu\text{eq/l/year}$. Similar trends were observed for chloride although they were slightly smaller in magnitude (-0.05 to -0.08 $\mu\text{eq/l/year}$). Such widespread trends in sodium and chloride have not previously been reported for NADP stations, particularly in Colorado. Several changes were made in NADP protocols over the period of record that affected sodium and chloride concentrations, including contamination from the bucket lid prior to 1994 and contamination from filters used prior to 1998 (<http://nadp.sws.uiuc.edu/QA/>).

Table 3 Trends in monthly precipitation-weighted mean concentrations and precipitation amount at 10 high-elevation NADP stations in Colorado for 1987–2008

Station name and number	Field H+	Ca	Mg	Na	K	NH ₄	NO ₃	Cl	SO ₄	Amt.
Dry Lake (CO93)	-0.53^\dagger	ns	-0.03^*	-0.08^\dagger	ns	ns	0.23*	-0.07^\dagger	-0.55^\dagger	ns
Summit Lake (CO97)	-0.49^\dagger	ns	ns	-0.09^\dagger	ns	ns	ns	-0.06^\dagger	-0.46^\dagger	ns
Beaver Meadows (CO19)	-0.33^\dagger	ns	-0.02^*	-0.09^\dagger	ns	0.24 [†]	ns	-0.06^\dagger	-0.19^\dagger	ns
Loch Vale (CO98)	-0.26^\dagger	0.08*	ns	-0.08^\dagger	0.01*	0.19 [†]	ns	-0.05^\dagger	-0.16^\dagger	ns
Sugarloaf (CO94)	-0.28^*	ns	ns	-0.08^\dagger	ns	ns	ns	-0.05^\dagger	-0.30^\dagger	-0.04^*
Niwot Saddle (CO02)	ns	0.15*	ns	-0.11^\dagger	ns	0.19 [†]	ns	-0.06^\dagger	-0.15^\dagger	0.14*
Four Mile Park (CO08)	-0.33^\dagger	ns	ns	-0.10^\dagger	ns	ns	ns	-0.08^\dagger	-0.23^\dagger	ns
Sunlight Peak (CO92)	-0.34^*	ns	ns	-0.10^\dagger	ns	ns	ns	-0.08^\dagger	-0.23^\dagger	ns
Molas Pass (CO96)	ns	ns	ns	-0.08^\dagger	ns	ns	ns	-0.06^\dagger	-0.23^\dagger	ns
Wolf Creek Pass (CO91)	ns	0.24 [†]	0.03*	ns	ns	0.17 [†]	ns	ns	-0.18^\dagger	ns

Concentrations in $\mu\text{eq/l/year}$, precipitation amount in cm/year, ns trend not significant

[†] $p \leq 0.010$

* $0.01 < p \leq 0.050$

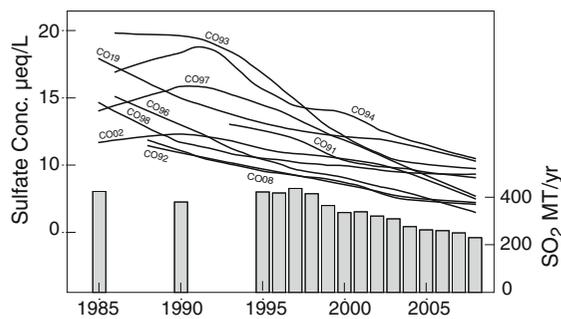


Fig. 3 LOWESS smooth lines of annual sulfate concentrations at 10 high-elevation NADP stations in Colorado and regional SO_2 emissions in megatons per year

However, these changes in protocol account for less than 10% of the total decrease in observed concentrations, indicating some of the decrease is likely caused by environmental change such as emission reductions. Although SO_2 and NO_x were the primary targets of the Clean Air Act Amendments, the controls put into place would likely also reduce HCl emissions related to coal combustion and waste incineration (Shapiro et al. 2007).

Trends in lake-water chemistry

Many significant trends were evident in lake-water concentrations in the three wilderness areas (Table 4 and Fig. 4). Trends in sulfate concentrations were detected in all 13 lakes with the Mount Zirkel and Flat Tops lakes showing downward trends (-0.12 to $-0.27 \mu\text{eq/l/year}$) and the Weminuche lakes exhibiting upward trends (0.87 to $3.82 \mu\text{eq/l/year}$). In the Weminuche Wilderness, the trends in sulfate largely were balanced by upward trends in calcium and magnesium concentrations, the sum of which ranged from 1.23 to $4.22 \mu\text{eq/l/year}$. Interestingly, three of the Weminuche lakes had significant increases in ANC while two had slight decreases and one remained unchanged. All 6 Weminuche lakes showed small increases in silica but only one lake (Upper Sunlight) showed an upward trend in sodium. Four of the six Weminuche lakes had sufficient nitrate data for trend analysis, but only White Dome showed a statistically significant trend increase of $0.14 \mu\text{eq/l/year}$.

Table 4 Trends in major-ion concentrations for 13 high-elevation lakes in 3 Colorado wilderness areas for 1985 through 2008

Station name	SC	ANC	Ca	Mg	Na	K	NO_3	Cl	SO_4	SiO_2
Flat Tops Wilderness										
Seven Lakes	ns	0.29^\dagger	ns	ns	ns	ns	–	ns	-0.12^\dagger	0.19^\dagger
Lake Elbert	ns	ns	-0.29^\dagger	ns	ns	ns	–	ns	-0.23^\dagger	ns
Summit Lake	0.07^\dagger	1.18^\dagger	0.70^\dagger	0.17^\dagger	ns	ns	–	ns	-0.26^\dagger	0.68^\dagger
Mount Zirkel Wilderness										
Ned Wilson Lake	0.06^\dagger	0.45^\dagger	0.23^\dagger	0.09^*	-0.10^\dagger	ns	–	-0.02^*	-0.16^\dagger	0.02^\dagger
Upper Ned Wilson Lake	0.07^\dagger	0.57^\dagger	0.47^\dagger	0.15^\dagger	-0.10^\dagger	ns	–	-0.02^*	-0.12^\dagger	0.16^\dagger
Lower Packtrail Pothole	ns	0.61^\dagger	0.36^\dagger	0.09^\dagger	ns	ns	–	ns	-0.27^\dagger	0.03^\dagger
Upper Packtrail Pothole	ns	0.66^\dagger	0.40^\dagger	0.17^\dagger	ns	ns	–	ns	-0.16^\dagger	ns
Weminuche Wilderness										
Big Eldorado Lake	0.25^\dagger	-0.70^\dagger	1.11^\dagger	0.99^\dagger	ns	ns	–	ns	3.10^\dagger	0.14^*
Little Eldorado Lake	0.25^\dagger	-0.35^\dagger	1.02^\dagger	0.21^\dagger	ns	ns	ns	ns	1.78^\dagger	0.38^\dagger
White Dome Lake	0.20^\dagger	ns	0.90^\dagger	0.36^\dagger	ns	ns	0.14^\dagger	ns	1.09^\dagger	0.17^\dagger
Lower Sunlight Lake	0.26^\dagger	1.42^\dagger	2.51^\dagger	0.33^\dagger	ns	ns	–	ns	1.45^\dagger	0.20^\dagger
Upper Sunlight Lake	0.52^\dagger	0.69^\dagger	3.50^\dagger	0.72^\dagger	0.17^\dagger	0.03^*	ns	ns	3.82^\dagger	0.17^\dagger
Upper Grizzly Lake	0.23^\dagger	1.42^\dagger	1.83^\dagger	0.27^\dagger	ns	ns	ns	ns	0.87^\dagger	0.16^\dagger

SC, specific conductance in $\mu\text{S/cm/year}$, concentrations in $\mu\text{eq/l/year}$ except SiO_2 in $\mu\text{mol/l/year}$, ns trend not significant, – insufficient data to calculate trend

$^\dagger p \leq 0.010$

* $0.01 < p \leq 0.050$

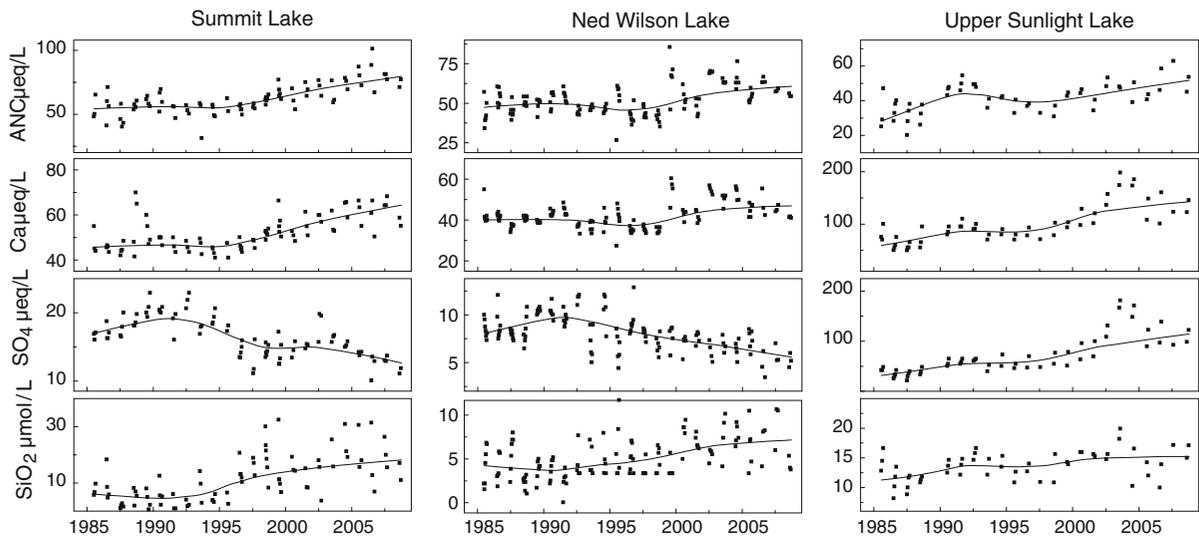


Fig. 4 Long-term trends in solute concentrations for Summit Lake in the Mount Zirkel Wilderness, Ned Wilson Lake in the Flat Tops Wilderness, and Upper Sunlight Lake in the Weminuche Wilderness for 1985–2008

In addition to sulfate, the Mount Zirkel and Flat Tops lakes also exhibited trends in ANC and base cations although average trend slopes were much smaller than those determined for the Weminuche lakes. Trends in the Mount Zirkel lakes showed a more mixed pattern. The smallest lake, Summit, exhibited upward trends in ANC, calcium and magnesium in contrast to the largest lake, Elbert, which showed no trend in ANC and magnesium and a small decrease in calcium. Seven Lakes showed a small increase in ANC with no associated change in base cation concentrations. Upward trends in ANC were significant at all four Mount Zirkel lakes with slopes ranging from 0.45 to 0.66 $\mu\text{eq/l/year}$. The increases in ANC were much larger than the decreases in sulfate and primarily were balanced by increases in calcium and magnesium concentrations. Many of the Mount Zirkel and Flat Tops lakes also showed small upward trends in silica (0.02–0.68 $\mu\text{mol/l/year}$), although none of the lakes showed upward trends for sodium or potassium.

Trends in air temperature and precipitation

Significant increases in annual air temperature were observed across most mountainous areas of Colorado throughout the past two decades (Table 5). Trends using the regional Kendall test were statistically significant at the 0.010 confidence level for 13 of the

14 mountain groupings and ranged from 0.45 to 0.93°C per decade. The trends appear to be similar among the groupings indicating the warming trend is fairly uniform across Colorado. For the 77 individual SNOTEL sites, 69% of sites had upward trends in annual air temperature at the 0.010 confidence level and 82% had upward trends at the 0.050 level. By month, the strongest increases in air temperature were during winter (November, December, and January) and midsummer (July) with trends ranging from 1 to 1.6°C per decade. Few significant trends were detected for February and June and none for October. The observed trends at SNOTEL stations are substantially greater than those estimated for Colorado as a whole based on trend analyses performed on data collected at National Weather Service cooperative observer stations throughout a similar period (Ray et al. 2008). The trends in SNOTEL data appear to be in agreement with predictions from general circulation models that indicate temperatures are projected to rise more in high mountains than at lower elevations (Bradley et al. 2006).

Trends in annual precipitation amounts at the SNOTEL stations were much weaker than those observed for air temperature (Table 5). Of the 14 groupings, only 2 showed significant trends at the 0.010 confidence level. In the Sangre de Cristo Range in southern Colorado, the trend for annual precipitation was -0.20 cm per year and in the Sawatch

Table 5 Trends in average annual air temperature and precipitation amount determined from the regional Kendall test for 14 geographic groupings of Colorado SNOTEL stations for the period of record through 2007

Geographic site groupings	Sites/group	Begin date	Air temp	Ppt Amt
Southern San Juans	5	1984	0.62 [†]	ns
Sangre de Cristo	6	1987	0.92 [†]	−0.20 [†]
San Miguels	7	1986	0.86 [†]	ns
San Juans	7	1987	0.82 [†]	ns
Las Garitas	5	1987	0.85 [†]	ns
Grand Mesa	4	1986	0.93 [†]	ns
Elk Mountains	3	1986	0.83 [†]	ns
Sawatch Range	7	1986	0.59 [†]	−0.15 [†]
Mosquito Range	5	1986	0.89 [†]	ns
Southern Front Range	4	1986	0.60*	−0.14*
Northern Front Range	7	1990	0.75 [†]	−0.10*
Medicine Bow	6	1986	0.59 [†]	ns
White River Plateau	5	1986	0.77 [†]	ns
Park Range	6	1987	0.45 [†]	ns

Air temperature in °C/decade, precipitation amount in cm/year, *ns* trend not significant

[†] $p \leq 0.010$

* $0.01 < p \leq 0.050$

Range in central Colorado, the trend was -0.15 cm per year. Although less significant, similar downward trends also were detected at the two Front Range groupings. When broken out by season, the SNOTEL data revealed significant decreases in winter precipitation at 11 of the 14 groupings. Because changes in annual precipitation were not significant at most sites, the downward winter trends may indicate a shift in the seasonal distribution of precipitation. NADP stations showed a similar lack of trends in annual precipitation amount with one site showing an increase and one site showing a small decrease (Table 3).

Discussion

Effect of atmospheric deposition

To evaluate the effect of atmospheric deposition on lake chemistry, we analyzed precipitation chemistry collected at 10 high-elevation NADP stations in Colorado. Sulfate and hydrogen-ion concentrations decreases are in agreement with trends in precipitation chemistry observed elsewhere in the U.S. (Lehmann et al. 2007; Nilles and Conley 2001). The sulfate trends

at NADP stations in Colorado appear to correspond to reductions in SO₂ emissions that have occurred during the same period (Fig. 3). Estimates of regional SO₂ emissions (Arizona, Colorado, New Mexico, Utah, and Wyoming) obtained from the EPA Clean Air Markets Program (<http://www.epa.gov/airmarkt/>) indicate SO₂ emissions have declined by 44% between 1985 and 2008, with most of the decline occurring after 1995. This is very close to the average decrease in sulfate concentrations of 46%, which indicates that sulfate and associated acidity in precipitation in high-elevation areas appears to reflect regional patterns of SO₂ emissions. By contrast, trends in nitrogen species were not as widespread, with four stations showing upward trends in ammonium and one showing an upward trend in nitrate. Estimates of regional NO_x emissions show decreases of less than 15% between 1995 and 2008 (<http://www.epa.gov/airmarkets/>). Most precipitation stations with upward ammonium-concentration trends are located on the east side of the Continental Divide (Beaver Meadows, Loch Vale, and Niwot Saddle) in proximity to large population centers (Fig. 1) and agricultural areas in eastern Colorado. This spatial pattern suggests that ammonium deposition in high-elevation areas may be more strongly influenced by local-scale sources and deposition processes.

As observed for deposition, substantial decreases were observed in sulfate concentrations in lakes in the Mount Zirkel and Flat Tops wilderness areas. All seven of the lakes in these 2 areas showed statistically significant trends in sulfate for 1985–2008 with a mean decrease of $-0.19 \mu\text{eq/l/year}$. The rather uniform decline in lake-sulfate concentrations combined with the isotopic evidence for an atmospheric source (Fig. 2) strongly indicate that decreases in SO_2 emissions and atmospheric-sulfate deposition are driving the lake response in these two wilderness areas. Although the response of surface-water chemistry to reductions in SO_2 emissions has been well documented in the eastern U.S. (Stoddard et al. 2003, Burns et al. 2006; Driscoll et al. 2003) and in Europe (Mosello et al. 2002), to our knowledge this is one of the first studies to document a response for aquatic ecosystems in the Rocky Mountain region. On average, the magnitude of lake-sulfate trends ($-0.19 \mu\text{eq/l/year}$) was about 30% smaller than the magnitude of trends for sulfate in precipitation ($-0.27 \mu\text{eq/l/year}$). The smaller magnitude trends in surface water suggest that some atmospherically deposited sulfate is being attenuated in these watersheds, resulting in a lag between deposition and surface-water response (Stoddard et al. 2003). If this is occurring, then further decreases in lake-water sulfate might be expected at some of these sites even if trends in precipitation began to flatten.

Interestingly, the average rate of decrease was similar in the Mount Zirkel lakes (mean decrease of $-0.20 \mu\text{eq/l/year}$) compared to the Flat Tops lakes (mean decrease of $-0.18 \mu\text{eq/l/year}$). Somewhat larger decreases might be expected for the Mount Zirkel lakes because they are directly downwind of two large coal-fired power plants (Fig. 1) where SO_2 emissions have decreased by more than 80% since 1998 because of installation of gas and particulate control systems (Mast et al. 2005). Consequently, sulfate trends were evaluated for the post-1998 period and a slightly different pattern emerged. The trend at Lake Elbert, for example, indicated a larger decrease of $-0.51 \mu\text{eq/l/year}$ ($p < 0.001$), which represents a 40% decrease in concentrations over the period when emissions were reduced by more than 80%. By contrast, the decrease at Ned Wilson Lake during this period ($-0.22 \mu\text{eq/l/year}$, $p = 0.006$) was less than half of the decrease at Lake Elbert but similar to the long-term trend, providing evidence that lakes in

the Mount Zirkel Wilderness have responded to emissions reductions at local upwind sources, as well as regional sources. The observations of actual improvements in lake chemistry to local emission reductions may be useful for refining protocols used in the Prevention of Significant Deterioration (PSD) process. PSD is a management tool used by federal land managers to predict changes in air quality in protected areas that would likely occur from a single point source of pollution with a proposed emission level (Blett et al. 2003).

In low ANC streams in the eastern U.S., decreases in stream-water sulfate typically are associated with decreases in base-cation concentrations because of decreased leaching of the cation exchange complex by strong acid anions (Driscoll et al. 2003, Stoddard et al. 2003). In the Mount Zirkel and Flat Tops areas, only Lake Elbert showed a corresponding decrease in calcium while most of the lakes showed increases in base cations that exceeded the decreases in sulfate and largely were offset by increases in ANC. Time-series plots for Summit Lake reveal that the increases in base cations and ANC occurred almost entirely after 1995 and did not show strong temporal coherence with trends in sulfate (Fig. 4). During the same period (1995–2008), lake-water chloride concentrations showed an increase in concentration of about 30%, similar to the increase in calcium. Assuming chloride behaves conservatively and that weathering contributions are minimal, this could reflect less dilution of soil and groundwater inputs by snowmelt and/or concentration by evapotranspiration (Campbell et al. 1995). In high-elevation areas of Colorado, 1995 and 1997 were some of the wettest years on record and 2002 was one of the driest (Doesken and Pielke 2003). Annual precipitation at SNOTEL stations in the vicinity of the Mount Zirkel and Flat Tops areas does in fact show a prominent decrease during the later part of the record particularly between 1995 and 2002 (gray boxes in Fig. 5a). Given these lakes are shallow and have small contributing drainages, it seems plausible that drier conditions could be a major factor driving increases in ANC, base cations, and chloride concentrations in the later part of the record.

Although wet deposition of nitrogen species exceeds that of sulfate at all the NADP stations, few of the study lakes had detectable nitrate concentrations, indicating that terrestrial and aquatic biota retain most atmospherically deposited nitrogen at

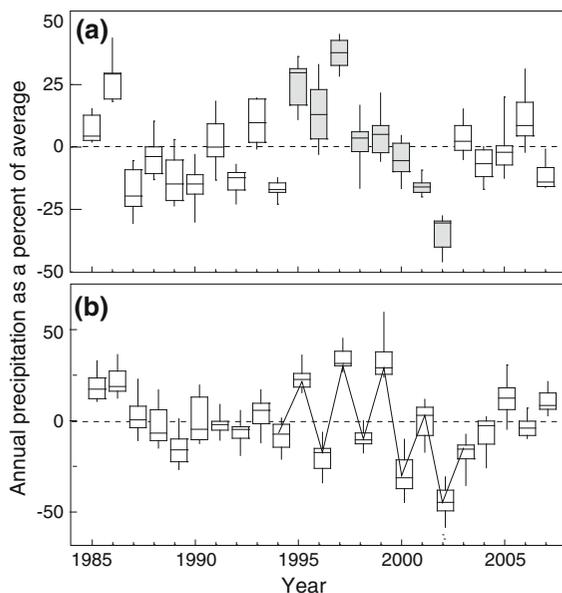


Fig. 5 Trends in annual precipitation expressed as a percent of average for SNOTEL stations in the vicinity of the **a** Mount Zirkel and Flat Tops Wilderness ($n = 11$) and **b** Weminuche Wilderness ($n = 7$). *Shading* in **a** highlights 1995–2002 downward trend in precipitation, and *connected boxes* in **b** indicate alternating wet and dry years

least during the growing season when lake sampling occurred. The low nitrate concentrations observed at our study lakes are in sharp contrast to lakes and streams in the Front Range of Colorado, which have summer concentrations exceeding 15 to 20 $\mu\text{eq/l}$ even when biological demand is highest (Williams et al. 1996; Campbell et al. 2000). These areas of the Front Range are reported to be at an advanced stage of nitrogen saturation because of prolonged atmospheric nitrogen loading from source areas in eastern Colorado (Baron et al. 2000; Burns 2004; Bowman et al. 2006). In this study, nitrate was most frequently detected in the Weminuche lakes, which are at higher elevations than lakes in the other two wilderness areas. This may reflect a lower capacity of these watersheds to retain nitrogen because of less soil coverage and steeper slopes, and lower in-lake productivity at higher elevations (Sueker et al. 2001; Sickman et al. 2002). Four of the Weminuche lakes did have sufficient nitrate data for trend analysis and one of those, White Dome, did show a significant upward trend in nitrate. It is not clear what is driving the trend at White Dome given that Molas Pass, the closest NADP station, showed no trends in nitrate or

ammonium over the same period. One possibility is the watershed is in an early stage of nitrogen saturation and nitrate might be beginning to leach to surface waters, although to a lesser degree than what is occurring in high-elevation areas of the Front Range (Baron et al. 2000; Burns 2004).

Effect of climate on weathering rates

In sharp contrast to the downward sulfate trends in the Mount Zirkel and Flat Tops lakes, the dominant pattern in the Weminuche lakes was a strong increase in lake-water sulfate over the study period. The trends in sulfate were quite dramatic in some of the lakes. At Upper Sunlight, for example, sulfate increased from a minimum of 21 $\mu\text{eq/l}$ in 1987 to a peak of 180 $\mu\text{eq/l}$ in 2004 (Fig. 4). The isotopic data discussed previously clearly show that sulfate in these lakes is derived primarily from weathering sources. Therefore, atmospheric deposition should have relatively little, if any, effect on lake sulfate concentrations in these lakes. In all the Weminuche lakes, increases in lake sulfate were balanced by calcium and magnesium with only modest increases in silica (Fig. 6). Because pyrite is the dominant source of sulfate, most calcium is likely released by strong-acid weathering of calcite, which occurs within mineralized veins (Steven et al. 1969) and is disseminated within the granitic rocks (White et al. 2005). Some studies have invoked sulfate minerals such as gypsum as the source of calcium and sulfate to alpine lakes and streams (Sommaruga-Wögrath et al. 1997; Lafreniere and Sharp 2005) but our isotopic evidence indicates this is not a significant source in the Weminuche

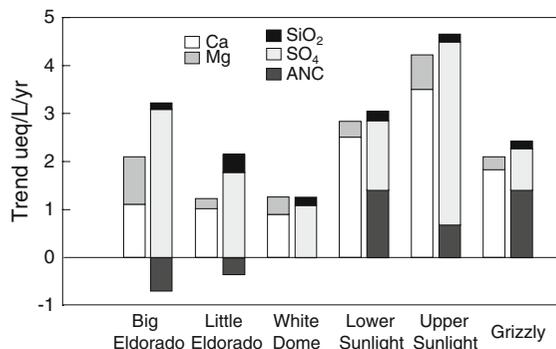


Fig. 6 Comparison of trend magnitudes in calcium, magnesium, sulfate, acid neutralizing capacity, and silica concentrations for 1985–2008 for 6 lakes in the Weminuche Wilderness

Wilderness. Silicate minerals are the most plausible source of magnesium; in particular chlorite, which occurs in metamorphic rocks underlying Big and Little Eldorado and White Dome Lakes, and hornblende, which occurs in granitic rocks underlying the other three lakes (Barker 1969). Other researchers analyzed the outflow from a rock glacier in the Colorado Front Range. Their analysis showed a similar enrichment of sulfate, calcium, and magnesium during late summer months (Williams et al. 2006) and they proposed a similar geochemical model with dissolution of pyrite, epidote, chlorite, and calcite best explaining elevated concentrations at the glacier outflow.

Trends in lake chemistry in the Weminuche Wilderness could partially be explained by below-average precipitation and runoff, which might result in less dilution of weathering-derived solutes and a greater proportion of base-flow contributions to surface-water bodies. Annual precipitation at SNOTEL stations in the southwestern part of the State showed no trends for 1985–2007, 1990–2007 or 1995–2007 although a period of considerable variability was noted in the middle part of the record, characterized by alternating wet and dry years (Fig. 5b). Trends in streamflow were evaluated at the Vallecito Creek gaging station located at the wilderness boundary approximately 25 km downstream from the lake study area. Similar to precipitation, significant trends were not evident in mean annual discharge during the period 1985–2007 ($p = 0.492$). Weak downward trends in monthly runoff were detected during June ($p = 0.031$) and July ($p = 0.055$), which might reflect warmer summer temperatures and a shift towards earlier snowmelt runoff as documented by Clow (2010) for high-elevation areas of Colorado. Overall, however, available data provide little evidence for substantial changes in runoff in the Weminuche Wilderness over the period that sulfate increases occurred. A more complex relation between sulfate and runoff does appear to be evident on shorter time scales. For example, following a severe regional drought in 2002, a sudden increase in sulfate persisted for the following 2 years (Fig. 4) despite increases in precipitation and runoff during this period. Pulses of sulfate-rich water following drought have been documented in headwater streams in North America; however, these pulses mainly occurred in wetland-dominated catchments

because of drought-induced reoxidation of reduced sulfur in organic rich soils (Laudon et al. 2004; Eimers et al. 2007).

Given that hydrologic patterns do not adequately explain the long-term changes in lake chemistry in the Weminuche Wilderness, it seems plausible that trends in air temperature may be playing a role. Similar increases in sulfate and base-cation concentrations have been observed for numerous alpine lakes in Europe (Sommaruga-Wögrath et al. 1997; Tait and Thaler 2000; Mosello et al. 2002; Rogora et al. 2003), and have been attributed to enhanced weathering rates and increased biological activity caused by increasing air temperatures (Sommaruga-Wögrath et al. 1997). The increase in annual air temperature in the Alps of $+0.57^{\circ}\text{C}$ per decade for 1974–2004 (Rebetez and Reinhard 2007) is similar to mountainous areas of Colorado where trends averaged $+0.74^{\circ}\text{C}$ per decade for 1984–2007. Seasonal analyses showed that the greatest temperature increase in the Alps occurred during spring and summer (Rebetez and Reinhard 2007), which is similar to the pattern in Colorado where significant warming occurred during May, July, and August (Clow 2010). Sommaruga-Wögrath et al. (1997) suggest one effect of higher air temperatures, particularly during summer, is a shorter period of snow and ice cover, which increases exposure of rocks and soils and enhances weathering rates. At nearby SNOTEL stations, we estimated snow-cover duration as the number of days per year with snow on the sensor pillow. Of the seven sites tested, only one showed a slight downward trend ($p = 0.020$), perhaps indicating that changes in snow cover duration did not play a major role in controlling chemical changes in the study lakes.

Several recent studies have suggested the effect of climate warming on water chemistry in alpine areas is related to enhanced melting of ice features such as permafrost, rock glaciers, and glaciers (Williams et al. 2006; Thies et al. 2007; Hill 2008; Baron et al. 2009). Thies et al. (2007) reported as much as a 26-fold increase in sulfate and unexpectedly high concentrations of nickel and zinc during the past 20 years in alpine lakes in the Austrian Alps. Baron et al. (2009) reported increasing concentrations of nitrate, calcium, and sulfate since 2000 in streams draining the Loch Vale Watershed in the Colorado Front Range. Both these studies attribute chemical

trends to greater contributions of rock-glacier melt-water, which can be highly enriched in dissolved solids because of high rates of chemical and physical weathering in periglacial environments (Brown 2002; Williams et al. 2006). Climate also can play a role in controlling nitrogen retention and release in watersheds (Murdoch et al. 1998; Watmough et al. 2004). Baron et al. (2009) proposed that recent increases in stream-water nitrate in the Loch Vale watershed are caused by melting ice in glaciers and rock glaciers that is flushing nitrogen from microbially active sediments. Enhanced melting of permanent ice in the Front Range is plausible given that recent air temperature trends have increased the altitude at which permafrost and permanent snow and ice can persist (Clow et al. 2003b). A marked decrease in the ratio of precipitation to runoff in Loch Vale Watershed was reported by Baron et al. (2009), who attributed it to additional runoff from melting ice in glaciers and rock glaciers. In a small alpine catchment just south of Loch Vale, increases in late-season discharge have occurred during the past 2 decades (Hill 2008). Half of the flow increase was accounted for by melting of a small glacier and the remainder was attributed to melting of subsurface ice in rock glaciers and permafrost. The effect of melting permafrost on lake chemistry in the Weminuche Wilderness is difficult to assess due to the unknown extent of permafrost as well as a lack of detailed hydrologic data for the study area. The lake basins do not contain snow or rock glaciers; however, they do contain numerous talus slopes and other periglacial features that could contain embedded ice or discontinuous permafrost (Millar and Westfall 2008). Regional joint and fracture systems in the bedrock also might provide some storage for permanent ice. Because such fracture systems can be mineralized, melting of ice could enhance weathering of pyrite and other vein-filling minerals, resulting in increased solute transport to lakes. The magnitude of this input is unknown; however, a recent groundwater study of a mineralized alpine catchment in central Colorado found that simple topography rather than faults and lithology controlled the occurrence and flow of shallow groundwater (Manning et al. 2008) indicating that contributions from fracture flow would likely be small.

In this study and other studies reporting a link between climate warming and water chemistry in alpine areas (Sommaruga-Wögrath et al. 1997; Tait and Thaler 2000; Mosello et al. 2002; Rogora et al.

2003; Baron et al. 2009), increases in lake-water sulfate and associated calcium were large compared to increases in silica (Fig. 6). Increased sulfate export in response to climate variability has been reported for low-elevation headwater catchments and generally is attributed to release of sulfate from wetlands and peatlands following periods of drought (Laudon et al. 2004; Eimers et al. 2007). Because alpine environments typically are not dominated by organic-rich soils, the observed chemical signature may indicate that warming is preferentially affecting the rate of pyrite weathering. Pyrite decomposition, unlike silicate weathering, is largely dependent on oxygen availability and can be accelerated by fluctuations in groundwater levels, which enhance exposure of mineralized rock to oxygen when water levels decline (Forstner and Salomons 1988). An increase in summer air temperatures of a few degrees coupled with earlier snowmelt could increase evaporation rates and cause the water table to decline without a change in annual precipitation (Laudon et al. 2004). At SNOTEL stations in southwestern Colorado, significant warming trends have been discerned in summer months, and particularly July, which might be increasing evaporation rates during snow-free months. The precipitation pattern in southwestern Colorado also showed a pronounced period of alternating wet and dry years from 1994 to 2003 (Fig. 5b). A possible result is that the water table declined during the warmer, drier years, enhancing pyrite oxidation and the buildup of soluble salts in the unsaturated zone. During the alternating wet years, newly produced soluble salts were flushed from soils and sediments resulting in increased concentrations in lakes. If climate change in mountain areas results in increased summer warming or a greater frequency of drought years, then the magnitude of sulfate export from mineralized watersheds may increase (Nordstrom 2009). Because pyrite in mineralized areas can be associated with other base-metal sulfides and its breakdown generates acidity (Plumlee 1999), climate warming might result in increased acidity and trace-metal concentrations in surface water to levels where effects on aquatic life may become evident. Moreover, climate induced increases in lake sulfate could confound the ability to detect responses in some high-elevation lakes from future changes in anthropogenic SO₂ emissions. Such climate-related effects should be taken into consideration by resource

managers when evaluating new pollution sources under the PSD process as well as in the development and application of critical loads for atmospheric pollutants.

Conclusions

The results of this study suggest that long-term trends in the chemical composition of high-elevation lakes in three wilderness areas in Colorado have been driven by changes in atmospheric deposition and climate variation during the past two decades. Sulfate and hydrogen-ion concentrations in precipitation were found to decrease throughout mountainous areas of Colorado during 1987–2008. This is in agreement with trends in precipitation chemistry observed elsewhere in the U.S. and likely is caused by regional reductions in SO₂ emissions related to implementation of the Clean Air Act Amendments of 1990. Data from lakes in two wilderness areas in northern Colorado showed similar downward trends in sulfate concentrations during 1985–2008. Sulfur isotopic ratios reveal that sulfate in these lakes is almost entirely derived from atmospheric inputs, which supports the hypothesis that decreases in atmospheric deposition are driving the lake response in these areas. To our knowledge this is one of the first studies to document a response of surface-water chemistry to reductions in SO₂ emissions for aquatic ecosystems in the Rocky Mountain region. In contrast to sulfate, nitrogen species in precipitation showed increases only at sites in proximity to urban and agricultural areas. In the study lakes, most nitrogen concentrations were at or below detection during the summer months indicating that terrestrial and aquatic biota retain most atmospherically deposited nitrogen. These results are in sharp contrast to lakes and streams in the Front Range of Colorado, which have elevated growing-season nitrate concentrations because of prolonged atmospheric nitrogen loading from source areas in eastern Colorado.

Despite downward trends in precipitation sulfate concentrations across Colorado, lakes in a wilderness area in the southern part of the State showed sharp increases in lake-water sulfate during 1985–2008 that were largely balanced by increases in calcium and magnesium concentrations. Similar increases in sulfate and base-cation concentrations have been

observed in numerous alpine lakes in Europe and have been attributed to enhanced weathering rates, increased biological activity, and/or melting of permanent ice features caused by increasing air temperatures. Analysis of climate records from the SNOTEL network shows increases in annual air temperature of 0.45 to 0.93°C per decade across most mountainous areas of Colorado indicating climate may be a factor influencing the chemistry of these southern Colorado lakes. Sulfur isotopic data for the southern lakes reveals that sulfate largely is derived from weathering of pyrite, which is associated with hydrothermally altered and mineralized bedrock. Unlike silicate weathering, pyrite breakdown is largely dependent on oxygen availability and can be accelerated by fluctuations of groundwater levels, which enhance exposure of mineralized rock to oxygen when water levels decline. We suggest that during warmer, drier years water-table declines might enhance pyrite oxidation and the build-up of soluble salts in the unsaturated zone. During the subsequent snowmelt, these salts could be flushed from soils and sediments resulting in increased solute concentrations in lakes. If climate change in mountainous areas results in increased summer warming or a greater frequency of drought years, then the magnitude of sulfate export from mineralized watersheds may continue to increase. Because pyrite in mineralized areas can be associated with other base-metal sulfides and its breakdown generates acidity, changes in climate could result in increased acidity and trace-metal concentrations in surface water to levels where effects on aquatic life may become evident.

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