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Water chemistry of high elevation Colorado wilderness lakes

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Abstract. High elevation alpine and subalpine Rocky Mountain lakes in Colorado and south-eastern Wyoming were examined to determine regional variability in water chemistry and their sensitivity to atmospheric deposition. Acid neutralizing capacity, pH, conductivity and concentrations of major anions and cations were compared. Regional differences in water chemistry are evident. The south-eastern most lakes have significantly higher pH, conductivity, ANC, and sums of acid and base concentrations than lakes in the other regions of the state. In contrast the north-western most lakes are significantly more dilute than those from other regions. Despite these two regional differences, most regions are similar in having a wide range of variability in potential sensitivity of their lakes to acidification and nitrogen export. Many wilderness areas in western and eastern regions contains lakes that are extremely sensitive and other lakes not susceptible to deposition. Overall, 70% of the Colorado lakes are sensitive to acidification and 15% are extremely sensitive to acidification. All of the regions had lakes that are classified as susceptible or sensitive to acidification, with 12 of the 17 areas having all of their sampled lakes susceptible or sensitive. Generally NO_3^{1-} concentration in surface waters decreased from mid-season to late season; yet a large number of the lakes export NO_3^{1-} late in the season, suggesting nitrogen saturation. The results confirm the sensitivity of high elevation wilderness aquatic ecosystems in all regions of Colorado to acidification and nitrogen deposition.

Introduction

Regional examination of chemical variability of lakes in Colorado has been limited to the Western Lakes Survey in the 1980's (Eilers et al. 1986, Landers et al. 1987). That study compared lake chemistry of lakes from the Southern Rocky Mountains (WY, CO, and NM) with other regions of the Western US. The study was not limited to high elevation, wilderness, headwater lakes. The Western Lake Survey concluded that lakes from the Southern Rockies had fewer dilute lakes and higher calcium (Ca^{2+}), nitrate (NO_3^{1-}), total phosphorus (P), sodium (Na^{1+}), potassium (K^{1+}), magnesium (Mg^{2+}), iron (Fe), dissolved organic carbon (DOC), conductance, and bicarbonate than other regions of the Western US (Landers et al. 1887).

Previous studies within Colorado have held that most of the waters in the Front Range of Colorado are susceptible to acidification and increased N deposition (Musselman et al. 1996; Baron et al. 2000; Williams and Tonnessen 2000; Wolfe et al. 2001. The Front Range of Colorado is increasing in population attended with growing concern that atmospheric deposition from anthropogenic sources may be impacting sensitive high elevation ecosystems (Musselman et al. 1996; Baron et al. 2000; Williams and Tonnessen 2000; Wolfe et al. 2001). Of particular concern are aquatic ecosystems having low buffering capacity and low concentrations of nitrogen. Lakes low in acid neutralizing capacity (ANC) are common in high elevation Rocky Mountain watersheds which characteristically have a high amount of exposed, slowly weatherable bedrock (Turk and Spahr 1991). Such catchments frequently occur in steep, complex terrain with little soil development and sparse vegetative cover. Aquatic ecosystems in these catchments often have low ANC, biomass, and productivity. Little historic data on water chemistry of high elevation wilderness lakes of Colorado are available. The 1985 Western Lakes Survey sampled 132 lakes in Colorado, with 51 of the samples collected in the Colorado Front Range area (Eilers et al.1987, Landers et al. 1987). Of the Front Range lakes sampled in Colorado, 44% were found to be susceptible to acidification (Eilers et al. 1987, Landers et al. 1987), based on ANC values $\leq 200\ \mu\text{eq l}^{-1}$ (Baker et al. 1990). Lewis (1982) has reported a decline in alkalinity of lakes in the Colorado Rocky Mountains. Caine (1995) has documented a recent decrease in ANC in a Colorado Front Range catchment.

Atmospheric deposition of nitrate (NO_3^{1-}) and ammonium (NH_4^{1+}) generally increased in the western United States from 1983 to 1993 (Lynch et al. 1995). In Colorado, deposition increases of NO_3^{1-} are most notable for higher elevation watersheds (Williams et al. 1996a, b; Williams and Tonnessen 2000). Data from Rocky Mountain National Park indicate wet deposition of 2.3–3.4 kg N $ha^{-1}\ yr^{-1}$ (Baron et al. 1995), but the deposition has not increased in recent years (Baron et al. 2000). Similar wet deposition of N (3.2 kg/ha) has been recorded at a high elevation site in SE Wyoming (Ellsworth 2002). Williams et al. (1996a) report that wet deposition of nitrogen has increased from values reported in the 1980s at Niwot Ridge west of Boulder, Colorado, a site closer to the Front Range Urban Corridor, but nitrogen wet deposition has remained at about 3 kg N $ha^{-1}\ yr^{-1}$ since 1992 (Williams and Tonnessen 2000). An equal amount of dry nitrogen deposition may occur at this site (Sievering et al. 1992).

The spatial variability in water chemistry and extent and effects of increased NO_3^{1-} deposition on Rocky Mountain ecosystems are largely unknown. The aquatic components of ecosystems are likely the most sensitive to nitrogen deposition, particularly those at high elevation in ecosystems with minimal soil development and sparse vegetation. Baron et al. (2000) suggest that increased N deposition has caused significant changes in Colorado Front Range terrestrial and aquatic ecosystems. They report increased soil N, lower C:N ratio in spruce forest stands, and changes in diatom flora in areas where deposition is higher. Limnological impact, co-occurring with increased N use in agriculture and industry in the 1950's, is evident against a 14,000-year post glacier core of one lake in the Front Range (Wolfe et al. 2001). Nitrogen oxides emissions from automobiles likely contribute to N deposition in Front Range ecosystems.

Soils and groundwater can regulate chemical composition of surface waters even in high elevation, complex terrain with much exposed bedrock, little soil development, and sparse vegetation (Campbell et al. 1995; Heuer et al. 1999; Clow and Sueker 2000). The snowmelt chemical pulse evident in spring outflow can represent a flushing of stored groundwater in shallow subsurface reservoirs (Kendall et al. 1995; Mast et al. 1995; Campbell et al. 2000, 2002). However, as complexity of the terrain increases, the changes in slope gradient, soil permeability, and rainfall intensity increases the contribution to stream discharge of surface flow compared to subsurface flow (Sueker 1995). Smaller catchments in complex terrain likely have a higher surface to subsurface flow ratio than larger catchments in less complex terrain. Because soils in high elevation catchments are minimally developed, NO_3^{1-} available from these soils can be low compared to NO_3^{1-} loads from atmospheric deposition. Nevertheless, the contribution of atmospheric deposition to export of N from high elevation ecosystems varies by geographic region depending on the different geology and watershed and landscape characteristics of the various regions. Further, during snowmelt, some alpine soils serve as nitrogen sources whereas some sub-alpine soils serve as sinks (Heuer et al. 1999).

Productivity of lakes in the Rocky Mountains of Colorado and southeastern Wyoming can be limited, perhaps seasonally, by nitrogen, by phosphorus, or by both (Wagner and Parker 1973; Lewis and Grant 1977; Morris and Lewis 1988). Field (Campbell et al. 2000) and modeling (Baron et al. 1994) studies have shown that high elevation catchments in the western U.S. can retain and use inorganic nitrogen during the growing season, with almost no export of inorganic nitrogen in surface waters after an initial, episodic snowmelt pulse (Williams et al. 1996a). Yet small increases in nitrogen deposition in these ecosystems may be detected in surface water outflow (Baron et al. 1994). Chemical concentrations of cations and anions in surface waters from high elevation landscapes decrease from the time of initial snowmelt throughout the summer (Caine and Thurman 1990; Williams et al. 1995, 1996a). Nitrates typically decrease downstream in high elevation catchments (Caine and Thurman, 1990; Caine 1995), as they become used by the biota, aquatic or terrestrial. However, some alpine lakes in Colorado export N all season (Baron and Campbell 1997; Campbell et al. 2000, Williams et al. 1996b).

Since most high elevation Rocky Mountain catchments are nitrogen limited, increasing available nitrogen results in increased growth and production of biomass. However, if organisms are unable to use all available nitrogen, it is exported, chiefly as NO_3^{1-}, in surface waters. A particular concern is that high elevation Rocky Mountain lakes are exporting NO_3^{1-} (Williams et al. 1996b) during the time of year when NO_3^{1-} is expected to be maximally used, with implications for the nitrogen balance of these aquatic ecosystems and on the associated downstream terrestrial ecosystems. These lakes with nitrogen in excess of what can be retained by soil or organisms can be called nitrogen saturated (Aber et al. 1989, Williams et al. 1996b). Possible sources of nitrogen exported through surface waters include increased nitrogen deposition, mineralization, nitrification, release in freeze thaw cycles, soil flushing too rapid for nitrogen to be captured by biota, productivity limitation by other nutrients, biotic nitrogen fixation and release, microorganism decay, or supply from rapid lake turnover or episodic up welling yielding nutrients from lower anaerobic or sediment layers (Mitchell et al. 1996; Jaeger 1999).

This study examined water chemistry of high elevation, alpine and subalpine lakes mostly located in US Department of Agriculture Forest Service wilderness areas in Colorado. Wilderness as discussed here refers to those areas specifically designated by the US Congress that are "…undeveloped federal land retaining its primeval character and influence, without permanent improvements or human habitation…" and "…protected and managed so as to preserve its natural condition." (The Wilderness Act, US Public Law 88-557). Included in this study are wilderness lakes from the Front Range of Colorado and a few lakes from southeastern Wyoming, and from wilderness areas in western Colorado. Focus is on differences in lake chemistry, especially sensitivity to acidification and atmospheric deposition of nitrogen. In contrast to the more general Western US analysis of the Western Lakes Survey of the 1980s (Eilers et al. 1986, Landers et al. 1987), attention here is directed first to differences between geographic regions of Colorado, then to differences between lakes near the Front Range Urban Corridor and lakes from Colorado wilderness areas farther west. Seasonal differences and lake inlet to outlet differences were also examined for some of the wilderness areas.

Methods

Study region

Lake samples represent 17 wilderness or other high elevation areas in Colorado and southeastern Wyoming. The original survey attempted to sample as many lakes as could be accessed for each wilderness area. Only lakes higher than 3000 m elevation were selected for this analysis. The collections were placed into six geographic regions, three on the eastern and three on the western side of the Southern Rocky Mountains (Figure 1), roughly divided by a line just west of the 106th meridian (to include the Rawah wilderness and Colorado State Forest lakes in the east). In north to south order in the East they are the Northern Front Range, Front Range, and the Sangre de Cristo Mountains. For the Western corridor they are the Northern Colorado Mountains, Central Colorado Mountains, and the San Juan Mountains (Figure 1, Table 1). The

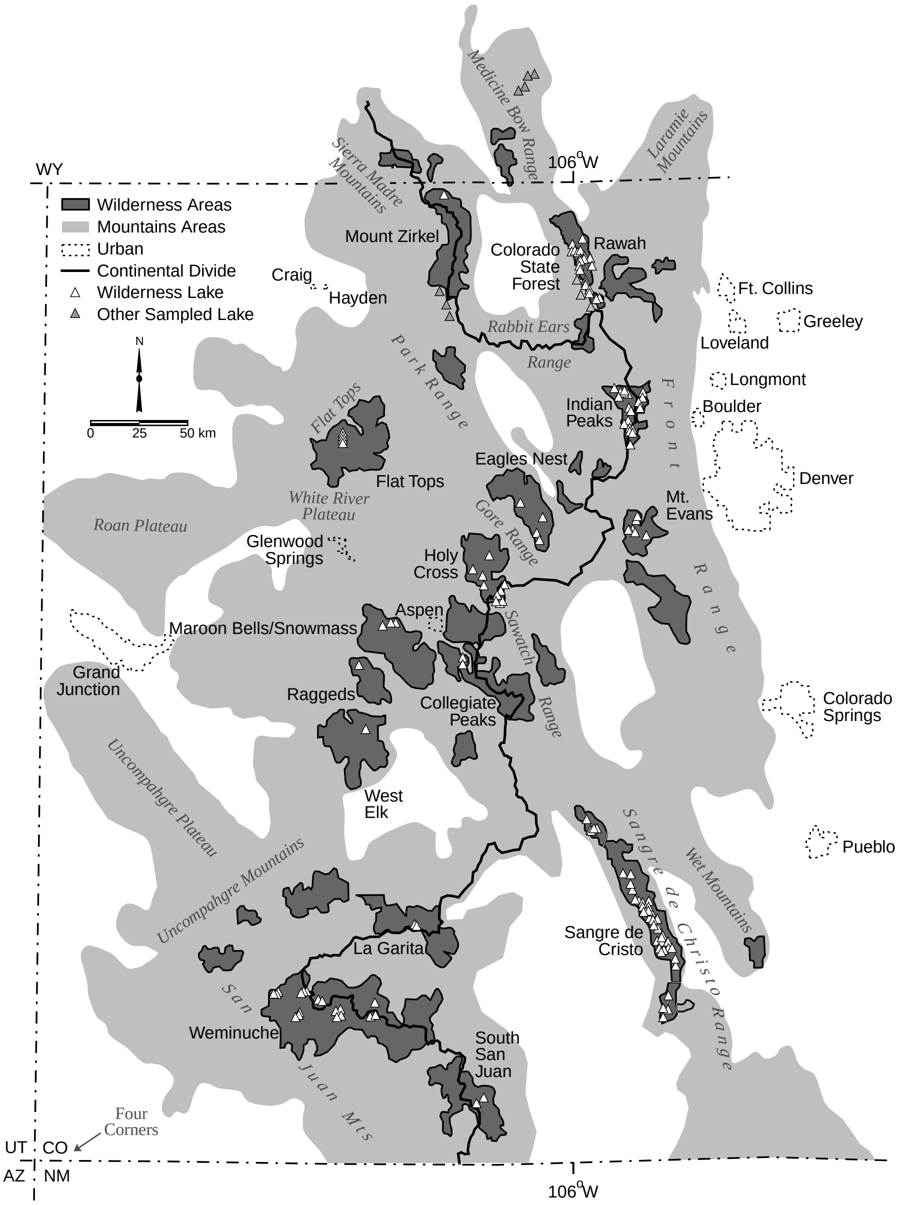


Figure 1. Location of 150 lakes sampled in 1995 in wilderness and other areas of Colorado and southeastern Wyoming.

Continental Divide is quite sinuous in Colorado (Figure 1), thus it cannot be used to delimit coherent geographic regions of eastern versus western areas of Colorado. In addition, eight of the wilderness areas included in this analysis straddle the Continental Divide.

Table 1. Geographic distribution of 150 high elevation Colorado and Wyoming Rocky Mountain lakes sampled for water chemistry in 1995

Geographic region	Wilderness area	Number of lakes sampled		
		Outlets	Early/late	Inlet/outlet
East				
Northern front range	Medicine Bow NF	4	1	2
	Colorado State Forest	3	1	
	Rawah	21	20	12
Front range	Indian Peaks	20 (12)	8	14
	Mount Evans	7[b] (2)	4	2
Sangre de Cristo mountains	Sangre de Cristo	44		
West				
Northern Colorado mountains	Mount Zirkel	4[c] (17)	3	
	Flat Tops	4 (8)	4	
Central Colorado mountains	Eagles Nest	4 (2)	2	
	Holy Cross	10 (2)		
	Maroon Bells-Snowmass	3 (2)	2	
	Collegiate Peaks	2 (1)	2	
	Raggeds	1		
	West Elk	1 (1)	1	
San Juan mountains	La Garita	2	1	
	Weminuche	18 (14)	6	
	South San Juan	2 (2)	1	
Total lakes		150 (63)	56	30

Geographic regions are arranged roughly north to south, first for the Eastern then for the Western mountain region. The number of lakes sampled for regional outlet comparisons, early/late season comparisons, and inlet/outlet comparisons are given.
[a]Numbers in paranthesis are number of lakes sampled in each wilderness for the Western Lakes Survey (Landers et al. 1987).
[b]One lake just outside wilderness area.
[c]Three lakes outside wilderness area.

The Front Range of Colorado is the series of mountain ranges on the eastern flank of the Southern Rocky Mountains from the Laramie and Medicine Bow Mountains of southern Wyoming to the Arkansas River south of Pike's Peak (Lovering and Goddard 1950). The Front Range Urban Corridor includes the cities just east of the Front Range from Fort Collins south through Denver and Colorado Springs to Pueblo (Long 1996). A dozen or more power plants and other point sources of nitrogen emissions also occur in this area (Williams and Tonnessen, 2000). For this paper the Northern Front Range lakes are separated from the rest. The Sangre de Cristo mountains are east of the Continental Divide south of the Front Range proper and west of the Wet Mountains, which distances them from the southern end of the urban area.

The Northern, Central Colorado, and San Juan Mountains are mostly west of the Continental Divide, but more importantly are more distant from eastern, urban pollution sources. However local urban areas, notably Grand Junction and the Glenwood Springs-Aspen corridor, affect wilderness areas in Northern and Central Colorado. The Northern Colorado wilderness areas are up slope and down wind of the Craig and Hayden coal fired power plants. Wilderness areas in the southern part of the Central Colorado Mountains and the San Juan Mountains are also affected by point sources associated with energy production in the Four Corners region (Blett et al. 1993; Williams and Tonnessen 2000).

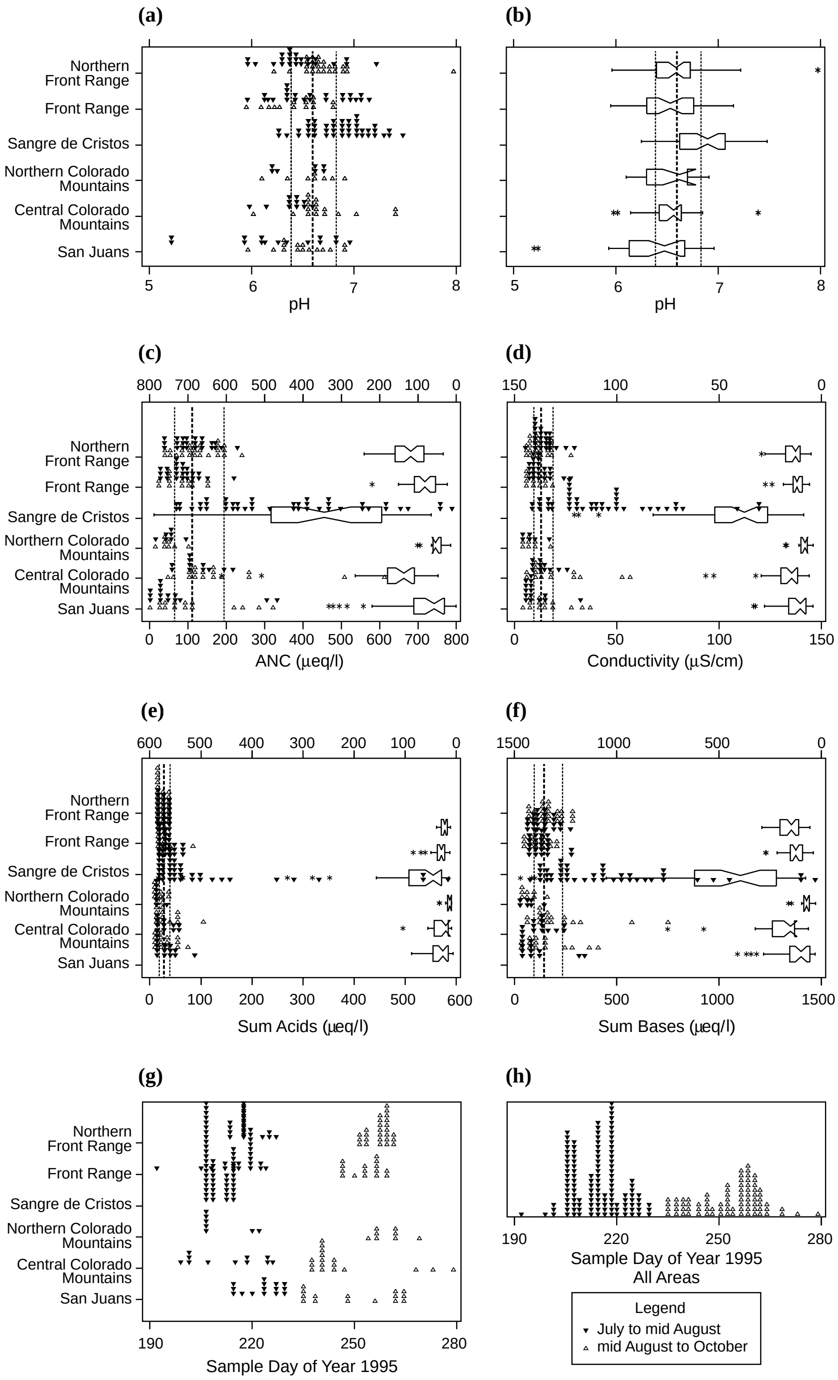
Precambrian igneous and metamorphic rock underlies the three Eastern geographic areas. In addition, the western side of the Sangre de Cristo's have substantial Paleozoic sedimentary rock (Lovering and Goddard, 1950; Bolyard 1960). Except for three wilderness areas, the Northern and Central Colorado Mountains of our classification are also generally composed of Precambrian igneous and metamorphic rocks. Flat Tops and West Elk are composed of Tertiary volcanic rock; and Maroon Bells-Snowmass is composed of Pennsylvanian, sedimentary, and younger rocks with igneous intrusions and rocks metamorphosed locally. The San Juans Mountains are predominantly Tertiary volcanic rock (Marsh et al. 1984).

Field methods

Most high elevation lakes in the Rocky Mountains had not been previously sampled. Lake chemistry data examined in this paper are primarily from a 1995 USDA Forest Service sampling (Musselman et al. 1996), and includes lakes sampled in 1995 by the University of Colorado (CU) and the US Geological Survey. CU samples comprise about 7% of all the samples and are primarily of Indian Peaks lakes. USGS samples comprise about 12% of the total and include all the Mount Zirkel and Flat Tops samples and some of the Weminuche samples. Collection dates for all samples ranged from 11 July to 6 October, 1995 (Figure 2h).

Sample collection followed strict protocols (USDA Forest Service and DOI USGS, unpublished) to insure sample integrity and standardization regarding sampling procedures. Training sessions were held for all staff and volunteers who collected the samples.

Typically one water sample was collected at or near each lake outlet. All samples were collected where one could stand without disturbing the water. This required sampling from solid ground or rock surface rather than from bog or wet meadow where stepping might disturb the water and contaminate the sample. Plastic gloves previously cleaned with deionized water were worn during sample collection. Samples were collected in 250 ml brown high density polyethylene bottles that had been pre-washed and filled with deionized water. The bottles were emptied just before sampling, taking care not to empty into the lake. Bottles were held 10 cm deep then filled with lake water, shaken and rinsed three times pouring rinse water over the inside of the cap and away from the lake surface, then filled completely, capped, and labeled. The samples were placed in a cooler containing an ice pack and delivered to the laboratory within 24 h of collection and filtered (0.45 mm). Protocols required collection of one



(a)
(b)
Northern Front Range
Front Range
Sangre de Cristos
Northern Colorado Mountains
Central Colorado Mountains
San Juans
pH
(c)
(d)
ANC (µeq/l)
Conductivity (µS/cm)
(e)
(f)
Sum Acids (µeq/l)
Sum Bases (µeq/l)
(g)
(h)
Sample Day of Year 1995
Sample Day of Year 1995 All Areas
Legend
July to mid August
mid August to October

duplicate sample approximately every 10 lakes, and one field blank every 20 lakes.

Laboratory methods

Water chemistry analyses included pH, conductivity (μS cm^{-1}), ANC (μeq l^{-1}), and concentration (μeq l^{-1}) of the cations Ca^{2+}, Mg^{2+}, Na^{1+}, K^{1+}, $NH_4{}^{1+}$, and anions $NO_3{}^{1-}$, Cl^{1-}, and $SO_4{}^{2-}$. Analyses were primarily conducted at the USDA Forest Service Rocky Mountain Research Station biogeochemistry laboratory in Fort Collins, but some were analyzed by the Department of Geography, University of Colorado (CU), and the US Geological Survey Water Quality Laboratory in Denver, Colorado. CU staff attended the Forest Service sample collection training sessions and used identical collection protocols and similar laboratory analytical methods for most chemical analyses (Williams and Tonnesson 2000). Alkalinity (μeq l^{-1}) rather than ANC (μeq l^{-1}) are reported for the eight samples analyzed by the US Geological Survey Water Quality Laboratory. Since ANC and alkalinity are often used interchangeably and are very similar for lakes with low ANC or alkalinity (Baker 1990), these alkalinity values were used in place of ANC in the results below. Samples collected by all laboratories used approved methods of analysis for surface waters (U.S. EPA 1987). Limits of detection in μeq l^{-1} for the USDA lab were Ca^{2+}, 0.680; Mg^{2+}, 0.353; Na^{1+}, 0.281; K^{1+}, 0.256; $NH_4{}^{1+}$, 0.674; $NO_3{}^{1-}$, 0.244; Cl^{1-}, 0.402 and $SO_4{}^{2-}$, 0.373 (Musselman et al. 1996).

Analysis methods

Samples with ion balance outside the range $\pm 15\%$ were not used. Seventeen lakes had replicate samples which were tested for differences in central tendency by the Wilcoxon signed rank test and differences in shape and location of

Figure 2. Summary water chemistry of 150 lakes by geographic region and sampling date. Dot density plots represent the chemistry of each lake and its sampling time. Dashed vertical lines through the dot plots mark the hinges and median (center darker line) of the overall distribution. Box and whisker plots summarize the distribution of early and late samples combined and are shown in reverse scale on the top axis. The reverse scale is utilized to avoid visual overlap of the box plots with the dot plots, yet show the box plot analysis in association with the dot plots. Box plots are read as follows: the arm or whisker on either end and individually plotted outliers (asterisks), if any, represent the first and fourth quartiles, the central box represents the inner 50% of the data with the median located along the abscissa (top axis) at the center of the notch. Notches span the approximate 95% confidence interval about the median thus overlapping notches indicates an approximate, nonparametric, pairwise, estimate (with 95% confidence) of no difference in medians (Velleman & Hoaglin 1981).

their distribution by the Kolmogorov-Smirnov two-sample test. They were not statistically different ($p < 0.01$) and were replaced by their average in subsequent analyses. Here and whenever samples were averaged, pH was recalculated from the average H^{1+} concentration.

In addition to the 11 measured water chemistry variables, two summary variables were computed from measured concentrations: sum of acids = Σ Acids = Σ (NO_3^{1-}, Cl^{1-}, SO_4^{2-}) and sum of bases = Σ Bases = Σ (Ca^{2+}, Mg^{2+}, Na^{1+}, K^{1+}, NH_4^{1+}). Inspection of normal probability plots indicated that, as anticipated, none of the water chemistry variables were normally distributed. This was confirmed by Lilliefors tests of normality for each variable across all samples ($p < 0.01$). Log transformation yields normally distributed values (Lilliefors, $p > 0.01$) for only eight of the 13 variables. Because of this and our interest in the nitrogen containing ions whose values were often below the level of detection and recorded as zero (log undefined), log transforms were not used. Rather for this paper non-parametric tests were used and results are presented graphically. Further, because samples were collected by individual national forests, with differing budgetary and other capacities, to represent as many lakes as possible there is no presumption that the samples represent an independent random sample of the wilderness area lakes addressed in this paper. Accordingly our statistical results must emphasize the descriptive, hence as a caution conservative *p*-values and tests are used. Nevertheless, the number of lakes sampled by wilderness in the study reported here (Table 1) is roughly comparable to those of the Western Lakes Survey (Landers et al. 1987). Their stratified random sampling included 89 Colorado wilderness lakes, with 63 of these occurring in wilderness areas of the present study. They included, in addition, four lakes from three other wilderness area and 22 lakes from Rocky Mountain National Park. We include 87 additional lakes from four other wilderness areas and two non wilderness areas.

Lake water samples were routinely collected near the lake outlets. But, some lakes were sampled at their inlets as well, and some lakes were sampled on two or more dates about a month apart. Accordingly three sets of data were considered: (1) Regional comparisons of 150 lake outlets; (2) seasonal likeness or differences of paired measurements in 56 lakes; and (3) inlet versus outlet changes in water chemistry for paired observations of 30 lakes in the two front range areas (Table 1).

Results and discussion

Regional comparison

Differences between geographic regions in chemistry or in vulnerability to acidification were examined. Collection dates for lake samples show a bimodal distribution with mode centers 40 days apart and with an 8-day gap between modes (Figure 2h). The early group contains samples taken 11 July–17 August;

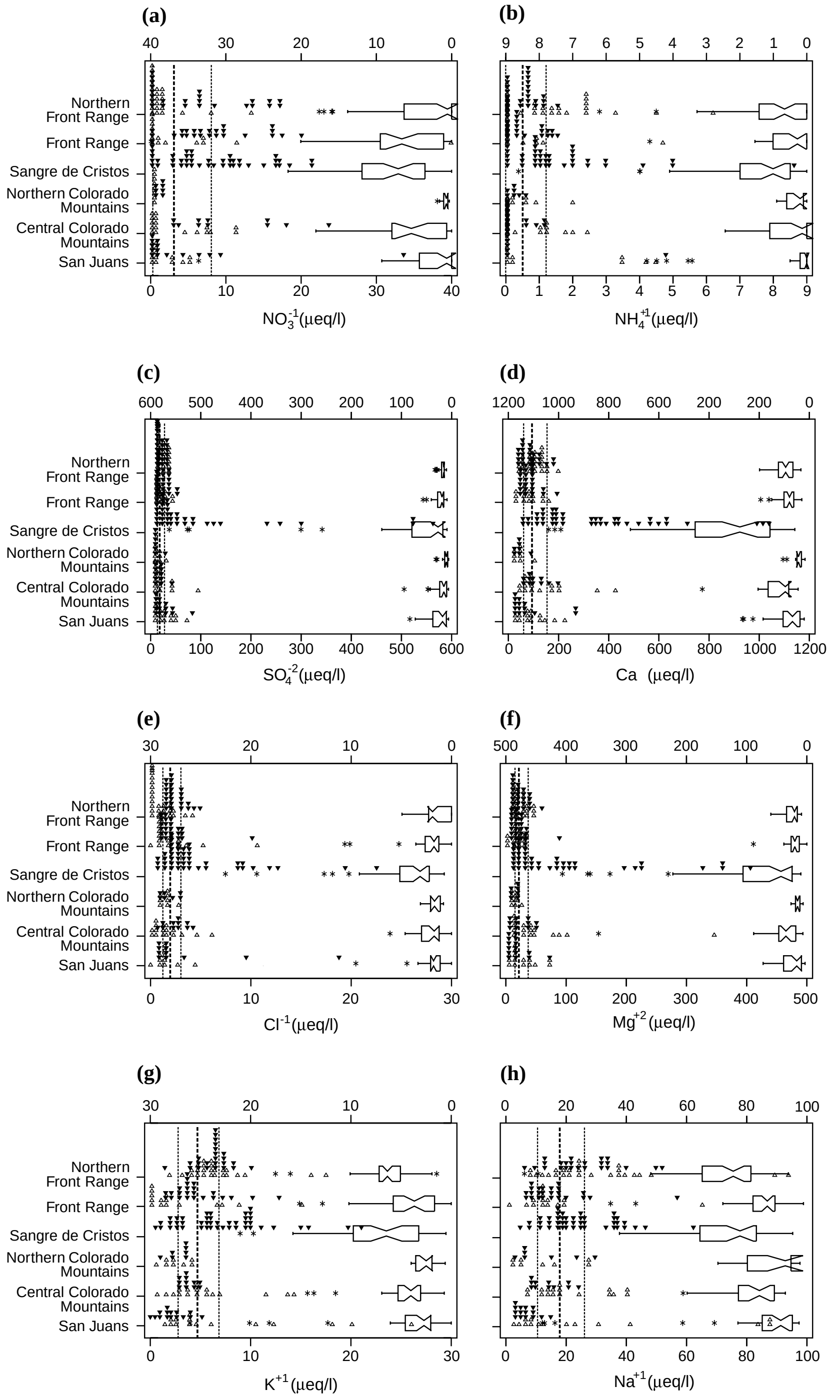
the late group contains samples taken 23 August–6 October. Because lake water chemistry can change throughout the year, early and late data are displayed separately. However, seasonal differences in variation within a geographic region made little or no difference when examining variation between regions. This is not to say that seasonal variation within a given lake does not exist or is not important and those results are presented below. Rather, for comparing populations of lakes from region to region, the same conclusions were reached here, whether the comparison was made with the early samples plus the single season samples, the late plus the single season samples, or with them all combined.

Water chemistry values for lakes within each geographic region are displayed in Figure 2a–g, Figure 3a–h. Early and late season samples, with different symbols, are shown by dot density plots. Three vertical lines drawn through the dot plots mark the upper and lower hinges (75- and 25-percentiles) and the median (50-percentile) of the combined sample. The distribution of values in each geographic region is summarized by a box plot.

Inspection of the dot and box plots (Figure 2 and 3) gives a synoptic picture of the water chemistry of these lakes because the data for each lake is individually represented by value and season, each region's distribution is summarized by a dot density and by a box plot, and quartiles of the overall distribution are represented. Further, grouped box plots can be read as a visual nonparametric analog of analysis of variance (non overlapping notches are an indication of differences (Velleman and Hoaglin 1981). The non normality of the data, the unequal variances revealed in the individual plots and the overall quartile lines, and the separation of some boxes calls for a nonparametric analysis of variance.

A Kruskal-Wallis analysis of variance shows that each of the 13 variables differs significantly across the six regional groups taken together ($p \leq 0.01$). Because 13 simultaneous analyses were performed the conservative Bonferroni adjustment was made. The adjustment multiplies each computed p-value by 13, which amounts to comparing test p-values to $0.01/13 = 0.00077$ (Sokal and Rholf 1995).

Since there are no standard nonparametric, post hoc, multiple comparison tests available, assessing significance of differences between regions was approached using another statistical procedure. The Mann–Whitney test, a nonparametric analog of the two-sample t-test, was computed between all possible pairings of the six geographic regions for each variable. Conover (1980, p. 226) reports that the asymptotic relative efficiency of the Mann–Whitney test is high relative to the t-test. Since there were 15 comparisons made for each of the measured variables, the Bonferroni adjustment used was $p \leq (0.01/15) = 0.00067$. To include all the outlet samples yet avoid using double samples for some lakes (early and late season) in any one Mann–Whitney test, the tests were carried out first on the early season samples plus the once sampled outlets and second on the late season plus the single season samples. This also avoids deciding which of the early or late samples, from



(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
Northern Front Range
Front Range
Sangre de Cristos
Northern Colorado Mountains
Central Colorado Mountains
San Juans
NO_3^{-1}(μeq/l)
NH_4^{+1}(μeq/l)
SO_4^{-2}(μeq/l)
Ca (μeq/l)
Cl^{-1}(μeq/l)
Mg^{+2}(μeq/l)
K^{+1}(μeq/l)
Na^{+1}(μeq/l)

some lakes, to use. Water chemistry variables significantly different in pairs of geographic regions, by these tests, are given in Table 2.

These results (Figures 2 and 3; Table 2) can be summarized as follows. Mainly the Sangre de Cristo lakes were different from all the others in having higher values for many of the variables. These lakes tend to be more concentrated. To a lesser extent the Northern Colorado lakes were different from all but the San Juan Mountains in having lower values. These lakes tend to be more dilute. This can be seen generally in Figures 2 and 3 by the spread towards the right by the Sangre de Cristo lakes and clusters of low concentrations for the Northern Colorado lakes for many of the chemistry measures. And it is apparent in Table 2 by the significant differences found being concentrated in the last column and in the first row. As for the rest of the table, of the 78 = 13(variables) × 6(pairwise tests) results computed, only two, NO_3^{1-} and Na^{1+}, were significantly different (Table 2) among the remaining regions.

Despite these differences in concentration between the south eastern most and north western most regions, the Colorado Mountain lakes display broad overlap and variability in lake water chemistry. First, most pH values (Figure 2a, b) were in the range 6-7. Only five San Juan lakes, two each of Front Range and Northern Front Range, and one Central Colorado Mountain lake had values less than 6.0. Second, ANC values and conductivity values for all but one region broadly overlap. The Sangre de Cristo Mountain lakes as a group stand out in having greater values than any other region (Figure 2c, d). But even here for ANC, 12 of the 44 lakes had values less than 200 μeq l^{-l}. Further, of all 150 lakes, 103 had ANC values less than 200 μeq l^{-l} as did both samples for all but two of the lakes sampled twice in a season (Figure 2c). Third, the distribution of individual anion and cation concentrations across geographic regions reveals the same pattern of broad overlap with possibly the Sangre de Cristo or the Northern Colorado Mountains standing out with especially high or low values for individual ions (Figure 3). The N containing ions deserve individual comment. More than three fourths of the NO_3^{1-} concentrations were less than 10 μeq l^{-1} across all lakes (Figure 3a). Concentrations were significantly higher in the Sangre de Cristos than the Northern Colorado Mountains, the San Juans, and the Northern Front Range. Only one other comparison reveals a significant difference for this ion: it is higher for the early season plus the single season outlets of the Front Range than in the San Juans (Table 2). Three-fourths of the NH_4^{1+} concentrations were below 1.2 μeq l^{-1} (Figure 3b) and along with NO_3^{1-} show the most divergence between the early and late sample groups with concentration reduced sometimes to below the detection limit at the late sampling. Both ions were especially low in the samples taken in the Northern Colorado Mountains (Figure 3a, b).

Figure 3. Summary of ion concentrations in 150 lakes by geographic region and sampling date. Plot types and symbols are as in Figure 2.

Table 2. Post hoc pairwise comparisons of geographic areas for water chemistry measurements found to be significantly different overall by the Kruskal-Wallis analysis of variance

Geographic area	Central Colorado mountains	San Juan mountains	Northern Front range	Front range	Sangre de Cristo mountains
Northern Colorado mountains	**ANC**, Ca^{2+}, **ΣAnions**	**ΣAnions**	ANC, **Ca^{2+}**, **K^{1+}**, **ΣAnions**	**ΣAnions**	**ANC**, **Conductivity**, **Ca^{2+}**, **Mg^{2+}**, SO_4^{2-}, **ΣAnions**, **ΣCations**
Central Colorado mountains					**ANC**, **Conductivity**, **Ca^{2+}**, **Cl^{1-}**, **ΣAnions**, ΣCations
San Juan mountains				NO_3^{1-}	**pH**, **ANC**, **Conductivity**, **Ca^{2+}**, Mg^{2+}, **NO_3^{1-}**, **Cl^{1-}**, **ΣAnions**, **ΣCations**
Northern Front range				Na^{1+}	pH, **ANC**, **Conductivity**, **Ca^{2+}**, **Mg**, NO_3^{1-}, Cl^{1-}, SO_4^{2-}, **ΣAnions**, **ΣCations**
Front range					**ANC**, **Conductivity**, **Ca^{2+}**, **Mg^{2+}**, **Na^{1+}**, **Cl^{1-}** **ΣAnions**, **ΣCations**

Variables shown are significantly different between indicated geographic areas as determined by individual Mann–Whitney tests $p = 0.01$. Since 15 tests were made for each variable the Bonferroni correction calls for computed *p*-values to be 15 times smaller than the nominal value or $p = 0.00067$. These tests were performed on two subsets of the data, the early season samples plus the single season samples and the late season plus the single season samples. Variables in bold were significantly different for both subsets, those underlined (three entries) were different only in the second subset, and the rest listed were different in the first. For each measure the value is greater in the area named in its column, except for NO_3 which has higher value in the San Juan mountains than the Front range.

East versus West.

Interest in increased NO_3^{1-} deposition in Eastern lakes, which are geographically near the Front Range Urban Corridor, and more remote Western lakes has recently been addressed on two scales. Williams and Tonnessen (2000), using a subset of our data (Musselman et al. 1996), find 'Lakes in Wilderness Areas of the Colorado Front Range had greater NO_3^{1-} concentrations than lakes from Wilderness Areas to the west of the Continental Divide' (Williams and Tonnessen 2000, p. 1656). They include the Sangre de Cristo lakes along with Mount Evans, Indian Peaks, and Rawah of the Front Range proper. They use Holy Cross, Eagles Nest, and Weminuche lakes to represent the western slope. It is unclear whether they include lakes west of the Continental Divide for Indian Peaks or east of the divide for Eagles Nest and Weminuche samples. Our analysis extends that of Williams and Tonnessen (2000) in two ways. We included additional lakes and divided them east or west as described in this paper rather than with reference to the Continental Divide (Figure 1, Table 1). We include five additional Western wilderness areas and include two additional Eastern (non wilderness) areas. Second we exclude the Sangre de Cristo lakes for reasons mentioned below and because they are not strictly in the Front Range and are farther from the Front Range Urban Corridor and separated from the Front Range by the Wet Mountains (Figure 1).

NO_3^{1-} concentration for early season samples are shown by Wilderness Area for the Eastern and Western mountains of Colorado in Figure 4. Sangre de Cristo lakes are not included but those data appear in Figure 3a. The Mann–Whitney test comparing Eastern versus Western lakes is not significant at $\alpha = 0.01$ ($p = 0.07$). The marginality of the significance, or lack of it, is visually evident in the paired box plots (shown in reverse scale). Here the notches do not quite overlap, thus this test shows significance at the approximate 0.05 level. If the Sangre de Cristo lakes are included in the east the Mann–Whitney test still is not significant ($p = 0.018$). Put another way, east–west differences is largely the effect of the Sangre de Cristo lakes, which we already know have significantly more NO_3^{1-} than some of the other geographic regions (Table 1).

Even though there may be a marginal tendency toward higher NO_3^{1-} values in the east, Figures 3 and 4 illustrates the large variability in lake chemistry both in small (Figure 3) and larger regional (Figure 4) spatial contexts. For example, concentrations in some Rawah lakes and all of the Medicine Bow lakes are as low as most of the Western lakes. In contrast all of the Maroon Bells-Snowmass lakes have higher NO_3^{1-} concentrations than most of the Eastern lakes. Caution should be used when generalizing from a few lakes or wilderness areas. If either the Maroon Bells-Snowmass or Medicine Bow lakes had been left out of our analysis, significant east–west differences such as those shown by Williams and Tonnessen (2000) may well have been evident. It should also be noted that conclusions may change from year to year since precipitation amount and local climatic conditions may influence lake

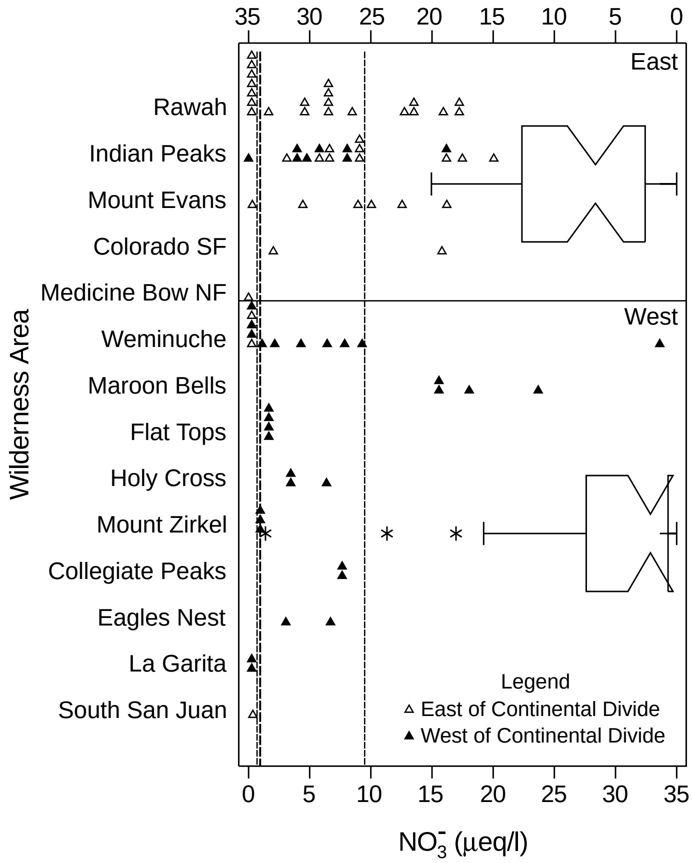


Figure 4. Dot density plots of NO_3^{1-} concentration for each sampled lake by wilderness or other area. Areas are arranged from bottom to top by increasing median NO_3^{1-} value within the Western and Eastern mountain regions. Dashed vertical lines through the dot plots mark the hinges and median (center darker line) of the overall distribution. Box plot summaries of the east and west combined data are shown in reversible scale, axis at the top. Box plots are read as in Figure 2. Notice that the extreme outlier in the west marked by the asterisk farthest to the left corresponds to the Weminuche lake with the highest overall value plotted on the right side.

chemistry. The year this study was conducted had heavy snowfall and late snowmelt for many areas of Colorado.

Eastern versus Western lake difference in NO_3^{1-} concentrations has also been examined on a finer scale. Baron et al. (2000) reported significantly ($p = 0.02$) more nitrogen in lakes east of the Continental Divide compared to those in close proximity but west of the divide, in the geographically more restricted area of Rocky Mountain National Park and the contiguous Indian Peaks wilderness. They included 30 Eastern and 14 Western samples from 1995, 1997, and 1998, with one eastern lake, Dorothy, mis-assigned to the west and identified as a 1996 rather than a 1995 sample. Their data were adjusted for

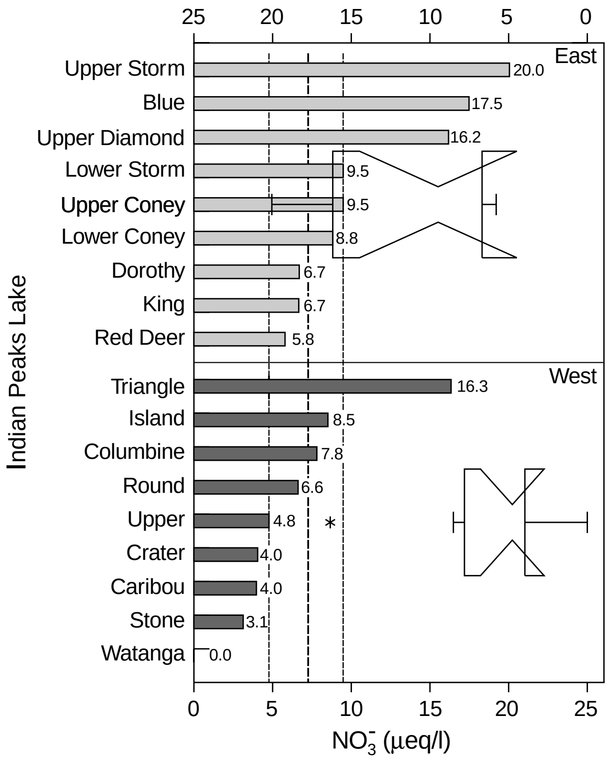


Figure 5. Bar plots of NO_3^{1-} concentration for each sampled lake in the Indian Peaks wilderness area arranged, bottom to top, by increasing NO_3^{1-} value first for lakes west then east of the Continental Divide. Dashed vertical lines through the dot plots mark the hinges and median (center darker line) of the overall distribution. Box plots, read as in Figure 2, summarize the lakes for each side of the Divide.

yearly and seasonal differences to The Loch, an east slope lake in Rocky Mountain National Park. They included one of the nine Eastern and eight of the nine Western slope Indian Peak lakes from Musselman et al. (1996) and reported here.

Our analysis shows NO_3^{1-} concentrations tend to be higher east of the Continental Divide using all the 1995 Indian Peaks data (Figure 5) with a Mann–Whitney test probability of no difference = 0.019. Judged by the arbitrary and conservative 0.01-level as explained above this is not significant. And judging from the overlapping notches in the reversed box plots in the figure the same conclusion follows. Baron et al. (2000) results are essentially equivalent ($p = 0.02$ [Baron et al. 2000] versus $p = 0.019$ reported here), despite the differences in the lake samples used, their dates, and their geographic coverage. Judgement on the critical threshold level deemed significant is an individual decision, but generalizations based on summary statistics should not discount importance of the range of variability within each grouping. Whether or not the tendency towards higher nitrates east of the Continental Divide is significant, and Wolfe et al. (2001) have other limnological evidence that it is, our attention focuses on the differences of individual lakes. For example, three of the Eastern lakes fall below the overall median value and Triangle lake in the west joins three other Eastern lakes in having the highest NO_3^{1-} concentrations. Indeed if Triangle lake is left out of the analysis the east west difference becomes significant at $\alpha = 0.01$ ($p = 0.005$). This shows that a single sample can dominate even a rank order analysis, further confirming that generalizations should be made with caution.

Seasonal change

The literature indicates that lake chemistry may change throughout the season after the snowmelt flush subsides (Bales et al. 1990). Nitrogen consumption by the biota in nitrogen limited lakes, especially, may cause nitrogen to decline during the season and downstream. However anthropogenic influx of inorganic nitrogen may exceed what the biota can use and be exported in surface waters. We report on the change in chemical composition of 56 of our sampled lakes that were measured twice in 1995. The median number of days between samples was 40, the range was 26–55 days.

Table 3. Early to late season change in water chemistry in lakes from the Eastern and Western Colorado mountains

	Western mountains			Eastern mountains		
Water chemistry measure[a]	Median increase (*n* Lakes)	Median decrease (*n* Lakes)	*p*-value[b]	Median increase (*n* Lakes)	Median decrease (*n* Lakes)	*p*-value[b]
pH	0.2 (15)	0.3 (7)	0.21	0.3 (27)	0.1 (7)	**0.00**
Conductivity	1.8 (16)	−0.9 (5)	0.04	1.1 (9)	−1.6 (25)	**0.01**
ANC	33.2 (11)	−9.6 (11)	0.41	8.9 (29)	−10.6 (5)	**0.00**
Ca^{2+}	15.0 (14)	−6.4 (8)	0.03	11.0 (29)	−5.4 (5)	**0.00**
Mg^{2+}	2.9 (16)	−2.1 (6)	0.02	2.9 (12)	−2.3 (22)	0.23
Na^{1+}	2.7 (14)	−0.6 (8)	0.08	3.0 (26)	−1.8 (8)	**0.00**
K^{1+}	0.6 (14)	−1.1 (8)	0.50	0.9 (12)	−0.9 (22)	0.06
NH_4^{1+}	0.0 (17)	−0.7 (5)	0.79	1.0 (22)	−0.6 (12)	0.02
NO_3^{1-}	3.1 (5)	−1.6 (17)	0.03	0.0 (9)	**−5.5 (25)**	**0.00**
Cl^{1-}	0.6 (11)	−0.8 (11)	0.72	1.1 (4)	−1.9 (30)	**0.00**
SO_4^{2-}	3.8 (17)	−1.9 (5)	**0.00**	2.0 (15)	−1.1 (19)	0.83

Median increase for lakes that increased in value or had no change and median decrease for lakes that decreased in value (along with the number of lakes that increased or decreased) are given. Changes significant at $\alpha = 0.01$ are in bold. Median changes biologically explainable are also in bold.

[a] Conductivity $\mu S\ cm^{-1}$; Ion concentrations $\mu eq\ l^{-1}$.

[b] Wilcoxon signed rank test. *p*-values displayed as 0.00 result from rounding, and are not equal to zero, for example, the eastern pH *p*-value, 0.0000152.

Table 4. Inlet to outlet change in water chemistry in lakes from the Front Range and Northern Front Range geographic areas

	Front Range			Northern Front Range Lakes		
Water Chemistry Measure[a]	Median increase (*n* Lakes)	Median decrease (*n* Lakes)	*p*-value[b]	Median increase (*n* Lakes)	Median decrease (*n* Lakes)	*p*-value[b]
PH	0.1 (14)	0.0 (7)	0.01	0.1 (11)	0.0 (3)	**0.01**
Conductivity	2.3 (12)	−1.0 (9)	0.15	0.8 (8)	−0.6 (6)	0.73
ANC	20.2 (12)	−8.6 (9)	0.09	11.5 (8)	−6.8 (6)	0.51
Ca^{2+}	21.9 (13)	−17.3 (8)	0.11	8.3 (6)	−5.2 (8)	0.98
Mg^{2+}	3.2 (14)	−1.5 (7)	0.20	2.1 (7)	−0.8 (7)	0.73
Na^{1+}	3.5 (14)	−2.7 (7)	0.07	1.1 (9)	−1.0 (5)	0.27
K^{1+}	0.8 (14)	−0.4 (7)	0.02	0.2 (2)	−0.3 (12)	**0.01**
NH_4^{1+}	0.3 (16)	−0.4 (5)	0.10	0.0 (9)	−0.1 (5)	0.72
NO_3^{-1}	1.1 (5)	**−2.8 (16)**	**0.01**	0.0 (6)	**−0.9 (8)**	**0.01**
Cl^{1-}	0.5 (16)	−0.3 (5)	0.02	0.0 (9)	−0.3 (5)	0.07
SO_4^{2-}	4.4 (17)	−0.7 (4)	**0.00**	0.4 (7)	−0.4 (7)	0.73

Median increase for lakes that increased in value or had no change and median decrease for lakes that decreased in value (along with the number of lakes that increased or decreased) are given. Changes significant at $\alpha = 0.01$ are in bold. Median changes biologically explainable are also in bold.

[a] Conductivity μS cm^{-1}; Ion concentrations meq l^{1-}.

[b] Wilcoxon signed rank test. *p*-values displayed as 0.00 result from rounding, and are not equal to zero, for example the eastern H^{1+} *p*-value, 0.0033138.

Lakes from the Eastern and Western mountain regions were analyzed separately for seasonal change by the Wilcoxon Signed Rank Test (Table 3). In general most of the differences occurred in the Eastern rather than the Western lakes. Western lakes showed a significant change only by an increase in SO_4^{2-} concentration, whereas Eastern lakes were significantly different for seven of the 11 variables (pH, Ca^{2+}, and Na^{1+} increase; conductivity, ANC, NO_3^{1-}, and Cl^{1-} decrease). Biological significance is another matter, for if the magnitude of the changes are either small or small compared to the range a variable typically takes, then biotic effects cannot be projected nor causes proposed. Comparing the median changes in Table 3 to the corresponding plots in Figures 2 and 3, reveals that this is the case for all but one of the statistically significant variables. For example a decrease in ANC of 10.6 μeq l^{-1} in the Eastern mountains represents a small segment of the greater than 200 μeq l^{-1} range seen for these lakes in the top of Figure 2c. The exception is the significant 5.5 μeq l^{-1} median drop in NO_3^{1-} concentration in the Eastern lakes, which represents a median percent change in concentration of −95.5%. The presumption is that this NO_3^{1-} is used by organisms. The variation in water chemistry seasonal changes, even where significant, tended to be smaller than the range of variation found geographically for the whole set of lakes. However, a few of these results are worth noting with respect to the condition of these particular lakes. Relatively stable ANC and pH values over the season showed them to be resilient to acidification, at least in 1995. And decrease of NO_3^{1-} demonstrates that the biota were managing to assimilate nitrogen.

Lake inlet to outlet changes

Results comparing inlets to outlets of 30 Front Range and Northern Front Range lakes lead to similar conclusions, *viz*, general differences in water chemistry are not perspicuous (Table 4). Wilcoxon Sign Rank Tests registered some differences between inlets and outlets for lakes in each of these geographic areas: a slight increase in pH for Northern Front Range lakes and a decrease in NO_3^{1-} concentration for both areas. Increase in pH of 0.1 units is small compared to the range 5.9–7.2 found in these lakes (Figure 2a). The only biologically relevant difference found was the decrease of NO_3^{1-}. The average change in the Northern Front Range was -68% compared to -26% in the Front Range, suggesting that proportionately less nitrogen is consumed and more exported from the Front Range area closest to urban sources of nitrogen deposition.

Inlet–outlet comparisons yield modest conclusions complementary to those reached in the early versus late season comparisons. The variation in water chemistry tends to be smaller than the range of variation found geographically for the whole set of lakes. Stability in ANC and pH indicates these lakes have no problem with acidity changes as water goes through them. Decrease in NO_3^{1-} shows that the biota manage to assimilate some amounts of nitrogen.

Fragile lakes

Because of interest in the vulnerability of wilderness area and other high elevation lakes to anthropogenic changes, we identify fragile lakes among those sampled, as those that are sensitive to such change. Since anthropogenic sources could lead to lake acidification and nitrogen saturation, we attend first to lake ANC and then nitrogen export.

Lakes with ANC values between 100 and 200 μeq l^{-1} are classified as susceptible to acidification and lakes with values below this are considered acid sensitive. Lakes with values ≤ 50 μeq l^{-1} are considered extremely acid sensitive (Schindler 1988; Baker et al. 1990). We use the general term 'fragile' for any lakes with ANC < 200 μeq l^{-1}. Table 5 lists 64 Eastern Mountain lakes and Table 6 lists 41 Western Mountain lakes in any of the three sensitivity categories by name and geographic region along with their ANC and pH values. These lakes represent 70% of the 150 lakes included in our sample and 22% of these (23 lakes) were extremely acid sensitive. The median pH of the lakes in these three categories is 6.5.

In general 93% of the Northern Front Range and 96% of the Front Range lakes sampled were acid vulnerable or fragile as gauged by ANC

Table 5. Eastern mountain lakes sensitive or susceptible to acidification arranged by ANC value and geographic location

Area	Lake	ANC[b]	pH
Northern Front Range (93%)[a]			
Medicine Bow (100%)	West Glacier	35	6.0
	Lost	54	6.6
	South Twin	139	6.7
	North Twin	154	8.0
Colorado State Forest (33%)	Kelly	187	6.6
Rawah (100%)	Iceberg	44	6.0
	Rawah 4	44	6.0
	Island	68	6.2
	Rawah 3	77	6.3
	Rawah 2	83	6.3
	Lower Twin Crater	94	6.4
	Carey	94	6.4
	Rawah 1	95	6.4
	Sugarbowl	97	6.5
	McIntyre	104	6.4
	Upper Twin Crater	104	6.3
	Hang	115	6.4
	Upper Twin	121	6.9
	Upper Camp	125	6.6
	Upper Sandbar	137	6.8
	Lost	137	6.4
	Lower Sandbar	140	6.5
	Lower Camp	158	6.6
	Blue (Rawah)	160	6.5
	Lower Twin	166	7.0
	Rocky Hole	171	7.2
Front Range (96%)			
Indian Peaks (95%)	No Name	27	6.1
	Blue	28	6.1
	Lake Dorothy	32	6.4
	Round	42	6.0
	King	43	6.2
	Upper Storm	44	6.6
	Crater	52	6.1
	Lower Storm	70	6.9
	Triangle	71	6.7
	Upper Coney	72	7.0
	Stone	74	6.4
	Red Deer	78	6.6
	Upper Diamond	82	7.0
	Upper	88	6.4
	Lower Coney	91	7.1
	Columbine	112	7.0
	Island	120	6.4
	Watanga	128	6.5
	Long	148	6.5

Table 5. Continued.

Area	Lake	ANC[b]	pH
Mount Evans (100%)	Upper Middle Beartrack	58	6.2
	South	66	6.2
	Frozen	94	6.3
	Summit	98	6.9
	Abyss	102	6.7
	North	113	6.3
	Chicago	151	7.1
Sangre de Cristo Mountains (27%)			
Sangre de Cristo (27%)	West Creek	66	6.2
	Mas Alto	66	6.3
	Upper Stout Creek	78	6.3
	Upper Bushnell	79	6.8
	Upper Little Sand Creek	110	6.5
	Crater	128	6.5
	Banjo	136	6.6
	Lower Sand Creek	149	6.6
	Lower Stout Creek	152	6.6
	Lower Little Sand Creek	153	6.6
	unknown	195	6.6
	Upper Sand Creek	195	7.0

[a] Percent of all lakes sampled in the area with ANC values in any of the sensitivity categories.
[b] Susceptible to Acidification 100 > ANC $\leq 200\ \mu eq l^{-1}$; Acid Sensitive 50 > ANC $< 100\ \mu eq l^{-1}$; Extremely Acid Sensitive ANC $\leq 50\ \mu eq l^{-1}$.

$\leq 200\ \mu eq\ l^{-1}$. The Sangre de Cristo range had the lowest occurrence, 27%, of such lakes in any region east or west (Table 5). Western Mountain regions ranged from 73 to 100% fragile lakes. The Weminuche wilderness area had the lowest at 67%, however nine of its lakes fell in the extremely sensitive category (Table 6). Thus both Eastern and Western mountain wilderness areas were susceptible to acidification. These results stand in striking contrast to results from 1985, where (based on the same criterion of ANC values $\leq 200\ \mu eq\ l^{-1}$) only 44% of Front Range lakes were found to be susceptible to acidification (Eilers et al. 1987 and Landers et al. 1987). The Front Range and San Juan Mountains had more lakes with low ANC than other regions of Colorado Landers et al. 1987). Eilers et al. (1987) sampling did not focus only on high elevation lakes as in this study. Note that eight of the 17 wilderness or other areas studied here had 100% of their sampled lakes with ANC values $\leq 200\ \mu eq\ l^{-1}$ (Table 3).

Nitrogen export from high elevation wilderness lakes is also a concern. Of 150 lakes (either sampled once or the early season instance of those twice sampled) 121 (81%) exported NO_3^{1-} and of the remaining 29 lakes, 23 exported NH_4^{1+}. Only 14 (9%) lakes exported no (detectible) nitrogen in these forms. Exported nitrogen values however were material: for lakes exporting NO_3^{1-} the median value was 6.5 and the maximum value was 39.9 $\mu eq\ l^{-1}$; for NH_4^{1+} these values were 1.2 and 8.6. Further, slightly more nitrogen is

Table 6. Western mountain lakes sensitive or susceptible to acidification arranged by ANC value and geographic location

Area	Lake	ANC[b]	pH
Northern Colorado Mountains (100%)[a]			
Mount Zirkel (100%)	Seven Lakes (largest)	38	6.1
	Lake Elbert	56	6.2
	Summit	61	6.7
	Long Lake Reservoir	95	6.2
Flat Tops (100%)	Upper Ned Wilson	16	6.3
	Lower NWL Packtrail	43	6.7
	Upper NWL Packtrail	59	6.6
	Ned Wilson	61	6.6
Central Colorado Mountains (76%)			
Eagles Nest (75%)	Booth	145	6.5
	Willow	155	6.5
	Lost Eagles Nest	166	6.7
Holy Cross (70%)	Blodgett	62	6.7
	Upper Savage	64	6.0
	Missouri	111	6.4
	Upper Tuhare	112	6.4
	Upper West Tennessee	119	6.6
	Lower West Tennessee	124	6.6
	Slide	147	6.7
Maroon Bells-Snowmass (100%)	Moon	59	6.1
	Capitol	140	6.4
	Avalanche	194	6.5
Collegiate Peaks (100%)	Brooklyn	100	6.4
	Tabor	109	6.4
Raggeds (100%)	Deep Creek	48	6.0
West Elk (100%)	South Golden	121	6.6
San Juan Mountains (73%)			
La Garita (100%)	unnamed	54	6.3
	U-Shaped	75	6.3
Weminuche (67%)	West Snowdon	2	5.2
	Little Eldorado	3	5.9
	White Dome	6	6.1
	Upper Grizzly	24	5.2
	unnamed	27	6.1
	South of Ute	31	5.9
	Upper Sunlight	33	6.6
	Big Eldorado	33	6.7
	Middle Ute	44	6.1
	Lower Sunlight	63	7.0
	Little Granite	93	6.4
	Lake Phil	117	6.6
South San Juan (100%)	unnamed	27	6.0
	Glacier	80	6.7

[a] Percent of all lakes sampled in the area with ANC values in any of the sensitivity categories.
[b] Susceptible to Acidification $100 > \text{ANC} \leq 200\ \mu\text{eq l}^{-1}$; Acid sensitive $50 > \text{ANC} < 100\ \mu\text{eql}^{-1}$; Extremely acid sensitive $\text{ANC} \leq 50\ \mu\text{eql}^{-1}$.

exported from proportionately more lakes early in the season than later. In the early season samples 91% of the lakes exported NO_3^{1-}, with a median value of 8.2. In the late season 61% of the lakes exported NO_3^{1-} with a median of value of 1.1. All of the early and late season lakes exported NH_4^{1+}, but with small medians of 0.9 and 0.2 μeq l^{-1}.

A high percentage of sampled high elevation lakes exporting nitrogen indicates that many of these high elevation catchments are nitrogen saturated. The percentage is high in the early season indicating that the initial snowmelt chemical pulse continues through these lakes downstream. Some lakes are nitrogen saturated late in the season, demonstrating that nitrogen export can extend through the growing season.

Summary and conclusions

Regional differences. The Sangre de Cristo lakes were generally different from all the others, having higher pH, conductivity, ANC, and sum of acid and sum of base concentrations. In contrast the Northern Colorado lakes tended to be more dilute than all the others with conductivity and ANC lower than at least some of the other regions.

Regional similarities. Not withstanding the above mentioned differences, the major conclusion regarding the water chemistry of these high elevation, Colorado and southern Wyoming lakes is a pattern of broad overlap. Values over a wide range can be found in different lakes in any of the geographic regions for the chemistry variables measured.

East–west differences. East versus west differences in NO_3^{1-} concentration were examined regionally and more locally. Conservatively no significant ($p = 0.01$) difference was found at either scale. Lakes with low (or high) NO_3^{1-} concentration can be found in wilderness areas from both eastern and western mountainous Colorado; and low (or high) values can be found in lakes on either side of the Continental Divide in the Indian Peaks wilderness area.

Seasonal differences. In general, seasonal variability was smaller than the variability between regions and seasonal change was greater in Eastern over Western lakes. The only biologically significant difference detected was a decrease of NO_3^{1-} concentration through the season in the Eastern mountain lakes, perhaps suggesting Eastern lakes better handle nitrogen loading. Still a large number of the lakes had detectible levels of NO_3^{1-} in surface waters during the time of year when NO_3^{1-} should be maximally used by the ecosystem, suggesting nitrogen saturation and limitation by other nutrients for these high elevation ecosystems.

Inlet versus outlet differences. In general variability here was smaller than that between regions. The only biologically relevant difference found was a material drop in NO_3^{1-} concentration between the inlet and outlet for most lakes. This was expected and indicates biological consumption of nitrogen as water travels through these lakes. The decrease was greater in lakes from the Northern Front Range than in the Front Range.

Fragile lakes. Seventy percent of the lakes examined had low ANC (<200 μeq l^{-1}) indicating susceptibility to acidification. 96% of the lakes in the Colorado Front Range and 93% in the Northern Front Range were sensitive to acidification. More than 15% of the lakes can be classified as extremely sensitive to acidification (ANC <50 μeq l^{-1}). Even though the Sangre de Cristo had most lakes with a high ANC, one quarter of the lakes here can also be classified as sensitive to acidification. Nitrogen export was detected in 136 of 150 (91%) of the sampled lakes indicating that most of these high elevation lakes catchments are nitrogen saturated.

The results of this study are consistent with earlier site specific results indicating that high elevation Rocky Mountain surface waters have low ANC (Lewis 1982; Caine 1995), suggesting that they are susceptible to acidification. The data also confirm earlier findings (Baron et al. 1994, Williams et al. 1996a, b) that nitrogen is exported from high elevation Front Range ecosystems during the season when export should be minimal. Results presented here extend the findings of these earlier single catchment studies regarding low ANC and nitrogen export to most high elevation lakes in Colorado, as suggested by Baron et al. (2000) and Williams and Tonnessen (2000) for the Colorado Front Range.

Urbanization and deposition are increasing throughout Colorado. We have documented that these aquatic ecosystems are sensitive. Most are presumably still pristine. Periodic monitoring of selected aquatic ecosystems in this area is continuing to detect possible changes in surface water chemistry as urbanization and deposition increase. Similar ecosystems in other mountainous areas near urban corridors should also be monitored for sensitivity to atmospheric deposition.

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