

Changes in the chemistry of lakes and precipitation in high-elevation national parks in the western United States, 1985–1999

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[1] High-elevation lakes in the western United States are sensitive to atmospheric deposition of sulfur and nitrogen due to fast hydrologic flushing rates, short growing seasons, an abundance of exposed bedrock, and a lack of well-developed soils. This sensitivity is reflected in the dilute chemistry of the lakes, which was documented in the U.S. Environmental Protection Agency's Western Lake Survey of 1985. Sixty-nine lakes in seven national parks sampled during the 1985 survey were resampled during fall 1999 to investigate possible decadal-scale changes in lake chemistry. In most lakes, SO₄ concentrations were slightly lower in 1999 than in 1985, consistent with a regional decrease in precipitation SO₄ concentrations and in SO₂ emissions in the western United States. Nitrate concentrations also tended to be slightly lower in 1999 than in 1985, in contrast with generally stable or increasing inorganic N deposition in the west. Differences in alkalinity were variable among parks but were relatively consistent within each park. Possible effects of annual and seasonal-scale variations in precipitation amount on lake chemistry were evaluated based on climate data available for the parks and an analysis of climatic effects at two research watersheds with long-term records. Results suggest that rain prior to sampling in 1985 may have caused elevated NO₃ in some lakes due to direct runoff of precipitation and flushing of NO₃ from alpine soils, which may explain some of the decrease in NO₃ concentrations observed in survey lakes. *INDEX TERMS:* 1803

Hydrology: Anthropogenic effects; 1806 Hydrology: Chemistry of fresh water; 1845 Hydrology: Limnology; 1854 Hydrology: Precipitation (3354); 1871 Hydrology: Surface water quality; *KEYWORDS:* lake chemistry, atmospheric deposition, emissions, monitoring, alpine, talus

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1. Introduction

[2] In the 1970s, deposition of sulfuric acid was widely recognized as an important stressor of sensitive aquatic ecosystems [Likens *et al.*, 1977; Galloway *et al.*, 1983]. Since then, effects of nitrogen deposition on aquatic and terrestrial ecosystems have become better understood [Stoddard, 1994; Williams *et al.*, 1996; Campbell *et al.*, 2000]. Although sulfate deposition declined during the late 1970s and early 1980s at many sites in the western United States, deposition of nitrogen has remained level or increased [Lynch *et al.*, 1996; Nilles and Conley, 2001].

[3] During fall 1985, the U.S. Environmental Protection Agency (USEPA) conducted the Western Lake Survey, a synoptic sampling of 719 lakes in the western United States.

The goal of the Western Lake Survey and the companion Eastern Lake Survey, which occurred during the fall of 1984, was to document the chemical status of lakes in regions of the United States considered sensitive to acidic deposition. In the west, those regions generally coincide with mountainous areas having slow weathering bedrock, poorly developed soils, and snowmelt-driven hydrology. These geochemical and hydrologic characteristics limit the capacity of mountain ecosystems to buffer acidity or absorb nutrients in atmospheric deposition.

[4] The Western Lake Survey (WLS) was the first regional sampling of high-elevation lake chemistry in the western United States. It was intended to provide an index, or “snapshot,” of lake chemistry and establish a basis for future comparisons. An important finding of the WLS was the dilute nature of many western mountain lakes. For the target population of lakes, the median specific conductance (SC) was 16.5 $\mu\text{S cm}^{-1}$, and the median alkalinity was 119 $\mu\text{eq L}^{-1}$ [Landers *et al.*, 1987]. Lakes in federally designated wilderness areas were found to be particularly dilute, having a median alkalinity of 91 $\mu\text{eq L}^{-1}$ compared with a median alkalinity of 283 $\mu\text{eq L}^{-1}$ for nonwilderness lakes. The dilute, low-alkalinity nature of wilderness lakes makes them particularly sensitive to stressors, such as

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atmospheric deposition of pollutants and variations in climate.

[5] The Federal Clean Air Act (CAA) amendment of 1977 designated many Forest Service and National Park Service wilderness areas in the western United States as Class 1 areas. Federal land managers are required by the CAA to protect “air quality related values,” such as visibility, water quality, and biota, in Class 1 areas from degradation due to atmospheric deposition of pollutants. The CAA amendment of 1977 also established a permitting process for new sources of pollutants near Class 1 areas, which federal land managers are required to participate in. The need for water-quality monitoring in Class 1 areas has been recognized by federal land managers as a prerequisite for protecting aquatic ecosystems. However, lack of resources has prevented establishment of long-term water-quality monitoring for most Class 1 areas.

[6] In 1998, the National Park Service (NPS) and the U.S. Geological Survey (USGS) established a partnership, with the goal of addressing unresolved water-quality issues in national parks. This partnership provided a mechanism for conducting a resurvey of a subset of the WLS lakes in seven high-elevation national parks in the western United States, including Glacier, Yellowstone, Grand Teton, Rocky Mountain, Lassen Volcanic, Yosemite, and Sequoia/Kings Canyon. All of the lakes included in the resurvey were in remote areas far from roads and buildings, where point sources of pollution were unlikely. The objective of the study was to compare lake chemistry measured in the two surveys and evaluate possible reasons for any differences, including changes in atmospheric deposition and variations in climate. The approach taken in the new survey was similar to that of the WLS: collect a single sample at a suite of lakes during fall when most of the lakes are well mixed and chemistry is relatively stable. Although the approach is not as robust as a well-designed, long-term lake chemistry monitoring network, when combined with information from intensively monitored research watersheds and long-term climate and precipitation chemistry networks, lake survey data can provide important insights into patterns of change in lake chemistry. Sixty-nine of the 70 lakes sampled during the WLS in the parks listed above were resampled during the new survey, which was performed during late September and early October of 1999. A summary of lake chemistry measured during the 1999 survey, and the relation of regional patterns in lake chemistry to regional patterns in atmospheric deposition and bedrock geology was presented by Clow *et al.* [2002].

[7] This article presents a comparison of lake chemistry measured in the WLS and in the 1999 USGS/NPS lake survey. Changes in lake chemistry are compared to trends in precipitation chemistry and emissions during 1985–1999 to determine if the direction and magnitude of changes are consistent. Like changes in emissions, variations in climate (particularly precipitation amount) have the potential to alter lake chemistry, potentially confounding comparisons of survey results. Temporal patterns in annual precipitation, atmospheric deposition chemistry, and lake chemistry from two lakes with long-term records are compared to evaluate the coherence of signals and identify possible effects of variations in annual precipitation amount on lake chemistry.

Information from this analysis is combined with data on annual precipitation at the study parks during 1985 and 1999 to infer likely effects of differences in annual precipitation on survey lake chemistry. Storms prior to sampling also have the potential to affect lake chemistry. Possible effects of differences in rainfall prior to sampling were evaluated by (1) comparing daily precipitation during fall 1985 and fall 1999, and (2) inferring likely hydrochemical responses of survey lakes based on an analysis of changes in surface-water chemistry during rainstorms at a research watershed in Rocky Mountain National Park.

2. Methods

[8] During the Western Lake Survey, most samples were collected from the epilimnion at the deepest part of the lake using a pontoon-equipped helicopter. In the present study, lake access typically was by foot, without watercraft. Water samples were collected from the outlets of lakes using a peristaltic pump with a 0.45 μm polysulfone filter attached to the outlet end of the pump tubing. It was hypothesized that outflow chemistry would not be significantly different from epilimnion chemistry because most of the lakes sampled are small, shallow, and frequently mixed by wind and/or streamflow. To test for possible sample location bias, outflow and epilimnion samples (midlake, using a small raft) were collected at 14 randomly selected lakes. Paired *t*-tests indicated no significant differences in temperature or chemistry between outflow and epilimnion samples at $p \leq 0.05$, and median differences were $\leq 1 \mu\text{mol L}^{-1}$ for all solutes.

[9] All sampling equipment was cleaned and rinsed using 18 megaohm deionized (DI) water prior to use. Sample bottles were triple rinsed with filtered sample water before filling. Analytical methods were similar to those used in the WLS [Kerfoot and Faber, 1987] and are described by Clow *et al.* [2002]. Samples were analyzed for alkalinity, pH, specific conductance (SC), calcium (Ca), magnesium (Mg), silica (SiO_2), sodium (Na), potassium (K), ammonium (NH_4), sulfate (SO_4), nitrate (NO_3), chloride (Cl), dissolved organic carbon (DOC), and total phosphorus (TP). Data for SC, SiO_2 , Cl, and DOC are not presented in this paper, but are available at <http://co.water.usgs.gov/projects/CO335/CO335.html>. Quality assurance procedures included collection and analyses of field blanks and field splits, each of which comprised 10% of the total sample load. Solute concentrations in all of the field blanks were less than the detection limit for all constituents ($\leq 1 \mu\text{mol L}^{-1}$). Median differences of field splits were $\leq 1 \mu\text{mol L}^{-1}$, except for alkalinity and Ca, which had median differences $\leq 2 \mu\text{mol L}^{-1}$. Analytical results were checked by comparing measured and predicted specific conductance, and by ionic charge balance, i.e., the difference between total cation and total anion concentrations.

[10] Accuracy of analyses was evaluated based on results of repeated measurements of USGS standard reference samples and certified high-purity standards traceable to the National Institute of Standards, and by participation in blind-audit performance tests conducted by the USGS [Ludtke and Woodworth, 1997] and by Environment Canada [Blum and Alkema, 2000]. Accuracy of analyses was better than $1 \mu\text{mol L}^{-1}$ or 1.5% for all constituents. Quality

assurance tests during the WLS indicated analytical measurements were of similar quality [Silverstein *et al.*, 1987]. Analytical accuracy and precision estimates were used to estimate possible laboratory bias between the two lake surveys with 95% confidence intervals. Estimated bias between laboratories was less than $1 \mu\text{mol L}^{-1}$ or 1.5% for all constituents. The bias estimates were compared to the distribution of measured differences in lake chemistry, and the percent of differences in lake chemistry that might be due to analytical error was calculated. This allowed separation of “real” differences from those that might be due to analytical artifacts.

[11] Differences in lake chemistry between the 1985 and 1999 lake surveys were evaluated using the Wilcoxon signed rank test, which is a nonparametric test that analyzes for differences between matched pairs of data. Trends in the chemistry of precipitation at National Atmospheric Deposition Program (NADP) sites in the western United States were evaluated using the Seasonal Kendall test (SKT), which is a nonparametric test that is well suited for analyzing temporal trends in seasonally varying water quality data [Hirsch *et al.*, 1982]. The SKT analyzes trends separately for each season and sums the results. The SKT can be applied to concentrations as well as volume- or flow-adjusted concentrations, allowing one to filter out variations in chemistry that are due to variations in precipitation volume or discharge. In the present study, the SKT was applied to monthly average precipitation concentrations and to volume-adjusted monthly average precipitation concentrations. The SKT also was applied to long-term water-quality data from the outlets of two lakes, the Loch in Rocky Mountain National Park, and Emerald Lake in the Sequoia/Kings Canyon National Park, that were monitored for chemistry and discharge from 1984 to 1999 (discharge and water-quality monitoring methods are given by Melack *et al.* [1998] and Baron [1992a]). Data were binned into eight seasonal periods for the lake chemistry trend analyses, ranging in length from 30 days during snowmelt to 90 days during winter.

3. Results and Discussion

3.1. Differences in Lake Chemistry, 1985–1999

[12] Geographic patterns in solute concentrations during the 1999 lake survey were similar to those during the 1985 lake survey [Melack and Stoddard, 1991; Turk and Spahr, 1991; Clow *et al.*, 2002]. In both surveys, concentrations of SO_4 and NO_3 in the lakes exhibited regional geographic patterns that were similar to those of SO_4 and NO_3 in precipitation, with higher concentrations in the Rocky Mountains than in the Sierra/south Cascades parks [Clow *et al.*, 2002]. The highest alkalinity values occurred in Glacier National Park, where carbonate bedrock is prevalent, and in Yellowstone National Park, where hydrothermal activity affects lake chemistry [Clow *et al.*, 2002]. Fern Lake, in Yellowstone, was the only acidic lake in 1999 (alkalinity = $-38.8 \mu\text{eq L}^{-1}$, pH = 4.3), as was the case in the 1985 survey. The parks with lowest median alkalinity values were Yosemite and Lassen Volcanic National Parks, which are underlain by resistant granitic and volcanic rocks. Geographic patterns in base cation concentrations followed those of alkalinity, as expected,

because they are derived from similar sources (primarily mineral weathering).

[13] At most of the survey lakes, SO_4 concentrations were lower in 1999 than in 1985 (Figure 1). The magnitude of declines generally was small, with median changes for each park ranging from -1.3 to $-1.7 \mu\text{eq L}^{-1}$ (Yellowstone and Grand Teton excluded). Lakes in Yellowstone had the largest absolute changes in concentrations of SO_4 and most other constituents, reflecting the high solute concentrations in most lakes sampled there; however, in percentage terms the changes in the Yellowstone lakes were small. Only one lake was sampled at Grand Teton National Park in the WLS and in the 1999 survey, so statistics cannot be calculated. Although median differences in SO_4 concentrations for individual parks were small, 74% of the differences were greater than could be explained by analytical error. Decreases in lake SO_4 were statistically significant at four of the parks, including Glacier, Lassen Volcanic, Yosemite, and Sequoia/Kings Canyon (Figure 1).

[14] Data from long-term monitoring sites in the Sierra Nevada and in the southern Rocky Mountains support these regional patterns of change in lake SO_4 . Trend analyses indicated a strong decline in SO_4 ($p < 0.001$; Figure 2) and weaker decline in flow-adjusted SO_4 ($p = 0.04$) during 1985–1999 at Emerald Lake in Sequoia/Kings Canyon National Park. There was a downward trend in SO_4 over the same period at the Loch in Rocky Mountain National Park ($p = 0.007$; Figure 2), and a strong upward trend in flow-adjusted SO_4 ($p = 0.001$). The differences in trends in SO_4 and flow-adjusted SO_4 probably are due to the diluting effect of increased precipitation during the mid-1990s relative to the late 1980s, as discussed in more detail in a later section.

[15] At most of the survey lakes, NO_3 concentrations were lower in 1999 than in 1985, except at Yellowstone and Grand Teton National parks (Figure 1). As for SO_4 , the changes tended to be small; median changes in NO_3 ranged from -0.1 to $-1.2 \mu\text{eq L}^{-1}$ (Yellowstone and Grand Teton excluded). Nonetheless, 77% of the differences in lake NO_3 concentrations were larger than could be explained by analytical error. Declines in lake NO_3 were statistically significant at Lassen Volcanic and Yosemite National Parks. Long-term monitoring data indicated no trends in NO_3 or flow-adjusted NO_3 concentrations at Emerald Lake during 1985–1999, but inclusion of data back to fall 1983 yielded a downward trend in NO_3 ($p = 0.02$; Figure 2) [Sickman *et al.*, 2003]. At the Loch, there was no trend in NO_3 (Figure 2) and an upward trend in flow-adjusted NO_3 during 1985–1999 ($p = 0.04$).

[16] There were no significant differences in NH_4 concentrations (not shown) in the survey lakes at any of the parks between 1985 and 1999, but concentrations generally were near or below the analytical reporting limit during both surveys.

[17] Total phosphorus (TP) concentrations tended to be higher in 1999 than in 1985, and the changes were significant at all of the parks except Yellowstone and Grand Teton (Figure 1). Sickman [2001] reported a strong increasing trend in TP at Emerald Lake during 1985–1999. Increases in TP in high-elevation lakes in the Sierra Nevada might be due to increasing atmospheric deposition of aeolian P, as suggested by increasing trends in particulate emissions in

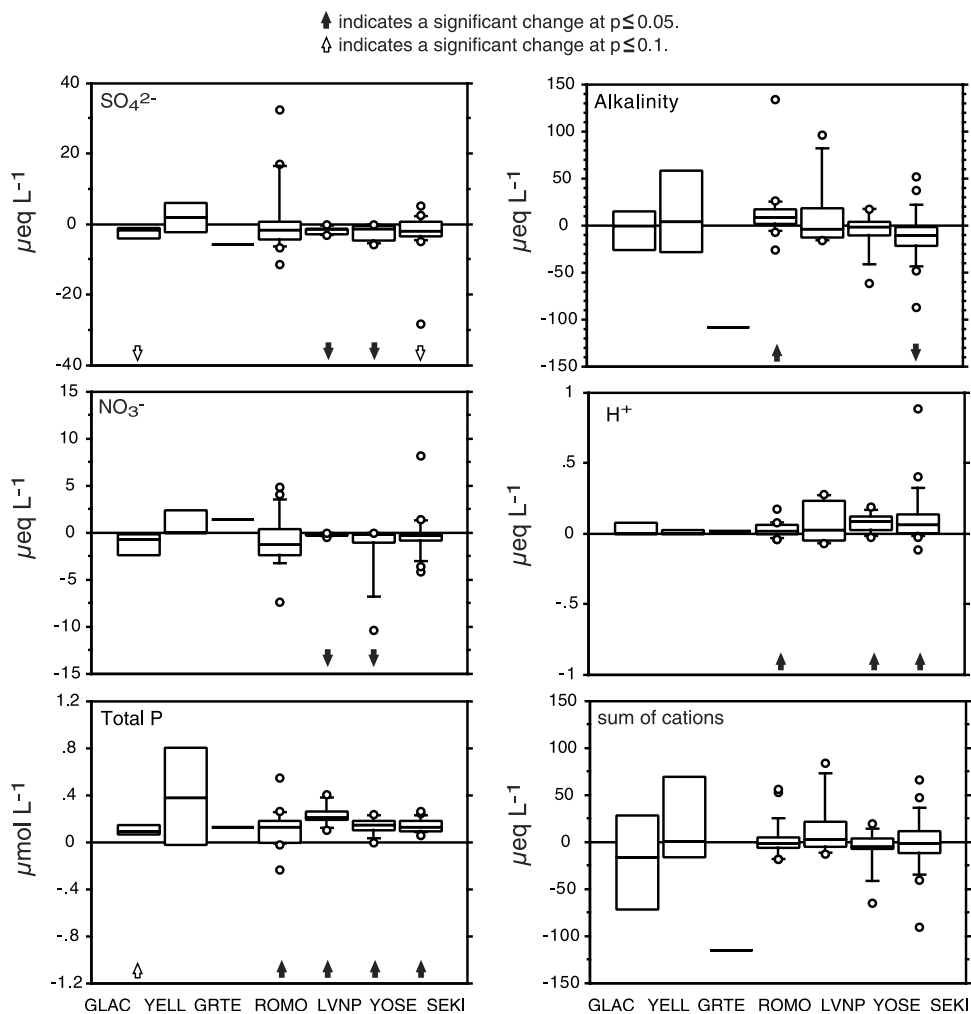


Figure 1. Box plots showing distribution of differences in concentrations measured in the 1985 and 1999 lake surveys. Abbreviations are GLAC, Glacier National Park ($n = 4$); YELL, Yellowstone ($n = 4$); GRTE, Grand Teton ($n = 1$); ROMO, Rocky Mountain ($n = 22$); LVNP, Lassen Volcanic ($n = 7$); YOSE, Yosemite ($n = 9$); SEKI, Sequoia/Kings Canyon ($n = 20$).

California's Central Valley [*California Air Resources Board (CARB), 2001*], which is adjacent to and upwind of the Sierra. Increased P deposition has decreased the incidence of P-limitation of phytoplankton in Emerald Lake and might be partly responsible for declines in summer and autumn NO_3^- levels observed during the late 1980s and early 1990s [*Sickman, 2001*].

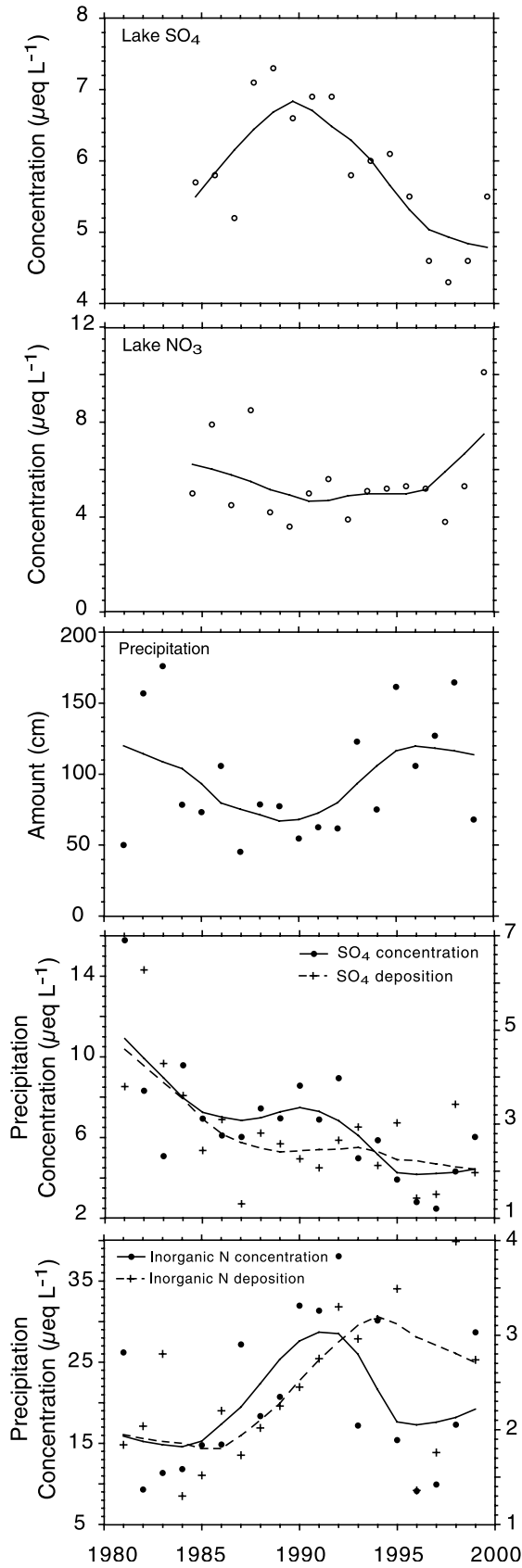
[18] Differences in alkalinity between the two surveys were variable among the parks, but were relatively consistent within each park (Figure 1). Alkalinity showed a statistically significant increase in Rocky Mountain National Park (median change = $8.7 \mu\text{eq L}^{-1}$), and a statistically significant decrease at Sequoia/Kings Canyon National Park (median change = $-9.9 \mu\text{eq L}^{-1}$). The increase in alkalinity at Rocky Mountain National Park reflects a change in the

balance of strong acid-anion:base-cation concentrations; strong acid anions decreased while base cation concentrations did not change substantially. The decline in alkalinity at Sequoia/Kings Canyon National Park reflects a general decrease in solute concentrations and specific conductance (Figure 1), which might be attributable to climatic variability or other influences.

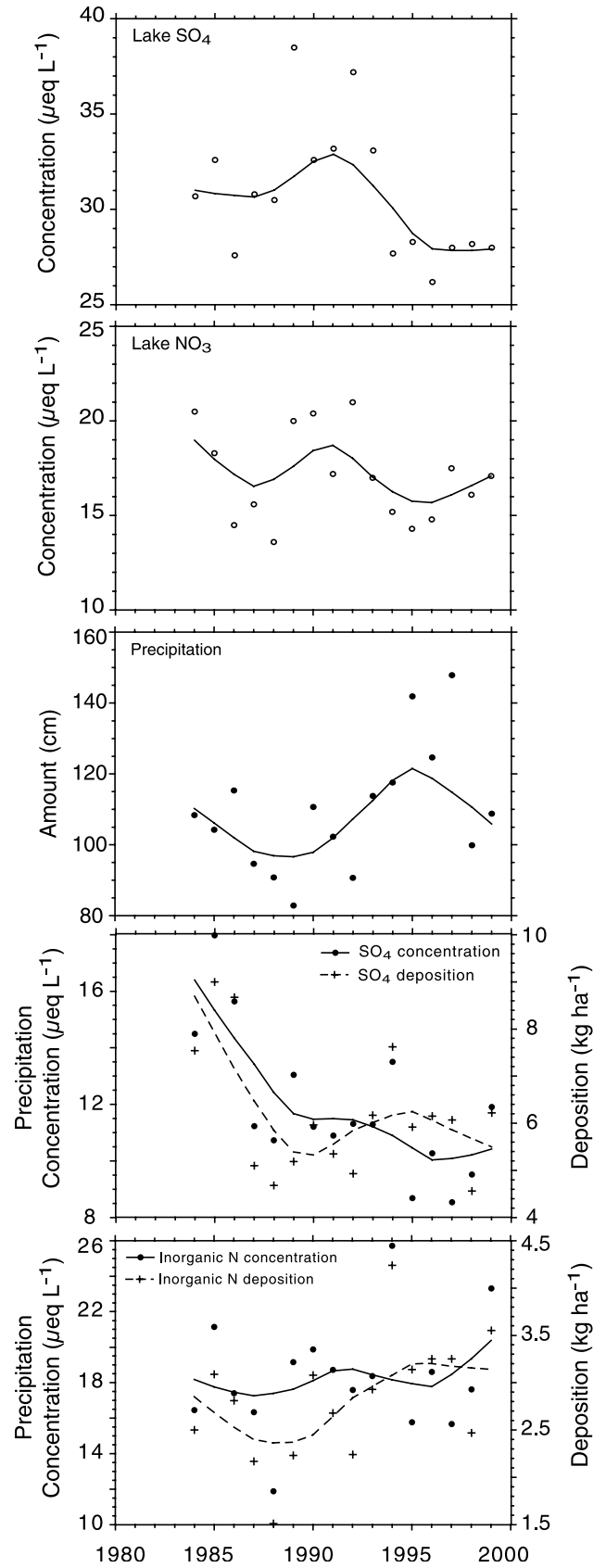
[19] Changes in pH were predominantly downward, but generally were less than 0.15 pH units. Tests for differences in H^+ concentrations indicated significant increases at Rocky Mountain, Yosemite, and Sequoia/Kings Canyon National Parks (Figure 1). However, many of the observed differences were not substantially larger than the analytical uncertainty of the pH measurements. Independent checks on the accuracy of pH and alkalinity measurements were

Figure 2. (opposite) Annual volume weighted mean (AVWM) concentrations of SO_4 and NO_3^- at the outlets of Emerald Lake and the Loch, and of annual precipitation, AVWM SO_4 , and inorganic N at nearest National Atmospheric Deposition Program (NADP) stations (CA75 and CO98). Locally weighted scatterplot smooth (LOWESS) lines are shown. Data for Emerald Lake were provided by J. Melack, University of California. Data for the Loch outlet were provided by J. Baron, U.S. Geological Survey/BRD. Plot of NO_3^- is after *Sickman et al. [2003]*.

Emerald Lake



The Loch



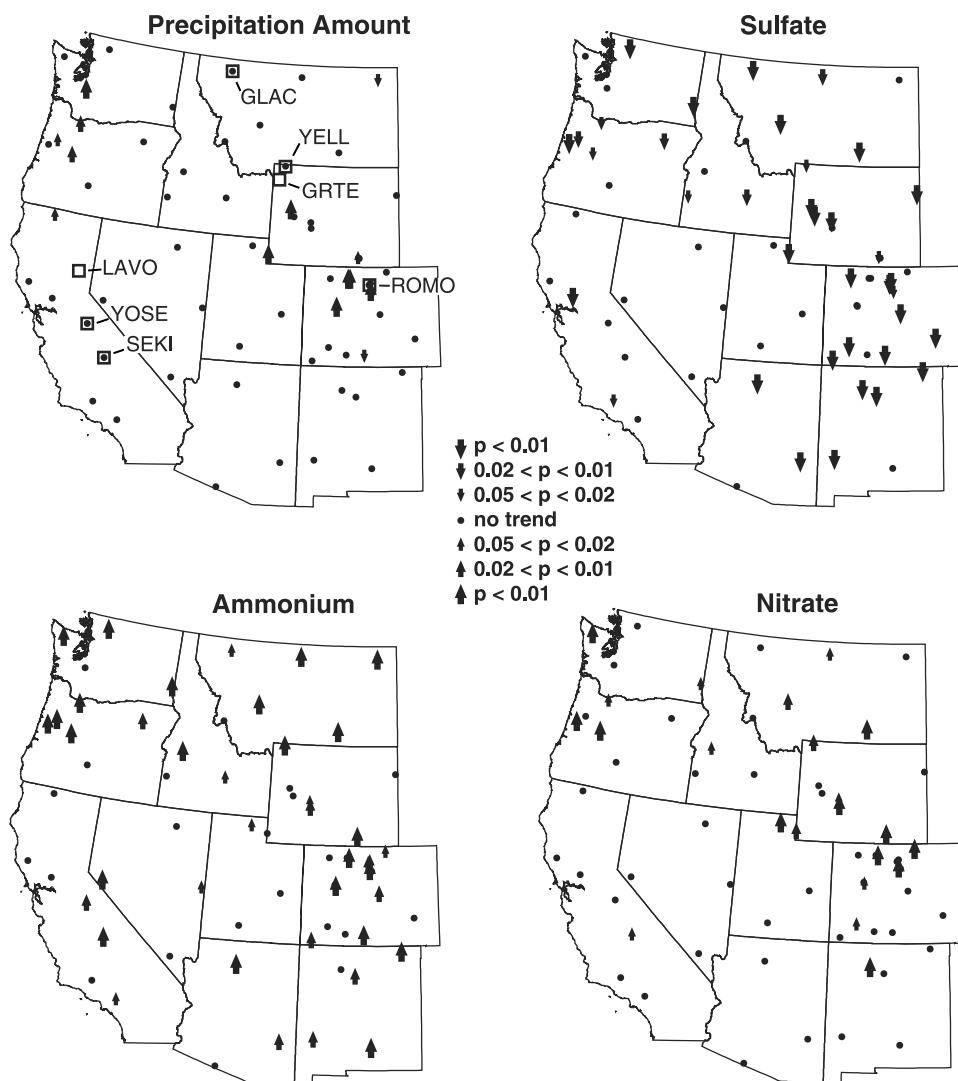


Figure 3. Trends in monthly volume weighted concentrations in precipitation, adjusted for precipitation amount, 1985–1999. Data were obtained from NADP [2000]. Parks are indicated on map as follows: LAVO, Lassen Volcanic; YOSE, Yosemite; SEKI, Sequoia/Kings Canyon; GLAC, Glacier; YELL, Yellowstone; GRTE, Grand Teton; and ROMO, Rocky Mountain.

not conducted during the 1985 survey, so it was not possible to evaluate whether analytical error might have been responsible for the observed differences in pH and alkalinity.

[20] There was little detectable change in base cation concentrations at most parks between 1985 and 1999 (Figure 1). Most of the differences in lake concentrations were smaller than the analytical uncertainty of laboratory measurements. The only statistically significant change for individual base cations was a downward trend in K at Rocky Mountain National Park (not shown).

3.2. Trends in Precipitation Chemistry, 1985–1999

[21] Differences in solute concentrations in the survey lakes in 1985 and 1999 could be caused by a variety of factors, including changes in atmospheric deposition of solutes and differences in precipitation prior to sampling. In the next three sections, trends in precipitation chemistry and differences in antecedent precipitation are examined and compared to changes in lake chemistry. The primary

focus is on sulfate and inorganic N ($\text{NH}_4 + \text{NO}_3$) because they are the most important acidifying compounds in atmospheric deposition [*National Acid Precipitation Assessment Program (NAPAP)*, 1998].

3.2.1. Sulfur

[22] During 1985–1999, monthly volume weighted mean (MVWM) SO_4 concentrations in precipitation declined at 81% of NADP sites in the western United States (51 of 63 sites); other sites in the west showed no trend. Increasing precipitation amount was at least partly responsible for some of the declines in SO_4 concentration, which tends to decline as precipitation amount increases. After accounting for variations in SO_4 due to changes in precipitation (12 increasing, 2 decreasing), 59% of western sites had declining SO_4 , mostly in the Pacific Northwest, Rocky Mountains, and desert southwest (Figure 3).

[23] Five of the parks in this study had NADP sites operating during 1985–1999, including Glacier, Yellowstone, Rocky Mountain, Yosemite, and Sequoia/Kings Canyon. MVWM SO_4 concentrations declined during

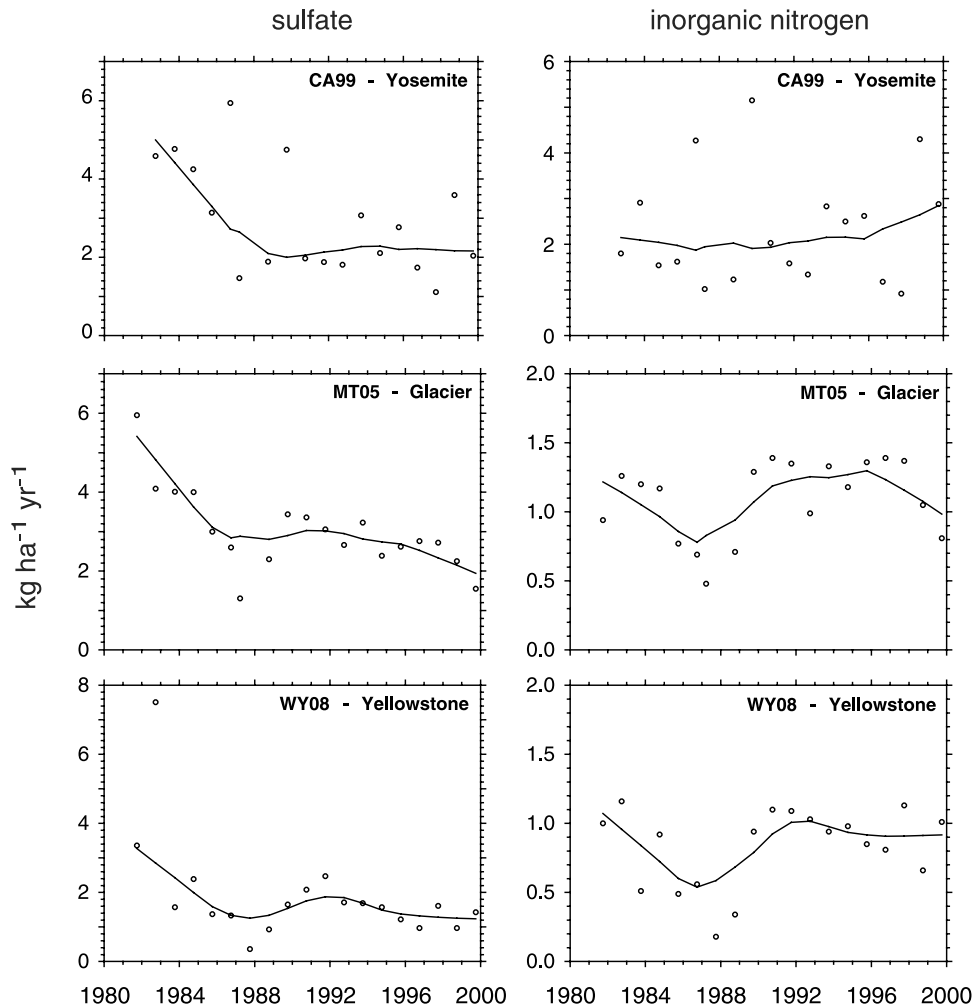


Figure 4. Annual deposition of sulfate and inorganic nitrogen at NADP sites in Yosemite, Glacier, and Yellowstone National Parks. LOWESS regression lines are shown. Data from *NADP* [2000].

1985–1999 at each of the parks, but precipitation-adjusted SO_4 concentrations declined only at the parks in the Rocky Mountains.

[24] Time series plots of annual volume weighted mean (AVWM) SO_4 concentrations at the NADP sites nearest to Emerald Lake (CA75) and to the Loch (CO98) indicate long-term declines, with subdecadal fluctuations that appear to be related to variations in precipitation amount (Figure 2). Annual wet deposition of SO_4 , which is the product of concentration and precipitation amount, is an important parameter in ecosystem studies because it defines the total annual loading of SO_4 in precipitation to an ecosystem. Annual SO_4 deposition at CA75 and CO98 declined during the early to mid-1980s and was relatively constant through the 1990s (Figure 2). Similar temporal patterns in SO_4 deposition occurred during 1985–1999 at the other parks in this study (Figure 4).

[25] The widespread declines in SO_4 concentrations in precipitation are consistent with changes in SO_2 emissions between 1985 and 1999 in the western United States. In general, SO_2 emissions have decreased in the western United States and nationally since 1985, although much of the decline in the west can be traced to emissions reductions in California during the early 1980s (Figure 5)

[CARB, 2001; USEPA, 2001]. USEPA data on emissions from utilities indicate that other western states have had relatively constant or increasing SO_2 emissions since 1985 [USEPA, 2001] (Figure 5).

3.2.2. Inorganic N

[26] NH_4 and NO_3 concentrations in precipitation were steady or increased at most NADP sites in the western United States during 1985–1999. NH_4 concentrations increased at 46% of sites and NO_3 concentrations increased at 19% of sites; one site had a downward trend in NO_3 and the others showed no change in NH_4 or NO_3 . Trends in precipitation-adjusted NH_4 and NO_3 concentrations were more widespread, with 65 and 35% of sites showing increases in precipitation-adjusted NH_4 and NO_3 , respectively (Figure 3). The difference in raw and precipitation-adjusted NH_4 and NO_3 is due to the diluting effect of increased precipitation that occurred at some sites.

[27] At the parks in this study that had NADP sites, there were no statistically significant trends in NH_4 or NO_3 concentrations, except Yellowstone, where NH_4 and NO_3 concentrations increased. However, precipitation-adjusted NH_4 increased at all of the parks, and precipitation-adjusted NO_3 increased at Sequoia/Kings Canyon and Yellowstone National Parks (Figure 3).

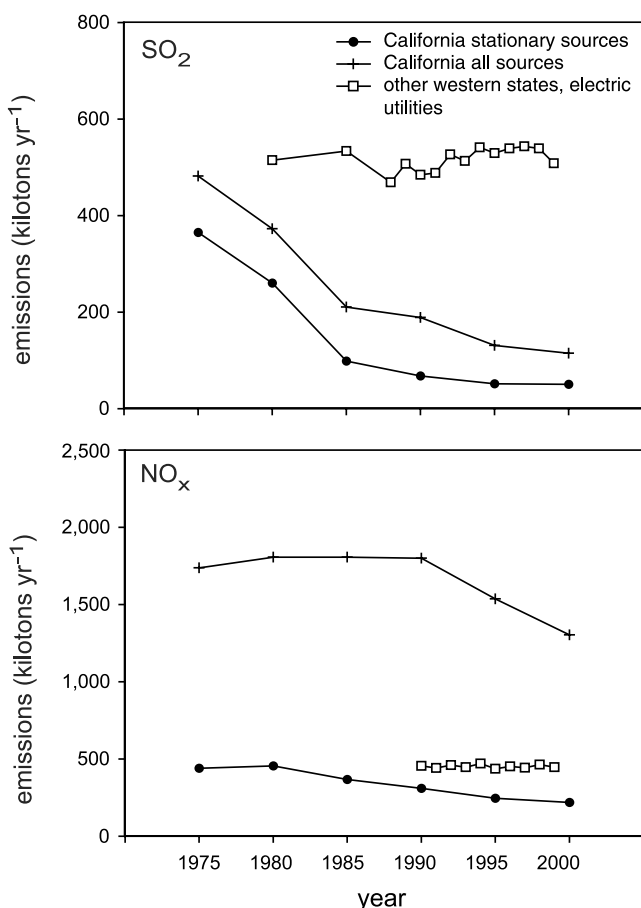


Figure 5. Trends in emissions of SO_2 and NO_x in the western United States, 1975–2000. California data are from the *California Air Resources Board (CARB)* [2001]. Data for other western states are from *U.S. Environmental Protection Agency (USEPA)* [2001]. Electric utilities accounted for approximately 66% of total SO_2 emissions and 28% of total NO_x emissions in the United States in 1995 [National Acid Precipitation Assessment Program (NAPAP), 1998].

[28] Inorganic N deposition at the study parks was highly variable from year to year, particularly at the sites in California (Figures 2 and 4). Most sites showed declines in inorganic N deposition during the early to mid-1980s and increases during the late 1980s to mid-1990s. Most of the interannual variability in inorganic N deposition can be explained by variations in precipitation amount ($r^2 = 0.68$), which also declined from the middle to late 1980s and then increased during the middle to late 1990s, reflecting subdecadal precipitation cycles in the western United States.

[29] Historical NH_3 and NO_x emissions data generally are less extensive than historical SO_2 emissions data. State NH_3 emissions data generally are not available prior to the mid-1990s, but national NH_3 emissions data, available beginning in 1990, indicate that NH_3 emissions increased during the 1990s [USEPA, 2001]. State NO_x emissions data indicate that NO_x emissions declined in California between 1985 and 1999 but have been relatively constant in the other western states (Figure 5) [CARB, 2001; USEPA, 2001]. National

NO_x emissions have been steady since the 1970s [USEPA, 2001].

3.3. Coherence of Trends in Lake Chemistry, Precipitation Chemistry, and Precipitation Amount

[30] Temporal patterns in AVWM SO_4 concentrations at the outlets of Emerald Lake and the Loch suggest a fairly direct response to variations in AVWM SO_4 concentrations in precipitation and/or to variations in annual precipitation amount (Figure 2). Lake SO_4 concentrations at Emerald Lake and at the Loch peaked during the late 1980s to early 1990s, coincident with a temporary increase in precipitation SO_4 concentrations and with a regional drought that affected much of the western United States (Figure 2). SO_4 concentrations in lake water and in precipitation subsequently declined during the relatively wet middle to late 1990s. Simple linear regression analyses indicated that annual precipitation amount accounted for 31% of the variance in AVWM lake SO_4 at Emerald Lake ($p = 0.03$) and 38% of the variance in AVWM lake SO_4 at the Loch ($p = 0.009$).

[31] The consistency in direction of changes in SO_4 concentrations at the survey lakes and in trends in SO_4 deposition and SO_2 emissions in the western United States indicates that lake SO_4 concentrations probably are responding to declining SO_4 deposition in the western United States. The long-term data from Emerald Lake and the Loch suggest that climatic-related variability is overlaid on a long-term decline in lake SO_4 concentrations. The relatively direct response of lake SO_4 to variations in atmospheric deposition is reasonable given the limited SO_4 adsorption capacity of soil in most high-elevation basins in the western United States [Lund et al., 1987; Baron et al., 1992].

[32] In contrast to the direct response of lake SO_4 , temporal patterns in AVWM lake NO_3 at Emerald Lake and at the Loch showed little direct relation to AVWM inorganic N concentrations in precipitation, to annual inorganic N deposition, or to annual precipitation amount (Figure 2). At Emerald Lake, NO_3 concentrations in the outlet declined from 1984 through 1992 ($p < 0.001$) and increased from 1993 through 1999 ($p = 0.025$). These trends are the opposite of those in precipitation NO_3 concentrations (Figure 2). Precipitation amount accounted for little variation in lake NO_3 at Emerald Lake, except during several drought years when AVWM NO_3 concentrations were approximately double the long-term average. At the Loch, AVWM lake NO_3 was weakly correlated with AVWM inorganic N concentrations in precipitation ($r^2 = 0.20$; $p = 0.07$). The existence of a correlation between lake NO_3 and precipitation NO_3 at the Loch and the lack of similar correlation at Emerald Lake may be attributable to the fact that the Loch Vale ecosystem is nitrogen-saturated while the Emerald Lake ecosystem is not.

[33] The mostly downward changes in NO_3 concentrations observed in survey lakes are not consistent with the generally level or upward trends in inorganic N deposition and NO_x emissions. Although variations in atmospheric deposition of N compounds undoubtedly affect lake NO_3 concentrations, other factors such as climate variability or increasing P deposition also must be considered [Sickman, 2001]. Climatic-related factors that may affect seasonal and AVWM NO_3 concentrations include the timing of snowmelt [Sickman et al., 2001], and the extent of snow cover [Brooks et al., 2000]. Summer storms also can strongly affect lake

Table 1. Annual Precipitation (in Centimeters) by Water Year (October–September) in National Parks in the Western United States, 1981–1999

Park	Median	Average ± 1 SD	1985	1999
Lassen Volcanic	71	84 \pm 35	55	76
Yosemite	114	118 \pm 49	86	113
Sequoia/Kings Canyon	78	97 \pm 42	73	68
Glacier	84	79 \pm 18	73	62
Yellowstone	39	38 \pm 10	34	38
Rocky Mountain	109	110 \pm 18	104	109

NO_3 concentrations by flushing NO_3 from catchment soils, as discussed in the next section.

[34] The possible effects of differences in annual precipitation amounts during 1985 and 1999 on survey lake chemistry were evaluated by comparing total precipitation during the 1985 and 1999 water years (October–September). Annual precipitation amounts were within one quartile of the 1985–1999 median at all of the parks, indicating that annual precipitation was within the “normal” range during both of the lake surveys (Table 1). Differences in annual precipitation during 1985 and 1999 were less than 15% at all parks except Lassen Volcanic and Yosemite National Parks, where annual precipitation amounts in 1999 were 32 and 39% higher than in 1985, respectively. Higher precipitation in 1999 compared to 1985 at Lassen Volcanic and Yosemite National Parks may partly explain the lower SO_4 and NO_3 concentrations measured in those parks during the 1999 survey.

3.4. Effects of Storm Events on Lake Chemistry

[35] Variations in precipitation amount can influence surface water chemistry, potentially confounding comparisons of water chemistry collected through synoptic surveys during different years. The influence of storm events on stream chemistry has been investigated at a number of forested watersheds in the eastern United States, Scandinavia, New Zealand, and elsewhere [Sullivan *et al.*, 1986; Hooper and Shoemaker, 1987; McDonnell *et al.*, 1991; Bazemore *et al.*, 1994; Burns *et al.*, 1998]. The response of stream water chemistry to storm events is complex, depending on a host of hydrologic and biogeochemical variables including antecedent moisture conditions, duration and intensity of precipitation, concentrations and mixing of source waters, and reaction rates along multiple flow paths. Most of the forested-catchment studies indicate that NO_3 , DOC, and aluminum concentrations increase with discharge during storm events due to flushing of these solutes from shallow organic soils. Concentrations of weathering products often initially increase due to flushing of shallow soils, but if the storm is of sufficient duration and intensity, increases usually are followed by a decline in concentrations as event water mixes with and dilutes groundwater discharge [Walling and Foster, 1975; McDuffett *et al.*, 1989; Caissie *et al.*, 1996].

[36] Little work has been done to characterize hydrochemical responses to storm events in high-elevation catchments in the western United States, which are largely alpine in character. Most studies in these basins have focused on hydrochemical variations during snowmelt because it drives the annual hydrologic cycle; rainfall typically accounts for only 5–30% of annual precipitation. The abundance of steep slopes, exposed bedrock, and highly permeable talus deposits suggest that interactions between rainfall and soils

would be minimal. However, recent observations in Loch Vale, an alpine/subalpine basin in Rocky Mountain National Park, have indicated that large summer storms can have a notable influence on surface water chemistry.

[37] Loch Vale is representative of many alpine/subalpine basins in the Rocky Mountains, with steep topography, sparse vegetation, and poorly developed soils. It is 660 ha in size, slightly larger than the average area of the 1999 survey lake basins (392 ha). The Loch, which is the lowest of three lakes in Loch Vale, is a small, shallow drainage lake with well-defined inlets and outlets and short residence times. During the 1985 and 1999 lake surveys, the residence time of water in the Loch was 3–4 days, based on lake volume and discharge data [Baron, 1992b]. Because of the short residence times of these systems, hydrologic and chemical responses to snowmelt and storm events are rapid.

[38] The influence of rain on surface water chemistry at Loch Vale was evaluated for the summer and fall of 1997; this period was chosen because there were several large rain events: one during early June, another during early August, and a third during late September (Figure 6). Surface water

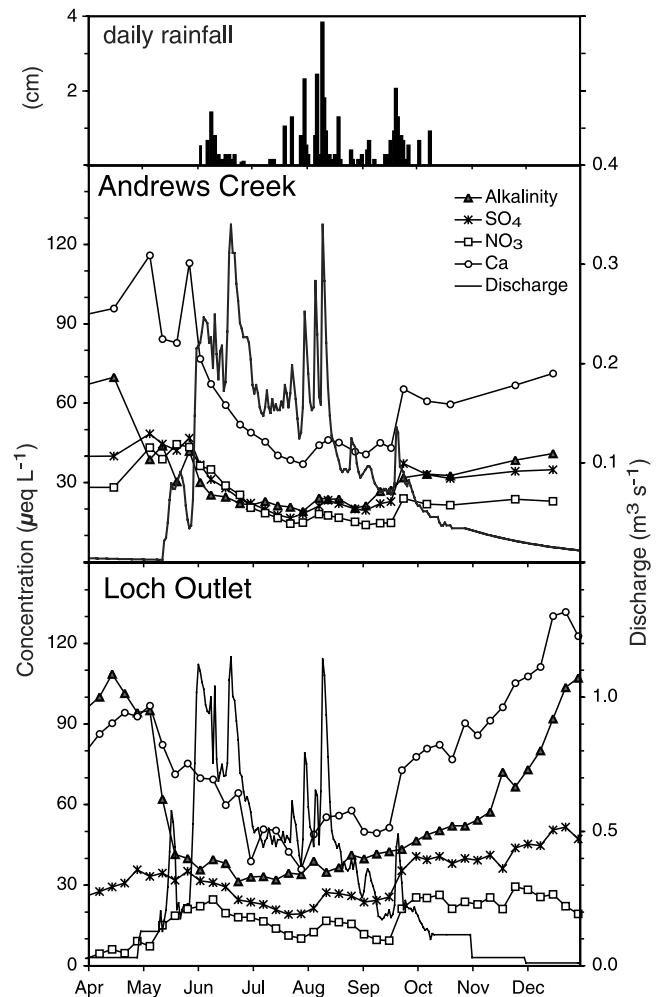


Figure 6. Response of discharge, alkalinity, SO_4 , NO_3 , and Ca concentrations at Loch Outlet and at Andrews Creek to rainfall during summer 1997. Precipitation data are from NADP [2000]. Loch outlet data provided by J. Baron, USGS/BRD.

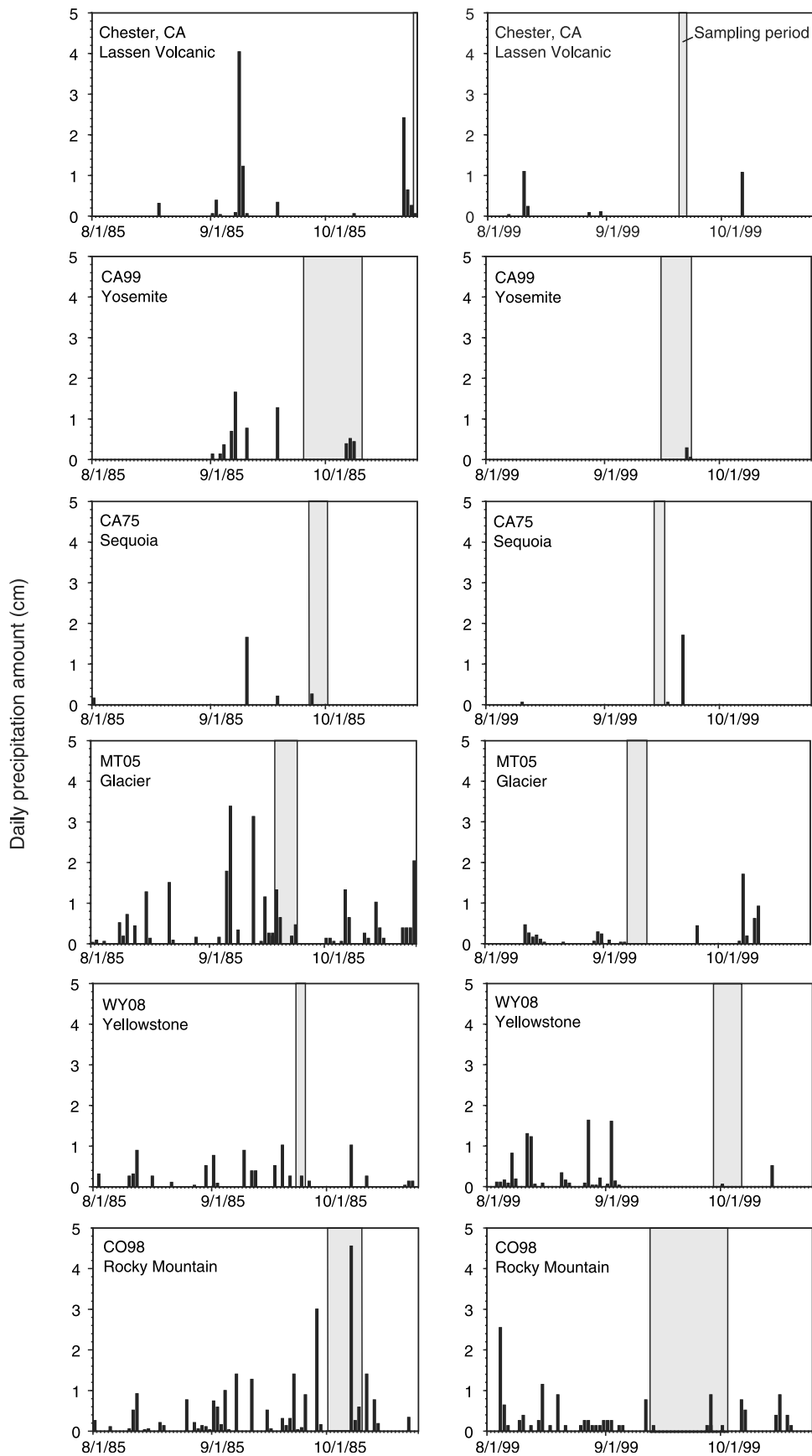


Figure 7. Daily rainfall for August–October 1985 and August–October 1999. Sampling period for each park is indicated by shaded area. Data are from *NADP* [2000], except for Chester, which is from National Climatic Data Center (<http://www4.ncdc.noaa.gov/>).

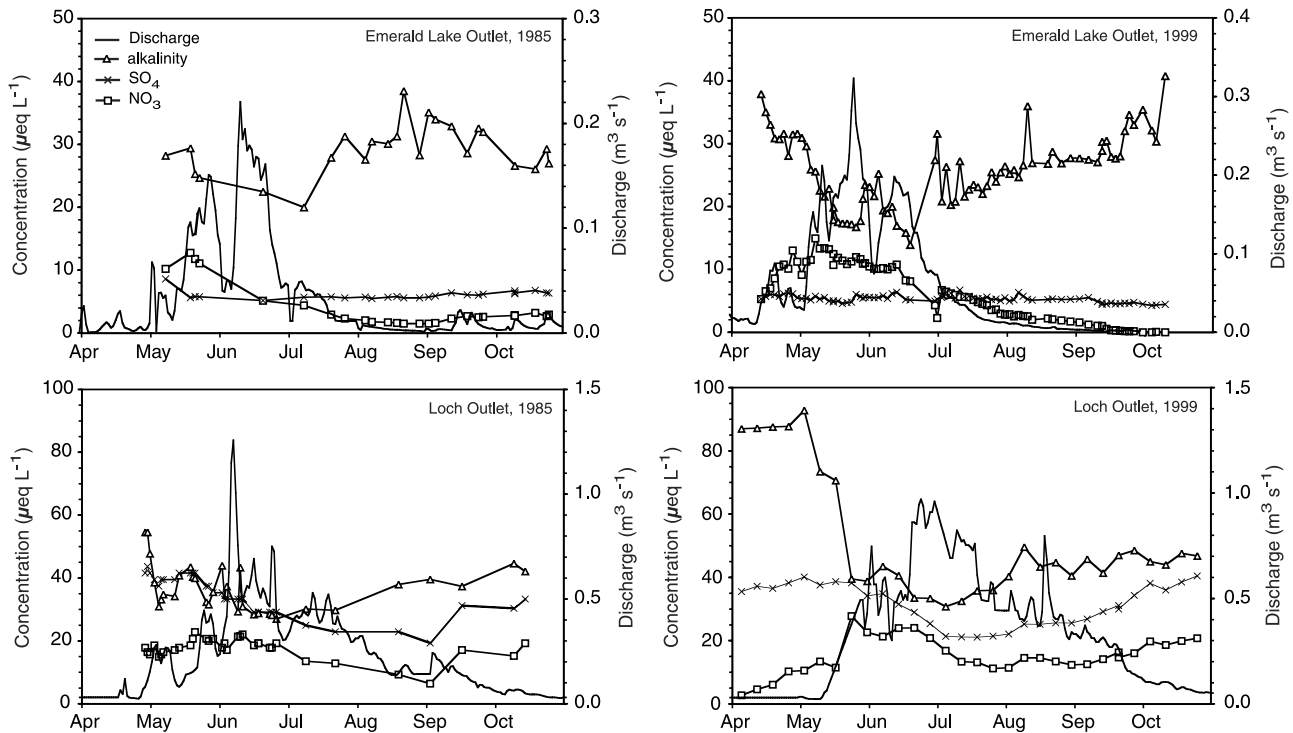


Figure 8. Discharge, alkalinity, SO_4 , and NO_3 concentrations at the Emerald Lake outlet (Sequoia/Kings Canyon National Park) and at the Loch outlet (Rocky Mountain National Park) during 1985 and 1999. Data for Emerald Lake were provided by J. Melack, University of California. Data for the Loch outlet were provided by J. Baron, USGS/BRD.

chemistry response to the early June rain was largely masked by snowmelt-related changes in chemistry, both at the Loch outlet and at Andrews Creek, one of two major tributaries to the Loch. During the middle-to late-summer rain events, surface water concentrations of all major constituents increased at both sites, and concentrations remained elevated after the September event (Figure 6). Analogous hydrochemical responses were observed during other years when there were large summer/fall rain events, including 1995 and 2001. The similarity of responses at the Loch outlet and at Andrews Creek suggests that processes driving the changes in chemistry were similar at those scales.

[39] It is noteworthy that while chemical responses to rain events during the summer were transient, chemical responses to rain events during the fall were more persistent. Solute concentrations in Loch Vale surface waters generally increase gradually during the fall as the relative importance of groundwater inputs to streams and lakes increase and uptake of nitrogen by vegetation declines. Rain events may simply hasten the normal increases in surface water concentrations that occur during fall by flushing solutes from soils, which accumulate through mineral weathering, evapotranspiration, dry deposition, and biologic processes (e.g., mineralization, nitrification).

[40] To determine the potential effect of antecedent rain on lake chemistry during the 1985 and 1999 surveys, daily rainfall data for fall 1985 and fall 1999 were compiled for the study parks. Rainfall was relatively common prior to and during the 1985 lake survey, especially at Glacier,

Rocky Mountain, and Lassen Volcanic National Parks (Figure 7). Rain was much less common prior to and during the 1999 survey (Figure 7).

[41] The rain prior to sampling in 1985 may have been sufficient to cause a hydrologic and chemical response at some of the survey lakes, as indicated by changes in discharge and chemistry at the Emerald Lake and Loch outlets (Figure 8). At Emerald Lake, there was a slight increase in NO_3 in response to the rain event in early September 1985 (2 weeks prior to sampling), but there were no substantial changes in SO_4 , alkalinity, or base cation concentrations. The small rain event that occurred in late September 1985 (during sampling) caused no discernable change in discharge or chemistry at Emerald Lake. At the Loch, rain during early September 1985 (4 weeks prior to the survey) caused an increase in discharge and in NO_3 and SO_4 concentrations (Figure 8). Base cation concentrations also increased, but alkalinity did not change, indicating that increases in acid anions and base cations offset each other. Additional precipitation during the rest of September and during early October 1985, when the lake sampling occurred in Rocky Mountain National Park, caused only small hydrologic and chemical responses at the Loch (Figure 8). In Rocky Mountain National Park as a whole, lakes sampled after the October 1985 storm ($n = 6$) had greater differences in NO_3 compared to 1999 survey data (mean = $1 \mu\text{eq L}^{-1}$) than lakes sampled prior to the October 1985 storm ($n = 15$). This supports the hypothesis that storm events may have caused a small increase in NO_3 in some of the lakes.

[42] Assuming that the hydrochemical responses at Emerald Lake and at the Loch were representative of other survey lakes, these results suggest that rainfall prior to or during sampling in 1985 might partly explain higher NO_3 concentrations in survey lakes in 1985 relative to 1999. This does not exclude the possibility of long-term declines in NO_3 concentrations at some lakes. The variable responses of SO_4 , alkalinity, and base cation concentrations to rain events indicate that changes in concentrations of other solutes are more difficult to predict, and additional study is needed before generalizations can be made.

4. Conclusions

[43] The consistency in direction of changes in lake SO_4 , precipitation SO_4 , and SO_2 emissions in the western United States suggests that lake chemistry is responding to decreases in SO_4 deposition in the west. These results are consistent with decreases in SO_4 in surface waters and precipitation, and in SO_2 emissions in the eastern North America and Europe [Stoddard *et al.*, 1999]. A comparison of long-term data on lake chemistry, precipitation chemistry, and precipitation amount from two lakes in the western United States indicates that annual variations in precipitation amount accounted for approximately one third of the variation in annual volume-weighted mean SO_4 concentrations in the lakes. These results are in agreement with previous studies that have documented the influence of climate on surface water chemistry [Bayley *et al.*, 1992; Webster and Brezonik, 1995], and reinforce the concept that variations in climate should be considered in any long-term trend analysis.

[44] Controls on lake NO_3 concentrations are complex; a direct response of lake NO_3 to changes in inorganic N deposition was not evident. As for SO_4 , these results are consistent with those found in a previous study in eastern North America and Europe [Stoddard *et al.*, 1999]. In the present study, precipitation prior to sampling in fall 1985 may have caused elevated NO_3 concentrations in some lakes during the 1985 survey due to direct runoff of atmospherically deposited inorganic N and flushing of NO_3 from alpine soils. Higher total phosphorus concentrations in lakes surveyed during 1999 may have contributed to decreases in lake NO_3 concentrations by stimulating phytoplankton productivity [Sickman, 2001].

[45] Process-oriented research and long-term monitoring of surface water and precipitation chemistry at two of the parks provided essential ancillary information to the lake survey study. Without this information, few interpretations about possible controls on lake chemistry would have been possible. The sparseness of long-term water quality monitoring data in the parks limits understanding of key processes, making it difficult to provide definitive interpretations of precisely how and why aquatic ecosystems respond to changes in atmospheric deposition and variations in climate. An improved long-term monitoring strategy would incorporate relatively frequent hydrologic and chemical measurements at a small suite of representative lakes and streams in combination with periodic, repeated hydrologic and chemical surveys of a larger group of lakes and streams. It must be recognized, however, that hydrologic and chemical monitoring in

wilderness areas will require substantial resources because these lakes and streams are in remote areas where access is difficult.

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