

Response of Ned Wilson Lake Watershed, Colorado, to Changes in Atmospheric Deposition of Sulfate

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The Ned Wilson Lake watershed responds directly and rapidly to changes in precipitation inputs of sulfate, which has important implications for effects of acid deposition on the aquatic system. Chemistry at three precipitation collection sites and three watershed sites (a pond, a lake, and a spring) has been monitored in and near the Flattops Wilderness Area in northwestern Colorado beginning in 1981–1983. Bulk snowpack concentration of sulfate in the watershed and volume-weighted annual mean concentration of sulfate in precipitation at two nearby sites generally decreased from 1981 to 1985, were small through 1987, and increased in 1988–1989. Changes in concentration of sulfate at the watershed sites are controlled by precipitation inputs. Responsiveness of the individual sites was dependent on their position along the hydrologic flow path. The fastest response was in the pond, which has a hydrologic residence time of less than 1 year; over 90% of the variance in concentration of sulfate in the pond was explained by changes in concentration in precipitation. The lake has a hydrologic residence time of 1 to 4 years; a regression model of the concentration of sulfate in the lake, as a function of the concentration in the lake during the previous year and the concentration in precipitation, explained 87% of the variance in concentration of sulfate in the lake. The hydrologic response time of the spring is unknown; it was not responsive to changes in concentration of sulfate in precipitation. The recent increase of sulfate concentration in precipitation and in the pond and lake is evidence for a rapid rather than a delayed response, which could not be determined when only a decreasing trend in sulfate concentration was reported in 1982–1987. Watersheds of this type are sensitive to acidification (acid-neutralizing capacity less than $60 \mu\text{eq L}^{-1}$), and these results indicate conservative behavior of sulfate. This is important in predicting effects of future changes in atmospheric deposition, which could potentially be caused by anthropogenic emissions or climatic change.

INTRODUCTION

Understanding the link between atmospheric deposition and surface water chemistry is important in predicting acidification of fresh waters. Considerable effort has been made to study this link in environments that have large sulfate deposition rates [Ryan *et al.*, 1989]. The U.S. Environmental Protection Agency (EPA), as part of the National Acid Precipitation Assessment Program, has sponsored the Direct/Delayed Response Project to address this problem in the eastern United States [Church, 1989]. However, little work has been done in the Rocky Mountain region, where many aquatic systems are sensitive to atmospheric deposition but have not been subjected to large deposition rates. These pristine watersheds are vulnerable to increases in the acidity of atmospheric deposition that could occur because of increased anthropogenic emissions [Turk and Spahr, 1991]. Such an increase in emissions could result from future development of the plentiful mineral and energy resources in the western United States or from population growth in the region. It is important to understand the potential effects of such development on federally protected land and water resources, many of which are located near point sources of emissions.

Changes in atmospheric deposition of sulfate have been reported for various sites in the Rocky Mountain region [Epstein and Oppenheimer, 1986]. This atmospheric deposition is the primary source of sulfate in many high-altitude

lakes and streams in the region [Turk and Spahr, 1991]. Therefore a major change in sulfate concentration of wetfall is expected to produce a change in sulfate concentration of the lakes and streams and potentially could change their acidification status. In many aquatic systems, such as those of the southeastern United States, there may be considerable time lag between deposition and acidification as hydrologic and geochemical processes mitigate the effects of acid deposition [Reuss *et al.*, 1987; Church *et al.*, 1990]. However, in alpine and subalpine watershed of the Rocky Mountains, soils are thin and poorly developed, and the snowmelt-runoff cycle flushes the systems rapidly. Consequently, a direct rather than delayed response is expected [Turk and Adams, 1983; Turk and Campbell, 1984].

The Flattops Wilderness Area (Figure 1) is located directly downwind (to the east) of the Piceance Basin, potentially a major center for development of oil shale in northwestern Colorado. As a class 1 wilderness area, all of the air, land, and water resources of the Flattops are protected by federal law from deterioration due to air quality degradation. Oil-shale retorting could result in large emissions of sulfate and nitrate, drastically altering atmospheric deposition in the Flattops. Therefore it is important to understand what effect changes in deposition are expected to have on the aquatic systems in the region.

Herein we examine changes in sulfate concentrations in wetfall (wet-only deposition) that have occurred since 1981, and the response of three sites in the Ned Wilson Lake (NWL) watershed in the Flattops. The responsiveness of the watershed to variations in atmospheric deposition may provide an indication of how these aquatic systems will respond

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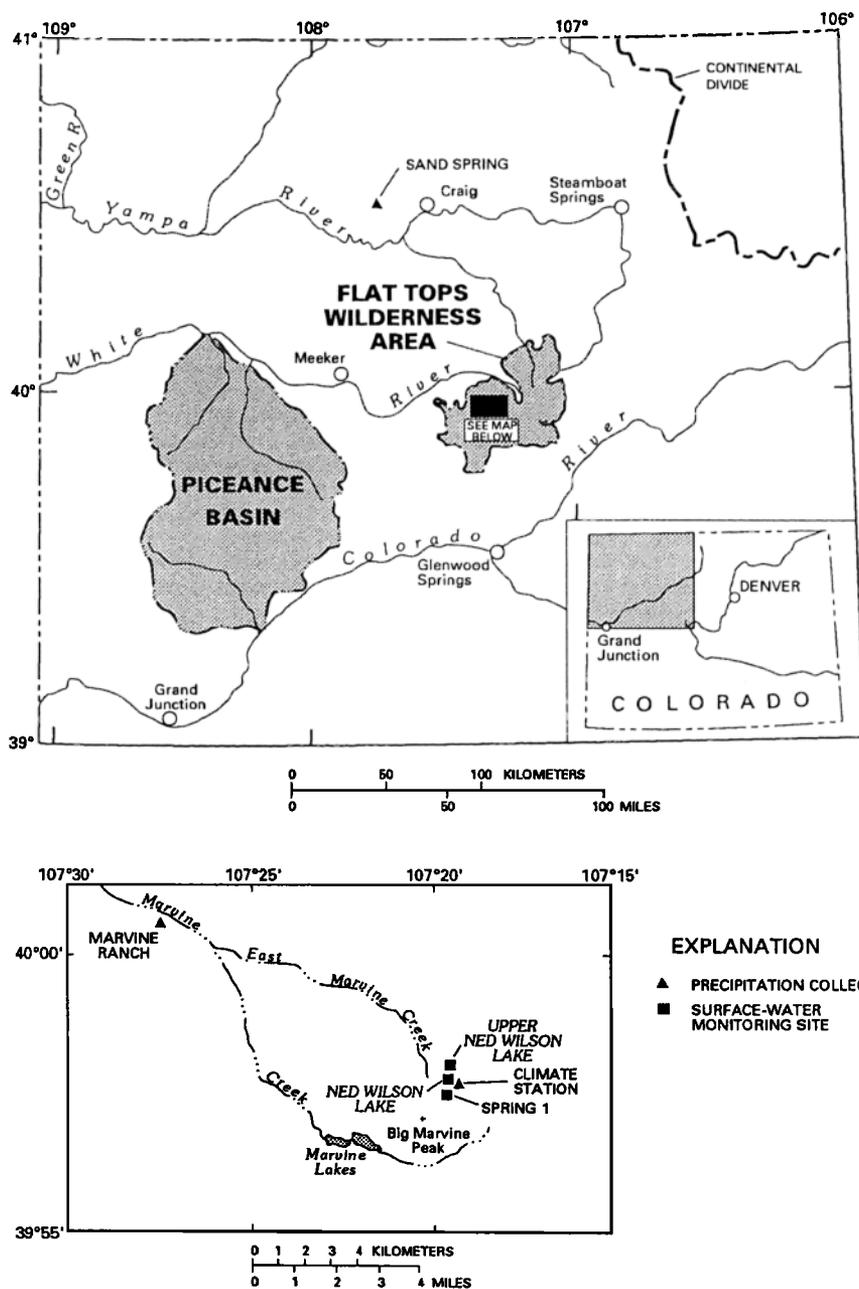


Fig. 1. Location map.

to possible future changes in deposition caused by changes in anthropogenic emissions or climate.

DESCRIPTION OF THE STUDY AREA

Precipitation Sites

Data from three precipitation chemistry monitoring sites (Figure 1) were compared because the record measured directly in the NWL watershed is not as complete as measurements made nearby. The three sites for which chemistry data are presented are affected by the same precipitation-producing storm tracks; the primary difference is in the amount of precipitation they receive.

The most complete and longest period of record is from the National Atmospheric Deposition Program/National

Trends Network (NADP/NTN) site at Sand Spring, Colorado. The site is located approximately 80 km north of the NWL watershed at an altitude of 1998 m. The completeness and length of the record make Sand Spring useful for comparison to the other precipitation collectors and the surface water monitoring sites.

Wetfall chemistry and precipitation amounts also were measured at Marvine Ranch, located in a valley approximately 11 km west of Ned Wilson Lake at 2379 m in altitude. This precipitation collection site is at lower altitude than the watershed.

Snowpack sulfate-concentration data from the NWL watershed are presented for comparison to the wetfall data from the above sites. Though this is the most direct measurement of atmospheric deposition in the watershed, the

TABLE 1. Water Budget for Ned Wilson Lake Watershed

Water Year	Precipitation,* cm	Runoff,† cm	Residence Time,‡ years
1983	...	4.48	1.7
1984	178	3.42	2.2
1985	135	2.23	3.3
1986	162	3.21	2.3
1987	124
1988	130	2.33	3.2
1989	115

*Precipitation calculated as maximum accumulation snow water equivalent, plus weighing-bucket rain gage amount for remainder of water year.

†Runoff calculated as total measured outflow from lake, divided by watershed area.

‡Hydrologic residence times are calculated as lake volume divided by mean annual discharge.

record is incomplete, lacking late-spring snowfall and all of the warm-season precipitation.

NWL Watershed

The NWL watershed has been the primary focus of long-term monitoring in the Flattops since 1982, when it was selected for its representativeness and sensitivity to acidification from 27 lake watersheds that were sampled during a synoptic survey of lake chemistry in the region during 1981 [Turk and Adams, 1983]. The watershed is 3389 m in altitude at the lake and has a surface drainage area of 50 ha. The Flattops are part of the White River Plateau, which is a large plateau of thick basalt. This basalt forms a homogeneous bedrock geology throughout the area, simplifying interpretation of the geochemical processes controlling surface water chemistry and providing an excellent opportunity to examine the effects of position in the hydrologic flow path on aquatic chemistry. There is little runoff on the land surface, even during peak snowmelt periods; most of the snowmelt infiltrates the thin soils and flows through the porous, fractured basalt bedrock. Three surface water sites in the NWL watershed were sampled during the study period: a pond, the lake itself, and a spring.

The pond (Upper Ned Wilson Lake) is located on a bedrock shelf just above Ned Wilson Lake. It has a surface area of 0.26 ha, a total watershed area of approximately 0.5 ha, and an average depth of 1.5 m. Direct annual precipitation exceeds the capacity of the pond, and groundwater seepage into the pond is believed to be small, owing to its topographic position. Therefore the chemistry of the pond is strongly affected by precipitation and evaporation.

Ned Wilson Lake has a surface area of 1 ha, a total watershed area of 50 ha, and an average depth of 5.5 m. The inflow stream has no measurable flow during most years; the outflow stream flows for about 3 weeks each year during June, and total measured discharge constitutes only a small fraction of total precipitation in the watershed (Table 1).

The spring (spring 1) is located in a wet alpine meadow near Ned Wilson Lake. The spring discharges throughout the snow-free season from July through September. Although the local groundwater system has not been studied, the spring is believed to be chemically representative of groundwater throughout the NWL watershed due to the

homogeneity of the bedrock. Because of the hydrogeologic setting on top of a large plateau (there is no input from deep groundwater), the primary source of groundwater is precipitation from the immediate vicinity. Residence time in the groundwater system probably is short.

METHODS

Precipitation

Wetfall samples at Sand Spring were collected as part of the NADP/NTN; data were presented and methods described by the National Atmospheric Deposition Program [1980–1989]. Precipitation amounts are measured in a weighing-bucket rain gage, these amounts were used to calculate annual volume-weighted mean (VWM) concentrations for December–November.

Wetfall samples at Marvine Ranch were collected as part of this project and frozen within 24 hours after the end of each storm event. The samples were then thawed and decanted to remove particulates. In order to conserve the volume of sample, filtering was not done unless suspended material was visible. Sulfate analyses were performed on decanted, unpreserved aliquots. VWM concentrations were calculated using volume of sample collected. Means calculated similarly but using precipitation quantity from a weighing-bucket gage had slightly different values, but trends were the same. Precipitation amounts are from the weighing bucket. Annual VWM concentrations and precipitation amounts are calculated for December–November.

Snowpack samples from the NWL watershed were collected using a Mt. Rose/Federal sampler, a standard snow-coring device used in measuring snowpack depth and water equivalents. Each core was inspected and any contamination from the underlying soil removed. This coring device provided a sample that was depth-integrated for the entire snowpack; 10–20 cores were composited for each sample to minimize error caused by spatial heterogeneity. Samples then were treated the same as frozen wet fall samples from Marvine Ranch.

Snowpack snow water equivalent for the NWL watershed was calculated as the mean of 30–40 cores along a snow survey transect. Because of limited access during the winter months, the snowpack sampling was done anytime between late March and early May. Total precipitation for the NWL watershed is calculated as the snowpack measurement, plus precipitation measured in a weighing bucket during the previous October, plus precipitation from the date of the snow survey through the end of September. This calculation using both snow survey and weighing-bucket data provides the most complete and accurate record of total precipitation.

NWL Watershed

Major-ion data have been collected at the pond since 1983, at Ned Wilson Lake since 1981, and at the spring since 1982. Since 1984, at least six samples per year have been collected at each of the sites during the open-water season (July–September). Surface water samples were filtered (0.45 μm) in the field; sulfate analyses were performed on filtered, unpreserved aliquots. Unless otherwise noted, all sulfate analyses were made by ion chromatography in a research project laboratory.

Discharge in the lake outlet channel is measured in a

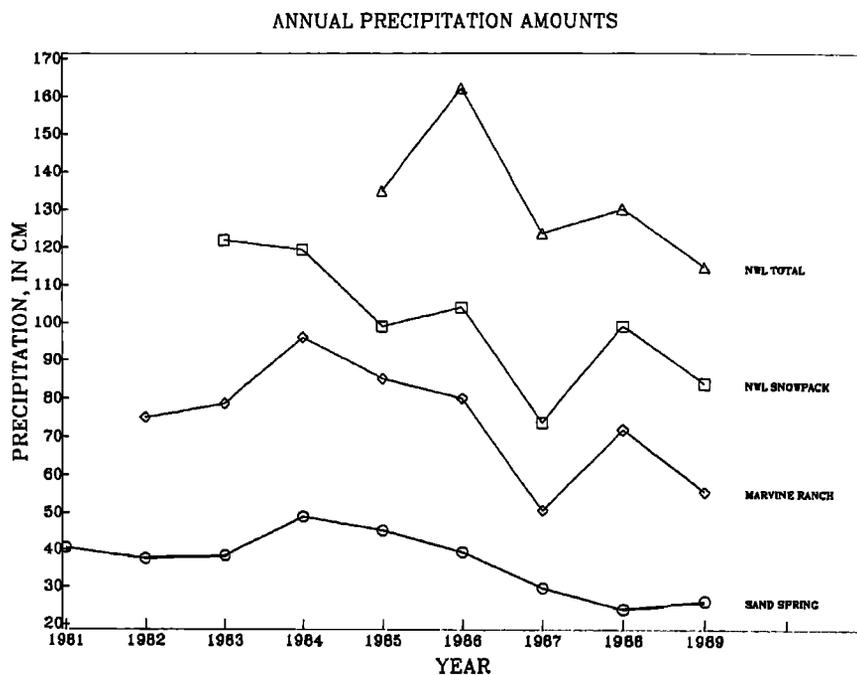


Fig. 2. Total annual precipitation amounts at Sand Spring, Marvine Ranch, and Ned Wilson Lake; and snowpack snow water equivalent at Ned Wilson Lake, 1981–1989.

Parshall flume. Stage is measured continuously from early June, when snowmelt runoff begins, through the end of September. Data are not presented for years in which a large part of the record was lost due to failure of the propane heater, damage caused by wildlife, etc. Because of legal and logistical constraints on work in wilderness areas, much of the knowledge of basic hydrology and geochemistry in the watershed has been gained by field observation and inference from the chemical data, rather than direct measurement.

Quality Assurance

Blind-audit samples were submitted for laboratory analysis; reported sulfate concentrations minus most-probable values had a mean of $0.05 \mu\text{eq L}^{-1}$; the greatest absolute difference for an individual sample was $0.52 \mu\text{eq L}^{-1}$ ($n = 4$).

During 1988–1989, duplicate samples from Ned Wilson Lake were submitted to the U.S. Geological Survey National Water Quality Laboratory (NWQL) in Arvada, Colorado, for sulfate analysis; the samples had a mean difference (Project-NWQL) of $-0.12 \mu\text{eq L}^{-1}$ and a standard deviation of $0.26 \mu\text{eq L}^{-1}$ (not significantly different from 0, $p = 0.10$, $n = 15$).

The U.S. Environmental Protection Agency (EPA) reported a sulfate concentration of $8.1 \mu\text{eq L}^{-1}$ in Ned Wilson Lake during the Western Lake Survey in September 1985 [Eilers *et al.*, 1987]; a similar sample collected for our project 1 day earlier also had a sulfate concentration of $8.1 \mu\text{eq L}^{-1}$.

Calculations of charge balance and specific conductance (calculated from major-ion concentrations compared to measured) were made for surface water and precipitation samples to validate ionic concentrations. Where EPA quality assurance criteria [Morrison, 1989] were exceeded for surface water samples, suspect analyses were rerun. Because of

the variable nature of precipitation chemistry, only gross analytical errors were detectable in wetfall samples; however, more than 75% of the samples with complete major-ion data met the EPA quality assurance criteria for charge balance and specific conductance.

The quality assurance results indicate good precision and accuracy for the sulfate data reported here. Charge balance and specific conductance checks further support a high level of confidence in the described trends in sulfate concentration of precipitation and surface water.

RESULTS

Sulfate concentrations at the three precipitation collection sites decreased through 1985, were small through 1987, and increased in 1988–1989. Changes in sulfate concentration in the pond and the lake showed a similar pattern, while the sulfate in the spring did not increase in 1988–1989.

Precipitation

Precipitation amounts vary consistently among the sites with $\text{NWL} > \text{Marvine Ranch} > \text{Sand Spring}$ (Figure 2). Larger precipitation amounts occur at higher altitudes in the Rocky Mountains, because most precipitation events show orographic effects. All three sites receive precipitation from the same storm tracks, as evidenced by similar pattern of year-to-year variability in precipitation amounts at each site. In general, precipitation amounts were smaller in the latter part of the record. Snow water equivalent at the time of the snow survey was 58–75% of total annual precipitation at Ned Wilson Lake.

VWM concentrations of sulfate in wetfall at Sand Spring generally decreased from 1981 to 1986 and then increased through 1989 (Figure 3). VWM concentrations of sulfate in wetfall at Marvine Ranch decreased from 1982 to 1987, increased in 1988, and decreased in 1989 (Figure 3). Snow-

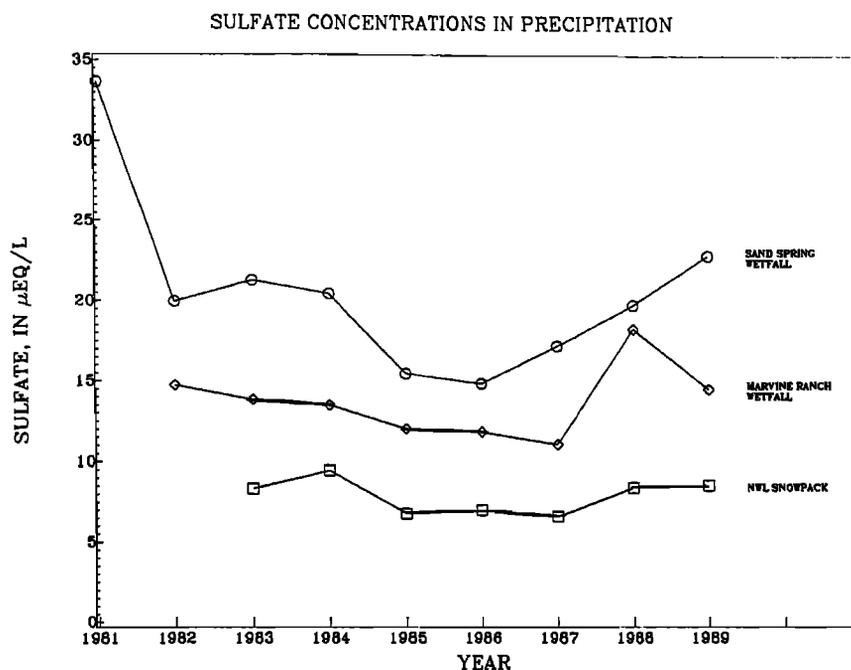


Fig. 3. Mean sulfate concentrations in precipitation at Sand Spring and Marvine Ranch and in Ned Wilson Lake snowpack, 1981–1989.

pack concentrations of sulfate in the NWL watershed increased from 1983 to 1984, were small in 1985–1987, and were larger in 1988–1989 (Figure 3). Sulfate concentrations show a consistent pattern of Sand Spring > Marvine Ranch > Ned Wilson Lake.

Precipitation chemistry data have large variability. Because of the large increase in sulfate concentration in Marvine Ranch wetfall during 1988, individual data were examined for outliers. A single-event value of $112 \mu\text{eq L}^{-1}$ occurred during March 1988, but chemical quality assurance did not indicate analytical error. Examination of sulfate concentrations from nearby NADP stations (including Sand Spring) verified the occurrence of a widespread event that had a large concentration of sulfate; therefore the large value at Marvine Ranch was not excluded from the data set. However, the VWM sulfate concentration at Marvine Ranch in 1988 was still much larger than would be predicted from the pattern at the other sites. Therefore it is treated as an outlier in the statistical analyses presented in the discussion section below.

NWL Watershed

Total precipitation, watershed runoff measured at the lake outlet, and hydrologic residence time for the lake are presented in Table 1. Runoff is less than 2% of total precipitation in all years for which data are available. Residence time in the pond is less than 1 year, based on direct precipitation exceeding average depth in the pond in most years. Residence time in the lake varies from 1.7 to 3.3 years, based on discharge at lake outflow compared to lake volume. Residence time of groundwater discharging at the spring is unknown.

Concentration of major ions and silica in the pond, lake, and spring are presented in Figure 4a–4i. Overall ionic

strength of water in the lake is slightly greater than in the pond, whereas the spring is 10–20 times more concentrated.

Sulfate concentrations in the pond during the open water season decreased from 1983 to 1987 and increased through 1989 (Figure 5). Sulfate concentrations for Ned Wilson Lake during the open-water season decreased from 1981 to 1987 and increased through 1989 (Figure 6). Sulfate concentrations in the spring during the open water season decreased from 1982 to 1987, increased in 1988, and decreased in 1989 (Figure 7).

DISCUSSION

Precipitation

Controls on precipitation chemistry are poorly understood, particularly in complex terrain such as the Rocky Mountains. Certain patterns are evident in the data presented here, many of which have been documented in other studies. The precipitation chemistry presented in this paper represents wetfall only at Sand Spring and Marvine Ranch; dry deposition during the snow accumulation period is included in the snowpack samples from Ned Wilson Lake. However, in the Rocky Mountains, dry deposition is believed to be small relative to wet deposition, particularly at high-altitude sites such as Ned Wilson Lake which receive large amounts of precipitation [Turk and Spahr, 1991].

For individual samples at a given site, concentrations of most ionic species are correlated, i.e., a sample tends to be low in all species (“clean”) or high in all species (“dirty”). An increase in an acid anion such as sulfate often is balanced by an increase in a base cation, usually calcium. In the western United States there is no consensus as to whether this occurs because most of the sulfate is paired with calcium at its source (“gypsum dust”) or whether anthropogenic

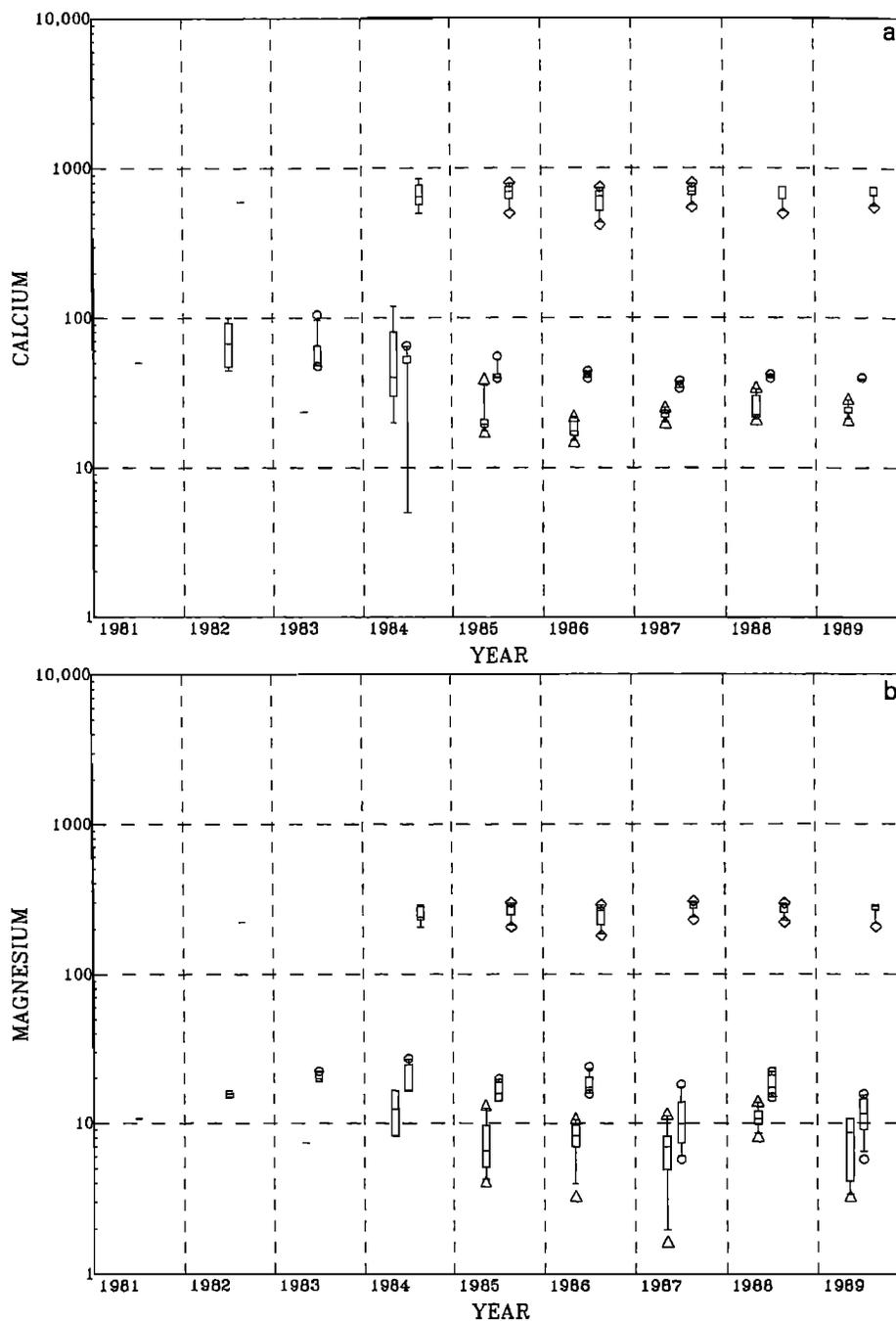


Fig. 4. Concentrations of major ions (in $\mu\text{eq L}^{-1}$) and silica (in $\mu\text{mol L}^{-1}$) in the Ned Wilson Lake watershed, 1981–1989. From left to right, for each year, pond (triangles), lake (circles), and spring (diamonds). Squares define 25th, 50th, and 75th percentiles; dashes define 10th and 90th percentiles. (a) calcium, (b) magnesium, (c) sodium, (d) potassium, (e) alkalinity, (f) silica, (g) sulfate, (h) nitrate, and (i) chloride.

sulfur dioxide emissions dissolve in atmospheric water to form sulfuric acid ("acid rain"), which then dissolves particulate calcium associated with carbonate or other species [Oppenheimer *et al.*, 1985; Hidy, 1986; Newman and Benkovitz, 1986]. It is difficult to determine if sulfate in precipitation came from an acid precursor and even more difficult to determine whether an increase in emissions will produce precipitation with greater acidity. Precipitation at the Marvine Ranch site was not acidified during this study (mean annual pH of 5.0 to 5.3), and sulfate was associated more closely with calcium than with hydrogen ion. Use of sulfur

isotopes presently (1991) is being investigated as a method to identify sources of sulfate in surface waters in the Rocky Mountains [Turk, 1990].

Precipitation quantities are greater at higher altitudes, and there generally is an inverse relation between sulfate concentration and precipitation quantity (small events produce "dirty" precipitation while large events are diluted and produce "clean" precipitation) [Campbell and Turk, 1988]. Consequently, in this study the precipitation that occurs in the NWL watershed is expected to have smaller concentrations than those reported for Marvine Ranch, which should,

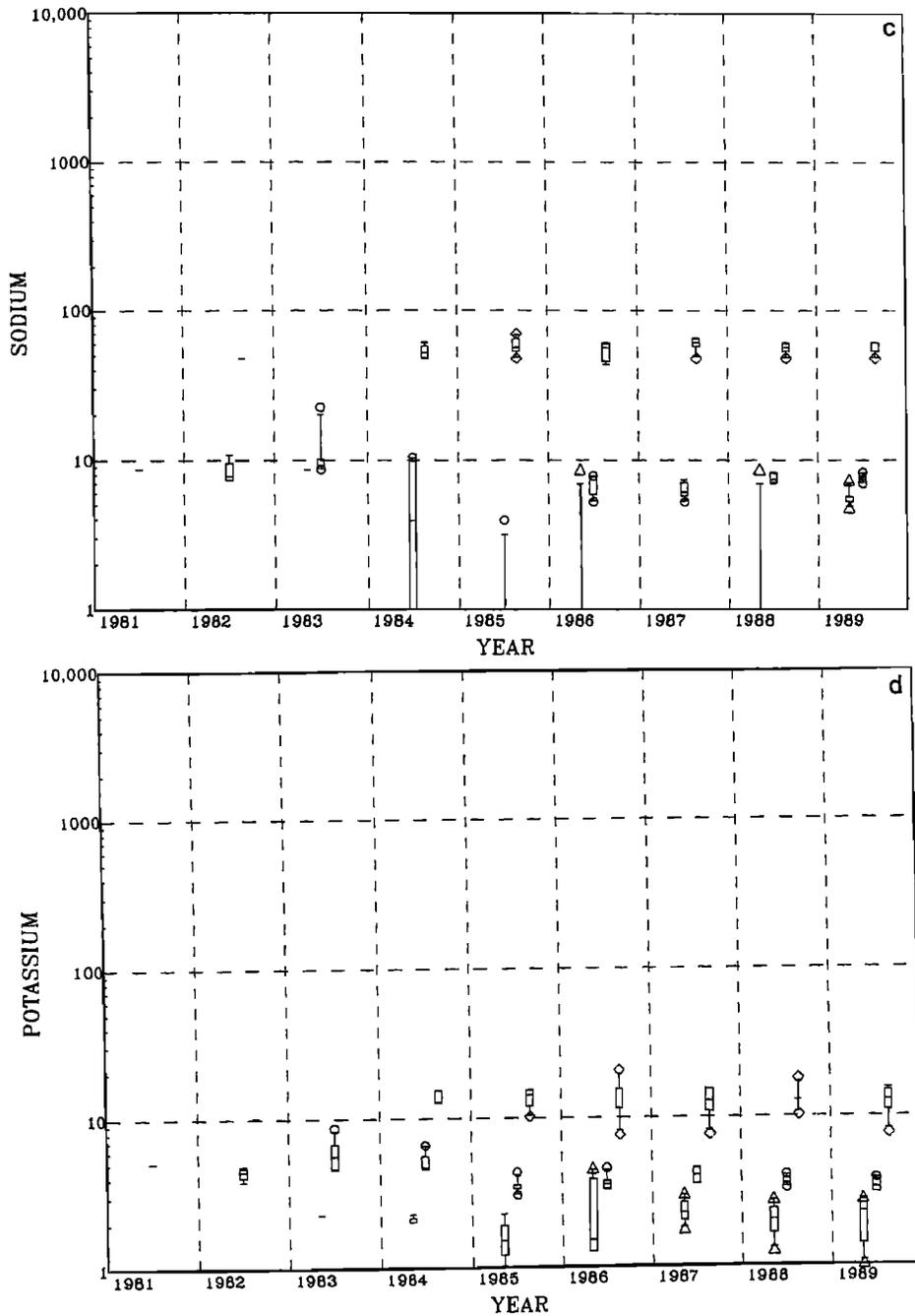


Fig. 4. (continued)

in turn, have concentrations smaller than those at Sand Spring. This relation is evident in Figure 3, which also shows that although concentrations are different, relative interannual variations are similar among the sites.

There is marked seasonality in sulfate concentrations in precipitation in the Rocky Mountains [Epstein and Oppenheimer, 1986; Campbell and Turk, 1988]. Sulfate values tend to be largest in summer and smallest in winter (caused in part by differences in precipitation quantity), which causes the snowpack samples from the NWL watershed to have sulfate concentrations that are less than would be expected for VWM concentrations for the entire year. Therefore seasonal distribution of precipitation can be just as important as the

total quantity of precipitation in determining the annual mean concentrations. Storm tracks also develop differently among seasons and years, which causes the air masses that produce precipitation to come from different source areas that have different sources of sulfate.

NWL Watershed

The water budget calculations indicate that the NWL watershed is predominately a groundwater recharge area, with less than 2% of total precipitation input leaving the system as surface water discharge (Table 1). This is not surprising given the fractured and highly porous nature of

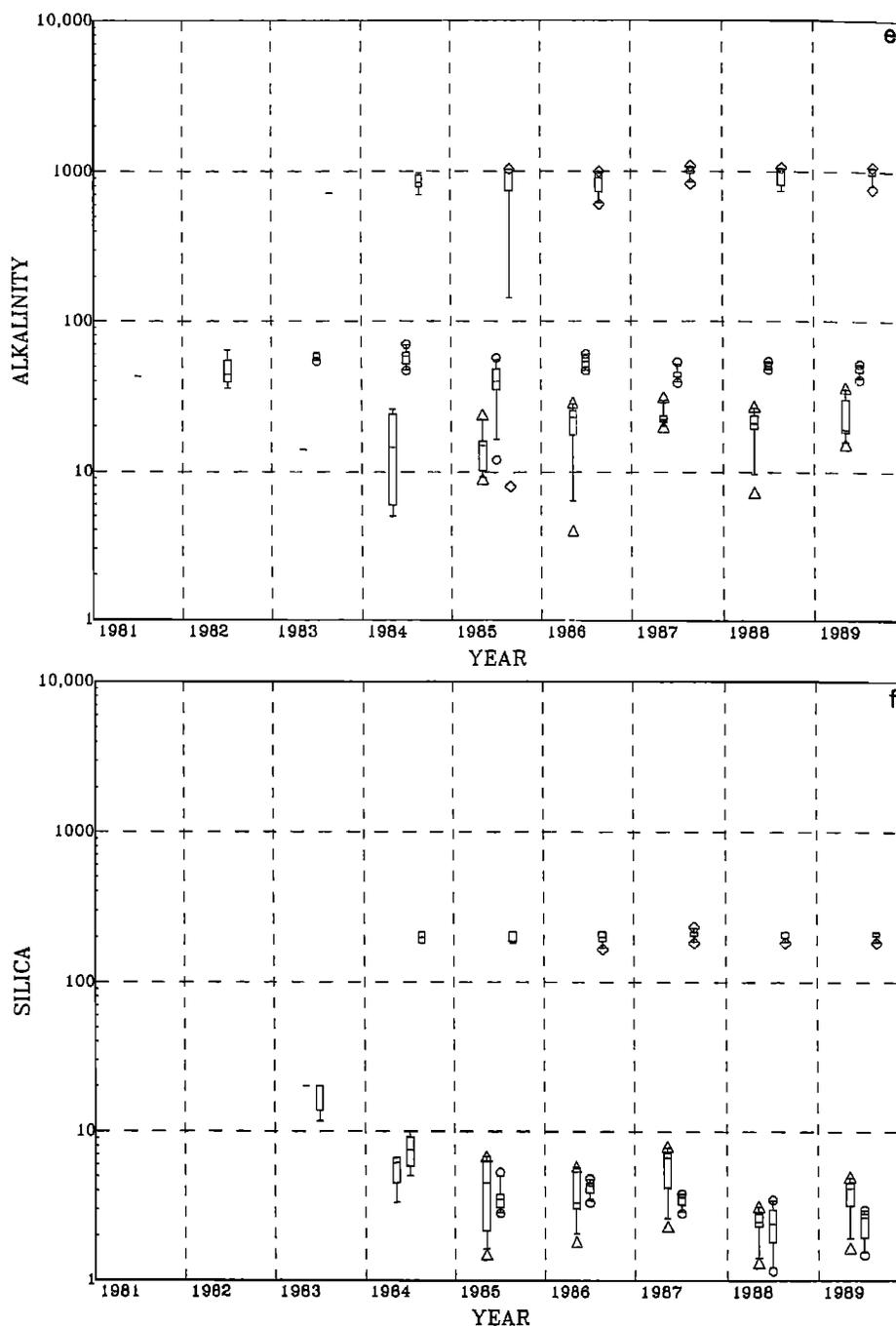


Fig. 4. (continued)

the basalt bedrock. Hydrologic residence time of the lake does not account for any water which moves from the lake into groundwater, therefore residence times are maximum estimates. Evaporation was estimated for the lake for 60 days during summer of 1983 and 69 days in summer of 1984; three separate methods yielded estimates of 20–27 cm for each of the two periods [Spahr and Turk, 1985]. A reasonable extrapolation to the entire open-water season indicates total evaporation of 25–40 cm. Winter season sublimation is accounted for in the snowpack measurement, therefore total evaporation is probably less than one fourth of the total precipitation of 115–180 cm measured in the NWL watershed.

The water in the spring has an ionic strength 10 to 20 times greater than the water in the pond. The spring water contains concentrations of calcium, magnesium, sodium, and bicarbonate (alkalinity) which are roughly an order of magnitude larger than those of the pond and the lake; chloride and sulfate concentrations are roughly equivalent in the three systems (Figure 4a–4i). Thus it appears that the base cations and bicarbonate are primarily weathering products, whereas chloride and sulfate are derived primarily from precipitation only. Potassium is a minor weathering product, and nitrate is detectable at low levels in the spring only.

Calcium concentrations in the lake showed larger variance in the early part of the record; large values of calcium

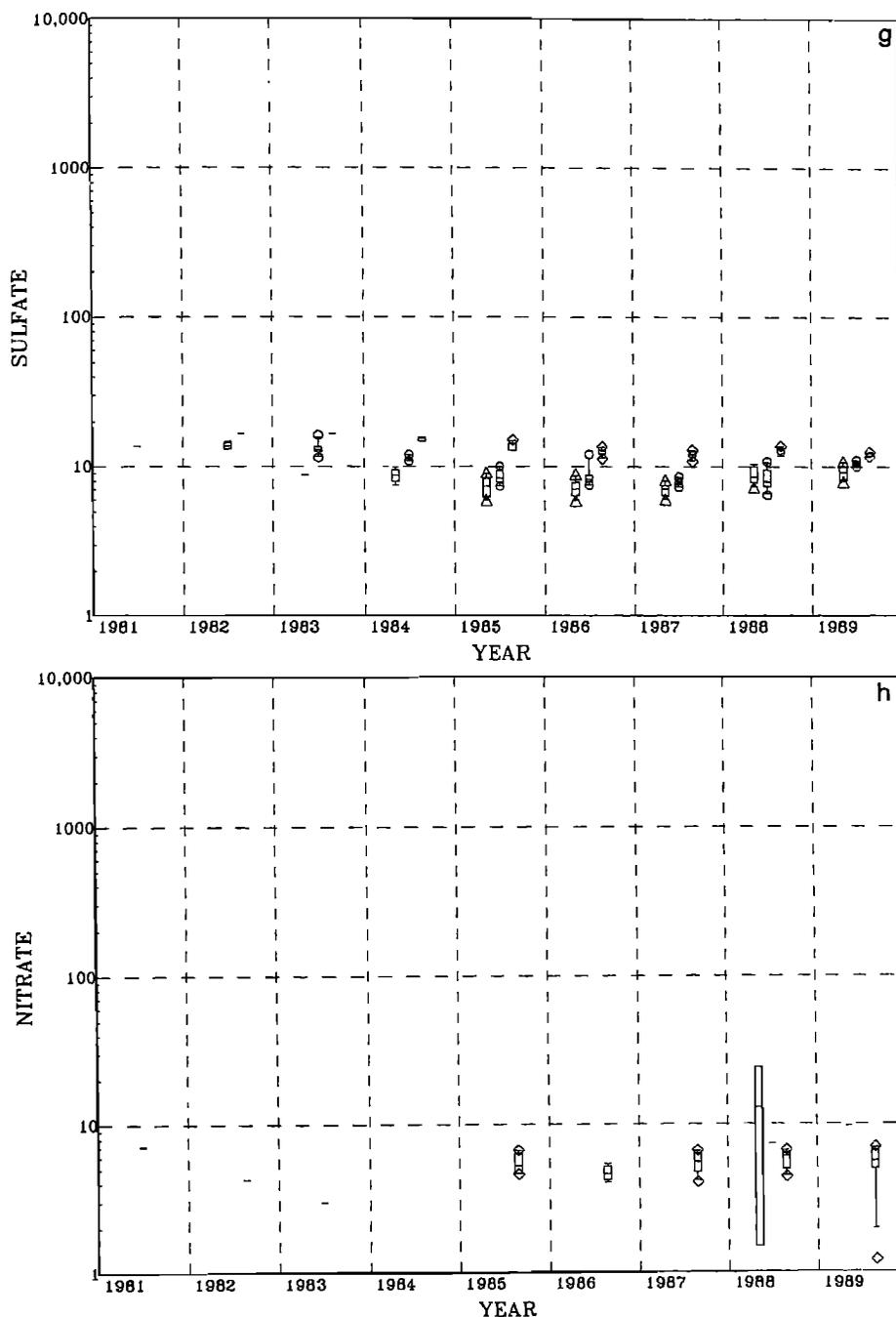


Fig. 4. (continued)

coincided with larger-than-normal anion deficits. Analytical bias for large calcium concentration is a possible explanation. Sulfate concentrations in the pond, lake, and spring were weakly correlated with calcium concentrations ($p < 0.10$; r square = 0.14, 0.35, and 0.08, respectively). Correlation of sulfate with calcium in the lake is strongly influenced by the suspicious calcium values early in the record; in recent years, sulfate increased but calcium did not. Because calcium concentrations in the lake are controlled by weathering and are 2–3 times as large as concentrations in precipitation, it is difficult to detect changes in calcium concentration in the lake caused by atmospheric deposition. It does appear that calcium increased in the pond in recent

years by an amount which roughly equals the increase in sulfate. This is probably the result of increases in calcium concentration in precipitation, as discussed above.

Dry deposition, evapotranspiration, and complex biogeochemical processes such as sulfate adsorption and sulfate reduction are not believed to be important in the sulfur budget of Rocky Mountain lakes [Turk and Spahr, 1991]. Sulfate thus moves through the watershed as a conservative constituent, with a number of processes affecting response time of surface water to changes in precipitation sulfate. Because of their locations at different points along the hydrologic flow path, the surface water sites are influenced differently by processes such as precipitation, snowmelt

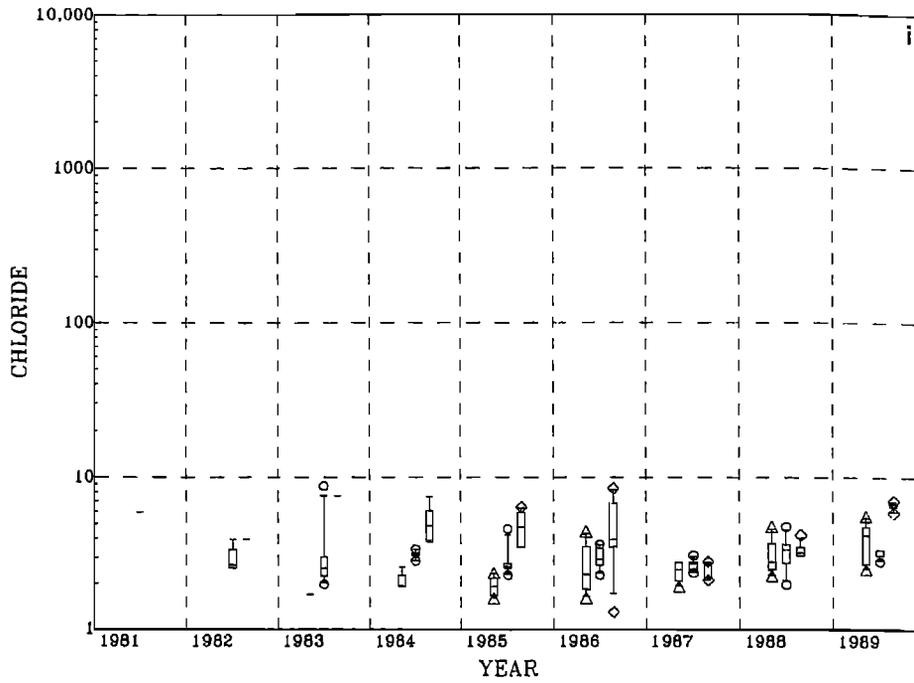


Fig. 4. (continued)

and direct evaporation, causing seasonal changes to differ for each site.

The sampling period for watershed data begins in July, which usually is the latter part of the snowmelt runoff period, and ends in late September, which marks the end of summer as the waters begin to freeze and precipitation occurs mostly as snow. Samples collected early in the season are most affected by the snowmelt runoff; later in the season, effects of evaporation and inputs from groundwater become more noticeable. Further, depending on the weather patterns, there may be significant precipitation input from thunderstorms during the summer months.

Annual mean, open water season sulfate concentrations were calculated for each of the surface water sites and compared to the annual sulfate concentration at each of the precipitation sites. Results of least squares correlation are presented in Table 2 and discussed below. Results also are included for the Marvine Ranch data set with 1988 data omitted, as discussed in the results section.

The pond is the surface water site expected to be most responsive to changes in atmospheric deposition because of its small drainage, shallow depth, short residence time, and absence of substantial groundwater input. As the snowpack melts, the pond water is flushed completely and is replaced

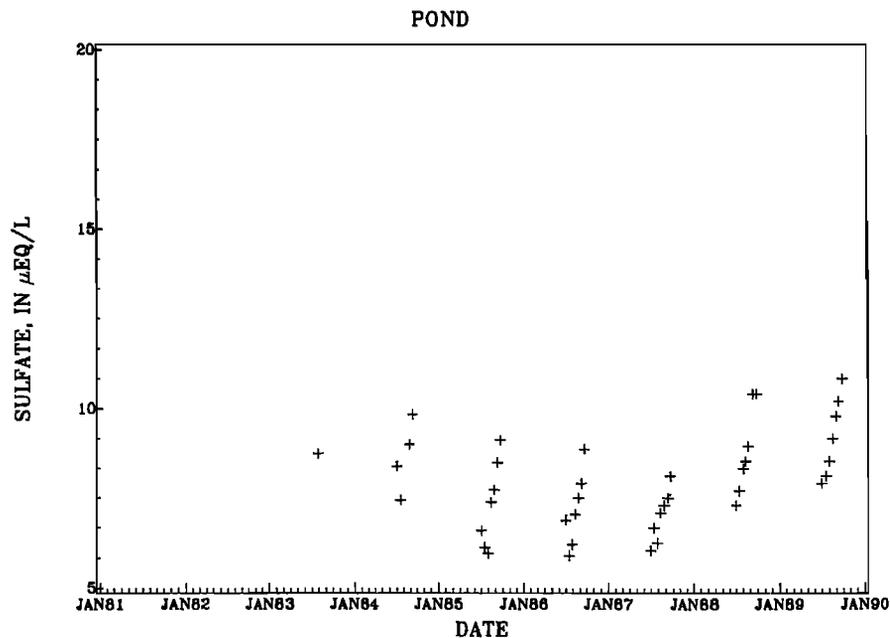


Fig. 5. Sulfate concentrations in the pond during open water season, 1983-1989.

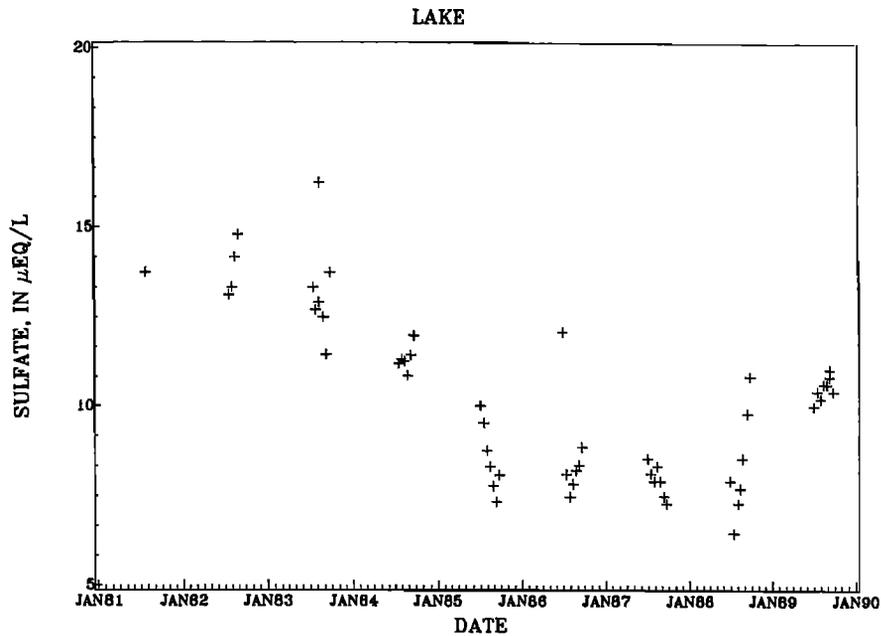


Fig. 6. Sulfate concentrations in Ned Wilson Lake during open water season, 1981–1989.

with water from the current year's snowmelt. However, particularly in years with a large snowpack, the pond may be flushed more than once (because the snow water equivalent depth in the snowpack is greater than the average depth of the pond). At the end of snowmelt the water in the pond is from the latter part of the snowmelt period. Because of the "ionic-pulse" effect, which causes a larger part of the ionic concentration of the snowpack to be delivered early in the snowmelt period, the snowmelt during the later part of the runoff period is more dilute than the overall snowpack [Cadle and Dasch, 1987]. Therefore, the runoff water remaining in the pond at the end of the snowmelt period (the

beginning of the sampling season for this study) is this dilute late-season snowmelt.

Sulfate concentrations in the pond at the beginning of July were generally slightly less than the annual mean sulfate concentrations in precipitation at Marvine Ranch (Figures 3, 5). During the open water months of July, August, and September, sulfate concentrations in the pond increased by approximately 50%. This increase was partly caused by input of summer precipitation, which has a larger sulfate concentration than the snowmelt, and partly caused by evaporation from the shallow pond (estimated open water evaporation from the pond is approximately 0.5 m, versus an

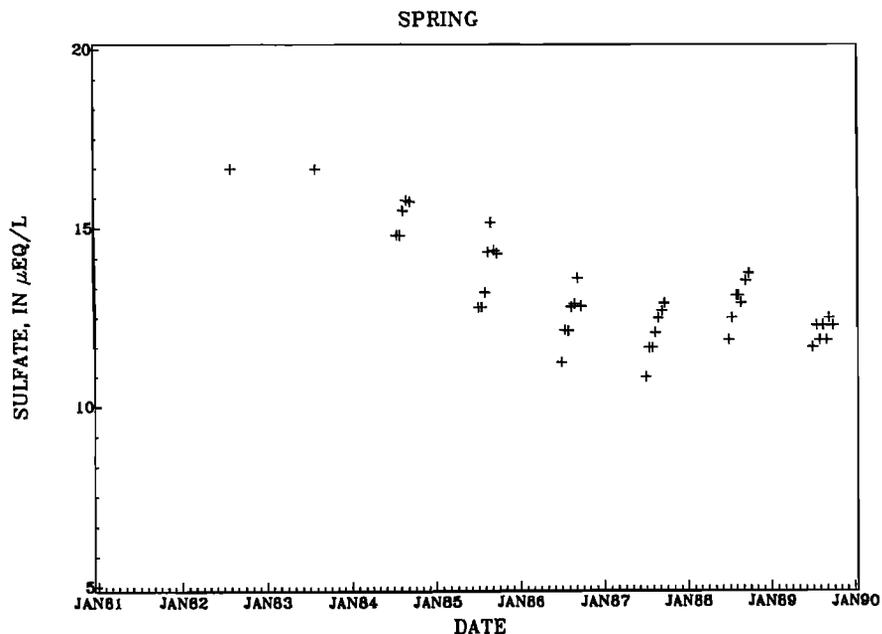


Fig. 7. Sulfate concentrations in the spring during open water season, 1982–1989.

SULFATE CONCENTRATIONS IN THE NED WILSON WATERSHED

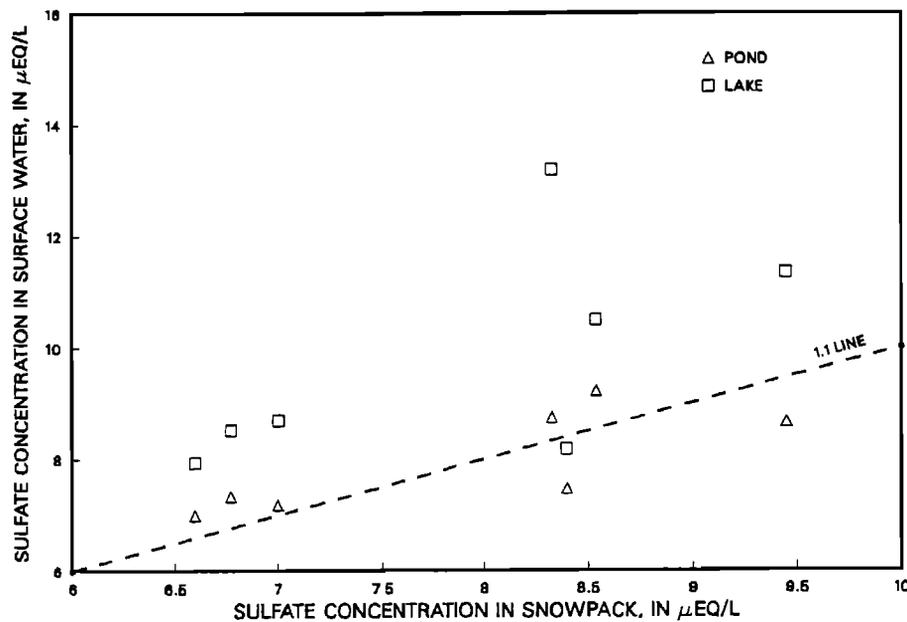


Fig. 8. Relation of sulfate concentrations in pond and lake to sulfate concentration in snowpack, 1983-1989.

average depth of 1.5 m). Annual mean sulfate concentrations in the pond were similar to sulfate concentrations in the snowpack (Figure 8). Annual mean sulfate concentrations in the pond showed little serial correlation (concentrations in a given year are independent of concentrations in the previous year), which would be expected because of the short residence time and absence of a groundwater reservoir. Most of the year-to-year variability can be explained by sulfate concentrations at any of the three precipitation sites (if the 1988 data from Marvine Ranch are omitted), which supports the concept of the pond functioning similarly to a cistern for snowmelt and precipitation (Table 2).

Ned Wilson Lake is located in a position along the flow path that is between the pond and the spring. The degree to which it is flushed during spring snowmelt is uncertain, both because the hydrologic characteristics of the local groundwater system are unknown, and because there may be incomplete mixing due to stratification. Estimates of maximum lake residence time are 1.7 to 3.3 years during the study period. A large snowpack may cause the lake to have lower ionic concentration at the beginning of summer because of more complete flushing and the "ionic-pulse" effect. Concentration by evaporation is greater during a hot, dry summer; direct precipitation may control concentrations during a rainy summer. If, for example, the shallow groundwater system is characterized by piston-type flow and an average residence time of about 2 years, a dry year will fail to flush the groundwater system, and groundwater discharge may be made up of water that originated in precipitation from previous years. On the other hand, a wet year may flush the groundwater completely, causing a fast response to changes in precipitation concentrations of sulfate.

In different years, sulfate concentrations increased by as much as 50% or decreased by as much as 30% during the summer months. Annual mean concentrations of sulfate in the lake tended to be larger than those in the snowpack

(Figure 8), probably because of a combination of evaporation, shallow groundwater input, and direct input of summer rain. For both the pond and the lake the points plotted in Figure 8 cluster near the 1 : 1 line, which indicates that a change in sulfate from precipitation produces a change of similar magnitude in sulfate in surface water. Despite the complications of interpreting seasonal variability in the lake, annual mean sulfate concentrations in the lake are correlated with sulfate concentrations at the three precipitation sites, although the relation is not as strong as it is for the pond (Table 2). The sulfate concentrations in the lake are serially

TABLE 2. Correlation of Sulfate in Surface Water to Sulfate in Precipitation

Precipitation Sites	Statistics	NWL Watershed Surface Water Sites*		
		Pond	Lake	Spring
NWL watershed Snowpack†	<i>R</i>	0.79	0.65	0.46
1983-1989	<i>p</i>	0.03	0.11	0.30
	<i>n</i>	7	7	7
Marvine Ranch wetfall‡	<i>R</i>	0.29	0.17	0.13
1982-1989	<i>p</i>	0.53	0.68	0.76
	<i>n</i>	7	8	8
Marvine Ranch wetfall‡	<i>R</i>	0.99	0.86	0.58
1988 data omitted	<i>p</i>	0.0002	0.01	0.18
	<i>n</i>	6	7	7
Sand Spring wetfall‡	<i>R</i>	0.88	0.67	0.32
1981-1989	<i>p</i>	0.01	0.05	0.44
	<i>n</i>	7	9	8

Statistics presented are: Pearson correlation coefficient *R*; probability $> R$ under $H_0: \rho = 0$; and number of observations *n*.

*Annual mean.

†Single measurement at maximum accumulation.

‡Volume-weighted mean.

correlated; because the lake residence time is greater than one year, the lake is not completely flushed each year. Multiple regression using the sulfate concentrations in the lake from the previous year and current year Marvine Ranch VWM sulfate in precipitation (omitting 1988 data) to predict current year concentrations of sulfate in the lake produces the following relation: (sulfate in the lake) = 0.43 (sulfate in the lake, previous year) + 1.02 (sulfate in precipitation) - 7.51, where adjusted r square = 0.87, overall equation (probability > F) = 0.007, and both dependent variables (probability > T) < 0.05.

Similar relations can be produced for the other precipitation sites, indicating a strong relation between sulfate in the lake and sulfate in precipitation, when serial correlation of sulfate in the lake is accounted for. This relation suggests a lake response to precipitation input of a year or less, compared to a response that is essentially immediate in the pond.

Sulfate concentrations in the spring are slightly larger than those in the pond or lake (Figure 7). Direct snowmelt runoff during the early part of the field season dilutes groundwater that flows into the pool where the spring is sampled. Sulfate concentrations in the spring water increase by as much as 20% during the sampling season, because overland flow ceases later in the summer. Evaporation and precipitation during summer are believed to have little effect on the seasonal pattern in this system. Annual mean sulfate in the spring is poorly correlated with sulfate at all of the precipitation sites (Table 2) and is serially correlated. Although size of the groundwater reservoir and the residence time before recharge from precipitation discharges into the spring are unknown, the reversal in 1988 of the downward trend in sulfate concentration indicates a short residence time, which is plausible given the hydrogeologic setting and large quantities of precipitation. If large sulfate concentrations in precipitation persist in the early 1990s, an upward trend in sulfate in the spring is anticipated.

CONCLUSIONS

The pattern of changes in sulfate concentrations at the surface water sites following changes in sulfate concentration in precipitation is consistent with the concept of atmospheric deposition as a primary source of sulfate in the surface waters of the Flattops Wilderness Area. Furthermore, the reversal in 1988–1989 of a downward trend in 1981–1987 indicates that the response of surface water chemistry to changes in deposition is direct and rapid. Differences in responsiveness of the individual sites were determined by their position along hydrologic flow paths, which can be indexed by hydrologic residence times.

The direction and magnitude of changes in sulfate concentrations of the surface waters were similar to those of precipitation. It appears that watershed processes in the Flattops Wilderness Area have at most a slight effect on the sulfate concentrations in surface waters. Seasonal changes in sulfate concentration which are superimposed on the long-term trends at each of the surface water sites help provide information about processes that control watershed chemistry.

The absence of a watershed source of sulfate, homogeneous geology, and relatively simple hydrology provide a good opportunity for studying trends caused by precipitation

in this watershed. Within the Flattops Wilderness Area, it is likely that the other high-altitude watersheds are responding similarly to precipitation, while responses of lakes and streams located in the valleys may be complicated by more complex hydrologic flow paths and longer residence times for groundwater.

Other watersheds of the Rocky Mountains, including those with similar acid-neutralizing capacity, may respond differently to changes in atmospheric sulfate input, depending on their hydrology and geology. The processes controlling watershed chemistry are poorly understood in high-altitude wildernesses in the region. However, it does seem from this study that changes in atmospheric deposition can be expected to produce immediate changes in aquatic chemistry in watersheds such as Ned Wilson Lake.

Though these results indicate a direct and rapid response of surface waters to changes in sulfate concentration in precipitation, questions remain to be addressed in future work. What is the geographic scope of these changes in sulfate concentrations in precipitation? Are local- or regional-scale processes the cause? Are the changes in precipitation chemistry simply natural fluctuations or are they the result of anthropogenic activities, and will further increases in sulfate concentration cause precipitation to become acidic?

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REFERENCES

- Cadle, S. H., and J. M. Dasch, Composition of snowmelt and runoff in northern Michigan, *Environ. Sci. Technol.*, 21, 295–299, 1987.
- Campbell, D. H., and J. T. Turk, Controls on precipitation sulfate in Colorado, in *International Mountain Watershed Symposium*, edited by I. Poppoff, C. Goldman, S. Loeb, and L. Leopold, pp. 350–359, Tahoe Resource Conservation District, South Lake Tahoe, Calif., 1988.
- Church, M. R., Direct/delayed response project: Predicting future long-term effects of acidic deposition on surface water chemistry, *Eos Trans. AGU*, 70, 801–803, 812–813, 1989.
- Church, M. R., P. W. Shaffer, K. N. Eshleman, and B. P. Rochelle, Potential future effects of current levels of sulfur deposition on stream chemistry in the southern Blue Ridge Mountains, U.S., *Water, Air, Soil Pollut.*, 50, 39–48, 1990.
- Eilers, J. M., et al., Characteristics of lakes in the western United States, vol. II, Data compendium for selected physical and chemical variables, *Rep. EPA-600/3-86/054b*, U.S. Environ. Protection Agency, Washington, D. C., 1987.
- Epstein, C. B., and M. Oppenheimer, Empirical relation between sulphur dioxide emissions and acid deposition derived from monthly data, *Nature*, 323, 245–247, 1986.
- Hidy, G. M., Acid deposition in the western United States, (Response to [Oppenheimer et al., 1985]), *Science*, 233, 10, 1986.
- Morrison, M., *Quality Assurance Plan for the Long Term Monitoring Project*, Environmental Protection Agency, Corvallis, Oreg., 1989.
- National Atmospheric Deposition Program, *NADP/NTN Data Reports: Precipitation Chemistry* (10 vols., 1980–1989), Natural Resources Ecology Laboratory, Colorado State University, Fort Collins, 1980–1989.
- Newman, L., and C. M. Benkovitz, (Response to [Oppenheimer et al., 1985]), *Science*, 233, 11–12, 1986.
- Oppenheimer, M., C. B. Epstein, and R. E. Yuhnke, Acid deposi-

- tion, smelter emissions, and the linearity issue in the western United States, *Science*, 229, 859–862, 1985.
- Reuss, J. O., B. J. Cosby, and R. F. Wright, Chemical processes governing soil and water acidification, *Nature*, 329, 27–31, 1987.
- Ryan, P. F., G. M. Hornberger, B. J. Cosby, J. N. Galloway, J. R. Webb, and E. B. Rastetter, Changes in the chemical composition of stream water in two catchments in the Shenandoah National Park, Virginia, in response to atmospheric deposition of sulfur, *Water Resour. Res.*, 25, 2091–2099, 1989.
- Spahr, N. E., and J. T. Turk, Estimation of evaporation from Ned Wilson Lake, Flattops Wilderness Area, Colorado, *Rep. 85-4244*, Water Resour. Invest., U.S. Geol. Surv., Denver, Colo., 1985.
- Turk, J. T., Use of stable sulfur isotopes to identify sources of sulfate in alpine lakes in the Rocky Mountains, paper presented at Rocky Mountain Section Meeting, Geological Society of America, Jackson, Wyo., May 21–23, 1990.
- Turk, J. T., and D. B. Adams, Sensitivity to acidification of lakes in the Flat Tops Wilderness Area, Colorado, *Water Res. Res.*, 19, 346–350, 1983.
- Turk, J. T., and D. H. Campbell, Prediction of lake alkalinity in the Rocky Mountains, *Air Quality and Acid Deposition Potential in the Bridger and Fitzpatrick Wilderness*, U.S.D.A. Forest Service Intermountain Region, Ogden UT, 1984.
- Turk, J. T., and N. E. Spahr, Chapter 14, Rocky Mountains, in *Acidic Deposition in Aquatic Ecosystems: Regional Case Studies*, edited by D. Charles, pp. 471–501, Springer-Verlag, New York, 1991.
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