

By

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INTRODUCTION

The degradation of aquatic ecosystems in Scandinavia and northeastern North America has been attributed to atmospheric deposition of acidic pollutants. Other environmental consequences, such as increased soil leaching of exchangeable plant nutrients, and damage to building materials and painted surfaces, are also blamed on acid deposition. The leaching of solutes accumulated and stored in snow has been demonstrated by sudden increases of acidity in surface waters during spring snowmelt periods (Galloway *et al.*, 1980; Johannes *et al.*, 1980; Siegel, 1981) and by elevated solute concentrations from outflow at the base of the snowpack (Colbeck, 1981; Johannessen and Henriksen, 1978; Seip, 1980). Abrupt acidity increases in surface waters led to fish kills in Norway (Leivestad and Muniz, 1976) and inhibited amphibian reproduction in temporary snowmelt ponds in New York (Pough, 1976). Stream and lake pH values from 6.0 to 6.4 adversely affect the fry and embryo stages of brook trout, cause reduced growth in brook trout, and are responsible for population declines in rainbow trout (Kling and Grant, 1984).

At sites in Norway, Japan, and northeastern Minnesota the first fractions of snow meltwater contain higher solute concentrations than later fractions. Most of the chemical load is released in the first third of the melt volume, but in some situations as much as 50 percent of the total hydrogen and sulfate present can leach from the snowpack in the first 10 percent of water content loss (Johannessen *et al.*, 1980). Concentrations of solutes in early snowmelt can be as high as 6.5 times concentrations in the bulk snow (Johannessen and Henriksen, 1978).

During mid-winter melt situations the fractionation effect may not be as pronounced. Field experiments at Sapporo, Japan verified the fractionation phenomenon for spring melt periods but showed decreased solute concentrations during mid-winter melts (Suzuki, 1982). Ionic concentrations in the surface zone of the snowpack changed dramatically in response to meltwater percolation induced by solar radiation, whereas smaller concentration variations in lower layers appeared to depend upon the amount of melt water reaching them from overlying layers. At a Sierra Nevada site, when recently fallen snow was artificially induced to melt, acidity increased throughout the melt after the first two melt fractions (Berg and Woo, 1983).

Findings in Scandinavia, Japan and the northern United States may not be applicable to the Sierra Nevada in California. The strong maritime influence on meteorologic processes there can produce winter rain storms as high as the crest of the central portion of the range and cause significant periods of near-freezing snow temperatures at forested sites. And snowpack accumulations are much greater than those described elsewhere (Smith and Berg, 1982); mid-winter melts occur once or twice annually to the 2200 m elevation in the central Sierra Nevada and typically the snowpack forms a sequence of variable density layers, some of which may impede the vertical movement of rain or melt water (Berg, 1982). These latter two characteristics of Sierra Nevada snowpacks, the proclivity for mid-winter melts at low and moderate elevations over much of the range, and the heterogeneity of snowpack development, affect the disposition of the chemical constituents resident in the snowpack and also influence the timing and frequency of outflows to the streams.

Information about the effects of acidic deposition on stream and lake water in California is scant, and the actual extent of the problem of surface water acidification is unknown. Acid deposition (pH < 5.6) in mountainous areas, however, has been documented (California Air Resources Board, 1984; McColl *et al.*, 1982; Melack *et al.*, 1983), although monitored sites are few and records of short duration. More extensive data are needed--particularly because thin soils, granitic bedrock geology, and poorly buffered water characterize much of the State's mountainous areas. Such sites potentially have minimal

Presented at the Western Snow Conference, April 16-18, 1985; Boulder, Colorado.

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ability to neutralize excess acidity entering their watersheds and are generally deemed susceptible to ecological damage (Melack *et al.*, 1985; Tonnessen and Harte, 1983).

Two factors distinguish atmospheric deposition in the mountainous areas of the State from lowland sites. First, in contrast to more arid sections of California, the northern and central mountain ranges may receive significant amounts of their total atmospheric deposition as wetfall; in the central Sierra Nevada, measurable precipitation falls on fully one-half of all winter days (Berg, 1985). Second, even though hydrogen ion concentrations in deposition may be greater in urban pollutant source areas, total acid deposition in the Sierra Nevada could be greater than source area deposition because of the greater volume of precipitation at the higher elevations (Brown and Skau, 1975; McColl *et al.*, 1982).

This paper analyzes precipitation, snowpack, and meltwater chemistry at a site in the central Sierra Nevada. It assesses evidence for a spring surge in snow meltwater acidity, and describes the chemical changes associated with rainfall onto the snow surface. This is a case study in which a single site is monitored for one field season. Replication in time and space is needed before generalizations can be made.

METHODS

During the winter of 1983-1984 information on the acidity (pH), and nitrate and sulfate solute concentrations of precipitation, streamflow, and snowpack layers and basal outflow was gathered. Stream alkalinity and discharge, precipitation amount and timing, and the rate of water outflow from the base of the snowpack were monitored as well. Melt, rainfall, and mixed rain and snow precipitation events were identified and related to periods of elevated basal outflow and stream discharge. These potential fractionation events were analyzed for acidification of the layer, stream and basal outflow samples.

The precipitation, layer, and basal outflow samples were collected at a 1/2 hectare forest clearing at the Central Sierra Snow Laboratory (CSSL)--a USDA Forest Service facility located slightly below and west of the crest of the Sierra Nevada northwest of Lake Tahoe (39° 22' 19.5" N. Lat., 122° 22' 15" W. Long.). A maritime climatic pattern dominates this site, causing high winter precipitation (1000 to 2500 mm) and snowpacks accumulating up to 5 m depth by early April. The snow season spans November to June, and while snowfall predominates, rain and mixed snow and rain also occur at the 2100 m elevation of the Lab.

Storms move toward CSSL from the west or southwest and potentially entrain pollutants from northern California's San Francisco Bay Area and Sacramento metropolitan areas as well as agricultural operations in the Central Valley. Adjacent to CSSL are several all-season residences, and Interstate Highway 80 is 1 kilometer north of the study site. These local sources of atmospheric pollutants are thought to be small and their impact on the findings of this study minimal.

Precipitation

Precipitation samples were collected at CSSL on an event basis by scooping fallen snow into polyethylene bottles or capturing rainfall in plastic bags. Analysis of deionized water stored in the plastic bags typically showed non-detectable sulfate (SO_4) concentrations and nitrate (NO_3) concentrations (mean = 0.42 eq/l) appreciably below nitrate samples of collected rainwater. In a similar pilot study, nitrate and sulfate concentrations of deionized water stored in the polyethylene bottles were 4 to 5 times less than mean solute concentrations of snowfall. Snow sample containers were sealed immediately after collection and allowed to melt at room temperature. Among the 111 precipitation samples collected between November 9, 1983 and June 7, 1984, one-fourth were replicated to assess measurement error. Longer events were sampled several times.

An alter-shielded, Belfort Instrument Company¹ weighing bucket gauge--with a 24-cm orifice--monitored precipitation amount at a point 10 m from the sample collector. Visual observations, in combination with air temperature measurements, were used to determine precipitation type.

¹ Trade names are mentioned solely for information. No endorsement by the U.S. Department of Agriculture is implied.

Snowpack basal outflow

Water leaving the base of the snowpack was collected from 2 1-m by 2-m plastic-lined aluminum pans located at the base of the pack 5 m from the precipitation sampling point. The pans were embedded 8 cm below the ground surface and had rims rising 8 cm above the surface. The rim configuration inhibited lateral flows either into or out from individual pans. PVC tubing directed outflow liquid from plastic drains centrally located in each pan to an underground sump, where the liquid drained into linear polyethylene containers. All sample water flow was along PVC or linear polyethylene surfaces. The timing and magnitude of basal outflow were monitored by an array of rock-filled aluminum pans which drained into tipping bucket mechanisms. Samples were collected weekly during the snowpack accumulation phase and several times daily during melt or rain-on-snow events.

Snowpack layers

Layer samples were collected from the north-facing wall of a snowpit excavated in a forest clearing 20 m from the precipitation chemistry collector. Layers were identified, by snowfall events, and sampled weekly throughout the accumulation and melt season. Before each sample collection, the wall of the pit was dug back 1 m. Samples were excavated from the pit wall, stored in linear polyethylene containers, and allowed to melt at room temperature.

Streamflow

Lower Castle Creek drains into the Yuba River 3 km northwest of CSSL. The creek was sampled at the 1860-m elevation weekly during the snow accumulation period and daily during the main melt period by immersing a 1-liter linear polyethylene bottle into the water adjacent to the channel edge. The basin upstream from the sample collection point covers approximately 2000 hectares and includes numerous granitic outcroppings on an otherwise slightly acidic cryumbrept soil. Forest vegetation is dominated by red fir and lodgepole pine but includes other conifers.

The nearest stream gauging station--approximately 9 km southeast of the Lower Castle Creek sampling site--at 1870 m elevation on a tributary to Onion Creek, monitored stream discharge at 15-minute intervals. The tributary drains a 50-hectare basin underlain by slightly to strongly acidic, rhyolitic loam soils. Weekly samples were collected at this site throughout the winter.

pH and alkalinity

Within a few hours after sample collection pH and alkalinity of each sample were determined by Forest Service employees at CSSL. The remaining sample liquid was transferred to linear polyethylene containers and immediately frozen for later determination of major ion species. The linear polyethylene storage containers had been soaked 36 hours in deionized water and rinsed with sample liquid. To measure pH, a Fisher Accumet meter equipped with a flowing junction electrode (Beckman 39501) was used. The electrode was calibrated at the onset of each measurement session with pH 7 and 4 buffers. The measurement procedure involved copious rinsing of the electrode in deionized water and immersing the electrode in the aliquot for 8.25 minutes, while stirring the liquid during the first 15 seconds of immersion. Replicated measurements on standard samples yielded values repeatable to ± 0.05 pH units.

Alkalinity was determined for stream water samples by titration to a fixed endpoint of 4.5 (Amer. Pub. Health Assoc., 1975). Gran titrations of a subset of the samples verified that results from the fixed endpoint titration procedure did not need correction for samples in the range of pH 6 and higher.

Sulfate and nitrate concentrations

Spectrophotometric methods were used to determine SO_4 and NO_3 solute concentrations. A barium chloranilate reaction was used to determine sulfate. A hydrazine reaction, reducing nitrate to nitrite, was used to determine nitrate concentration. The detection limits for nitrate and sulfate were rated 0.06 and 1.5 $\mu\text{eq/l}$ respectively. Replicated samples were analyzed to assess measurement error.

RESULTS AND DISCUSSION

If fractionation is occurring, the initial portions of outflow from the base of the snowpack should show lower pH's than later portions. Specifically, depressed pH, and probably elevated nitrate and sulfate concentrations, during the first 10 to 25 percent of outflow period should be observed. The degree of acidification will depend upon the purity of the precipitation; "clean" snowfall ($5.1 < \text{pH} < 5.6$) will have relatively few pollutants available for fractionation. pH minima during melt under this condition are likely to be 0.2 to 0.3 units below the mean. More acidic precipitation can be expected to show pH minima greater than 1 pH unit below the mean during the first 10 percent of the outflow. At the least, relative pH minima should be associated with outflow events.

Depending upon the pathways taken by the basal outflow, stream water may or may not be acidified. And soil processes may affect basal outflow pH. If pulses of acidified water move through the snowpack, the layer samples should identify the surges. Periods of increased basal outflow and streamflow, potentially associated with rain-on-snow or melt events, should be related to chemical changes in the snowpack layer and basal outflow samples and stream surface water.

Precipitation, stream discharge, snowpack development and basal outflow

Snow accumulation at CSSL was less than average during water year 1984: 10 percent less snow fell than normal. And the maximum snowpack depth (277 cm) was also 10 percent less than average. The maximum snow water equivalent (89 cm) approximated the average, but the snowpack melted out about 1 week earlier than usual. A January drought, not uncommon in this area (Smith, 1982), preceded significant precipitation during mid-February.

Basal outflow at CSSL increased during the periods December 13-16, 24-26, and 29-31, 1983, and January 23-25, February 11-13, and March 12-15, 19-22, and 25-28, 1984 (Table 1). Daily stream discharge increases in the Onion Creek tributary coincided with periods of elevated basal outflows but probably due to soil water storage, several periods of basal outflow increases (e.g., January 23-25) were not mirrored in stream discharge peaks. The coincident increases were appreciable, however, with basal outflows rising 1.5 to 9 fold above base level values and stream discharges rising slightly less. Except for the March 19-22 event--in which outflow was associated with high air temperatures--each outflow/streamflow event paralleled to a mixed rain and snow or rainfall event (Figure 1, Table 1).

Mixed rain and snowfall monitored in December were, in water equivalent, 2.6 cm from the 13th to the 16th, 15.8 cm from the 24th to the 26th, and 3.5 on the 30th. Measured basal outflow volume was greater than measured precipitation for the two December events for which the outflow record is complete, and doubled precipitation for the December 30 event, suggesting that appreciable melt was occurring. After December, rainfall was less frequent and approximated 0.5 cm on February 11-12, 0.5 cm on March 13-14, and 1.1 cm on March 26. Measured basal outflow during these events increased 0.5 cm (360%), 5.8 cm (480%), and 4.0 cm (100%) respectively. Although the mid-February basal outflow increase was small in absolute magnitude, both this increase and the late-March increase equalled the largest recorded for those 2 months.

Precipitation chemistry

The standard deviation of 19 snowfall pH measurements replicated to assess measurement error equalled 0.012--a value appreciably smaller than the resolution limit of the instrumentation. The mean snowfall value, 5.34, is more acidic than the reference pH of 5.6 (Table 2). Relatively few values were above 5.6, the third-quartile value equalling 5.43, suggesting that snow at this site is more acidic than water in equilibrium with atmospheric carbon dioxide. Rainfall pH's, averaging 4.91, were more acidic than snow or mixed rain and snowfall. And hail and graupel pH's were even lower. The sample sizes for the rain and hail/graupel precipitation types were small. Although the standard deviation of the rain values was relatively low, 0.28, pH's varied considerably within the hail and graupel group. We did not detect a trend through time for snowfall and did not have enough observations of the other precipitation types to evaluate any trends.

The relatively high standard deviation for mixed rain and snowfall (Table 2) is due partly to extreme variabilities during November and early December when pH values ranged from 4.6 to 6.4. Influxes of alkaline dust following the summer drought may be the cause of

Table 1. Precipitation, streamflow discharge, snowpack basal outflow and pH for precipitation, streamflow, and basal outflow during rain and mixed rain and snowfall, northcentral Sierra Nevada, 1983-1984.

Date	Precip amount (mm)	Stream discharge (cfs)	Basal flow (mm)	Precip pH		Pan pH		Stream pH	
				snow	mixed	pan 1	pan 2	Lo Castle Creek	Onion Creek
12/83									
13	10.2	0.72	--- ⁸	4.7 ²					
14	5.1	1.23	5.1						6.4 ¹
15	2.3	1.30	8 ⁴	4.6 ¹				6.0 ¹	
16	8.1	1.13	4.2						
17	7.4	1.06	3.7						
24	59.2	1.90	36.3						
25	61.5	6.10	122.8						
26	37.1	5.30	19.8	5.7					
29	1.5	1.90	8.7					6.8	
30	35.3	4.10	60.3	5.8	5.5				
31	0.0	3.20	6.0						
1/23/84	0.0	0.52	1.4				5.6		7.0
24	0.0	0.54	7.8	5.7				6.3	
25	0.0	0.53	4.6						
2/11/84	3.3	0.46	1.4						
12	5.6	0.50	6.4	5.4		4.9 ² ₁	5.2 ² ₃		
13	38.9	0.65	6.0	5.4		4.9 ¹	5.3 ³		7.2
14	9.6	0.63	2.8	5.4				6.9	
3/12/84	0.3	0.60	12.0						7.2
13	47.5	1.20	70 ⁴	5.4	5.1				
14	21.3	1.09	---	5.3		5.6	6.5 ⁵	6.8	
15	24.6	0.82	5.1	5.5					
18	0.0	0.70	6.9						
19	0.0	0.77	4.1						
20	0.0	0.92	33.6					6.2 ²	
21	0.0	1.06	---				6.3 ⁶	6.9	
22	0.0	0.98	---				6.0		
25	2.5	1.09	39.6						
26	11.4	1.48	80 ⁴		5.1 ⁷		5.7		7.1
27	0.0	1.28	24.4					6.9	
28	0.5	1.18	34.0					7.0	

¹ Seasonal low ² 2nd seasonal low ³ 3rd seasonal low ⁴ Approximate
⁵ Seasonal high ⁶ 2nd seasonal high ⁷ Rainfall ⁸ ---: Missing data

the high pH readings during the 2 months, but detailed analysis of storm patterns are needed before these data can be properly interpreted.

NO₃ and SO₄ solute concentrations were much greater for hail and graupel and rainfall than for snow or mixed rain and snowfall (Tables 3, 4). The means for NO₃ and SO₄ were 1.2 and 7.6 µeq/l respectively, for all precipitation types combined, compared with values of 1.3 and <6 µeq/l reported by Melack *et al.* (1983) for precipitation at Mammoth Mountain, California during the 1981-1982 winter. Variability in the CSSL concentrations for SO₄ in particular was high, with the third quartile values being at least three times the magnitude of the median. The correlation between pH and NO₃ was moderate, and equaled -0.43 and -0.79 for snowfall and rainfall, respectively. SO₄:pH correlations were much lower.

Table 2. pH of precipitation, basal outflow, and snowpack layers, and pH and alkalinity ($\mu\text{eq/l HCO}_3$) of stream water samples.

Item	pH										HCO_3						
	Precipitation				Outflow		Snowpack Layer				Stream		Stream				
	Rain	Mixed	Snow	Hail	Pan 2	Pan 3	A	D	H	L	Lo	Cas	On	Crk	Lo	Cas	On
N ¹	7	13	89	5	31	22	18	19	15	9	67	38	67	38			
MEAN	4.9	5.4	5.3	4.7	5.3	5.6	5.6	5.5	5.4	5.4	6.9	7.1	149	234			
MEDIAN	5.0	5.3	5.4	4.5	5.1	5.5	5.6	5.4	5.4	5.4	6.9	7.1	148	233			
STDEV	0.3	0.6	0.2	0.6	0.4	0.3	0.3	0.2	0.3	0.1	0.3	0.2	47	67			
MAX	5.2	6.4	5.7	5.7	6.4	6.5	6.4	6.2	5.8	5.5	7.4	7.6	266	420			
MIN	4.5	4.6	4.5	4.2	4.9	5.1	5.1	4.7	4.4	5.2	6.0	6.4	60	56			
Q3 ²	5.2	5.9	5.4	5.1	5.6	5.7	5.7	5.6	5.5	5.5	7.0	7.2	180	270			
Q1 ³	4.6	4.9	5.3	4.3	5.3	5.0	5.5	5.3	5.4	5.3	6.8	7.0	118	218			

¹ Sample size

² Third quartile

³ First quartile

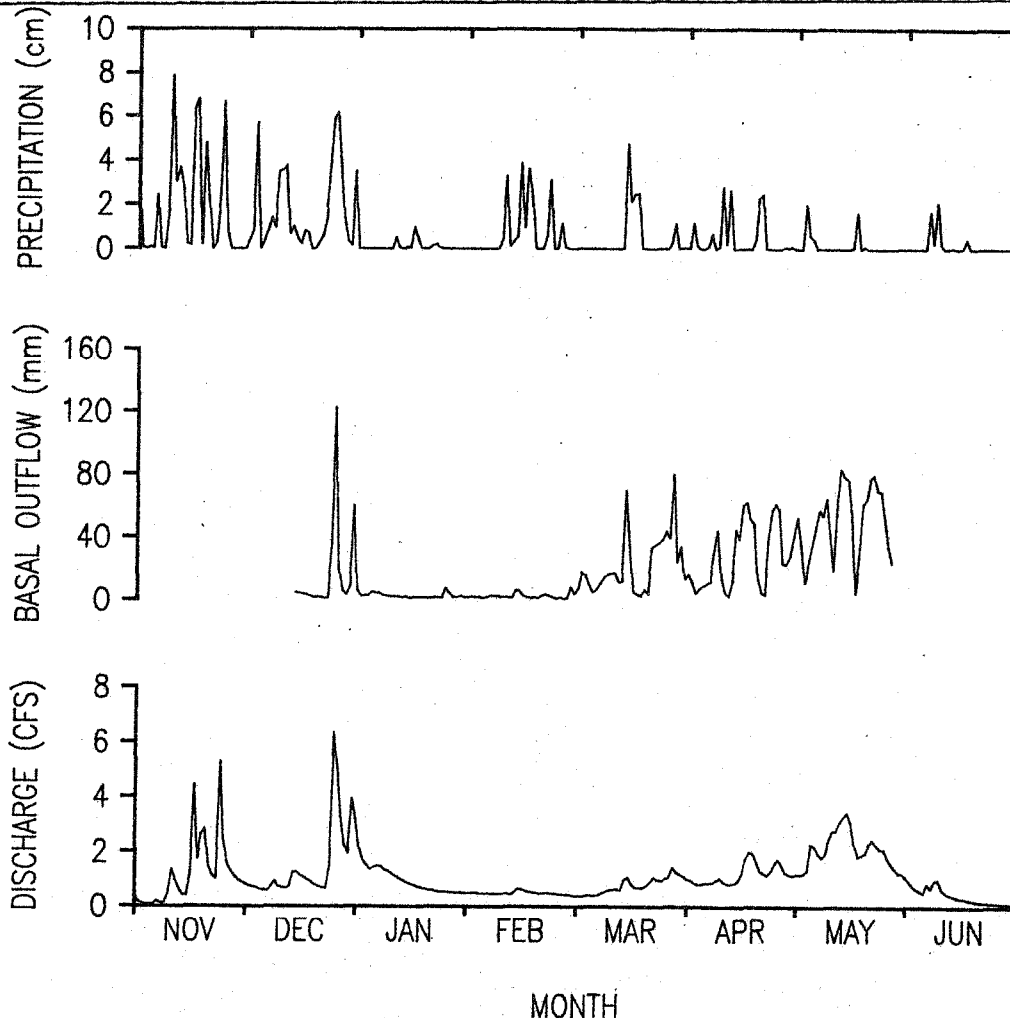


Figure 1. 1983-1984 precipitation amount and timing, stream discharge, and outflow from the base of the snowpack at the Central Sierra Snow Laboratory, northern California.

Table 3. Nitrate concentrations ($\mu\text{eq/l}$) of precipitation, basal outflow, snowpack layer, and stream water samples, Sierra Nevada, California.

Item	Precipitation				Outflow		Snowpack Layer				Stream	
	Rain	Mixed	Snow	Hail	Pan 1	Pan 2	A	D	H	L	Lo Cas	On Crk
N ¹	7	13	80	3	21	23	18	19	16	9	63	27
MEAN	2.4	0.6	0.9	7.4	1.6	1.2	0.2	0.4	0.7	0.3	0.2	0.1
MEDIAN	2.5	0.5	0.5	8.0	1.5	1.1	0.1	0.4	0.4	0.2	0.1	0.2
STDEV	1.5	0.4	1.0	4.6	1.1	0.5	0.2	0.3	0.7	0.1	0.4	0.4
MAX	5.0	1.6	6.4	11.7	3.3	2.7	0.6	1.2	2.8	0.5	2.7	1.7
MIN	0.7	0.2	0.0	2.6	0.1	0.3	0.0	0.1	0.0	0.2	0.0	0.0
Q3 ²	3.1	0.7	1.2	11.7	2.6	1.5	0.2	0.5	1.1	0.3	0.2	0.1
Q1 ³	1.0	0.3	0.3	2.6	0.8	0.8	0.1	0.2	0.2	0.2	0.1	0.0

¹ Sample size ² Third quartile ³ First quartile

Table 4. Descriptive statistics for sulfate concentrations ($\mu\text{eq/l}$) of precipitation, basal outflow, snowpack layer, and stream water samples.

Item	Precipitation				Outflow		Layer				Stream	
	Rain	Mixed	Snow	Hail	Pan 1	Pan 2	A	D	H	L	Lo Cas	On Crk
N ¹	7	13	80	3	21	23	18	19	16	9	63	27
MEAN	26.8	4.0	4.7	54.8	4.4	5.3	2.8	2.8	3.1	2.6	7.6	6.0
MEDIAN	7.3	1.3	1.9	21.0	4.2	2.5	1.4	1.5	1.5	0.8	3.9	5.0
STDEV	51.8	6.8	6.2	60.0	2.6	7.1	4.1	3.7	5.0	5.3	11.7	4.4
MAX	143	22	28	124	11	25	18	15	16	17	86	23
MIN	0.0	0.0	0.0	19.1	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0
Q3 ²	20	4.1	5.9	124	5.0	5.6	3.7	3.7	2.0	1.4	5.8	6.2
Q1 ³	3.9	0.3	0.4	19.1	3.0	1.5	0.4	0.2	0.5	0.6	2.5	3.5

¹ Sample size ² Third quartile ³ First quartile

Snowpack basal outflow chemistry

Evidence of fractionation should be most obvious in changes in the basal outflow chemistry when snow metamorphic processes alone shape the water chemistry and before soil effects complicate the situation. Nevertheless, several factors confound a simple association between outflow chemistry and fractionation. Stratigraphic features in the snowpack, such as high density horizontal layers, may direct liquid laterally, and potentially away from a ground-sited melt pan (Berg, 1982). Vertical conduits channel flow so that some sections of the snowpack are saturated while adjacent sections are dry (Kattelman, 1985). Such conduits were observed during the 1984 spring melt season. Depending upon the existing flow network and changes in its structure over time, water can vary widely in space and time in its release from the base of the snowpack. For instance, percolating water may force out liquid that has experienced some unknown amount of metamorphism so that displacement moves water further along the flow pathways, potentially leaving the pack and being sampled at a point in time asynchronous with the period of fractionation. The consequences of numerous percolation events, in combination with our poor understanding of the dynamics of water flow through the snowpack, inhibit a straightforward interpretation of the snowpack chemistry. The optimum time to identify fractionation in the field under maritime conditions on the West Coast may well be during the initial outflow events, before the confounding effects accumulate. The chemistry of early- and mid-winter outflows therefore take on added significance.

The two pans were sampled 31 and 22 times during the period December 30, 1983 to May 22, 1984. Unfortunately, outflow events before December 30 were not sampled, and data for that date suffer from the lack of preceding base level values for comparison. Outflow chemical characteristics from the two pans were similar. Samples from pan 1 were slightly acidic (mean pH 5.32) while the pan 2 samples had a pH mean of 5.58. Both pans showed elevated values during March and absolute or near-absolute minima during February, with pan 1 pH's 0.2 units lower during February than any other period and February 12 and 13 realizing pH's to 4.83 (Figure 2). The least acidic samples from pan 1 were collected in April and May, with the 3 highest pH's occurring after April 5. Except for one outlier, the pan 2 samples were exclusively in the range of 5.40 to 5.51 from April 8 to May 22.

The chemistries of the pre-spring outflow events which were associated with elevated streamflows and rainfall or melt conditions are of particular interest. pH at the initial samplings in both pans (on December 30 and January 4) approximated the respective means. Samplings on February 12 and 13, of outflow associated with the rain-on-snow event, were 4.86 and 5.23. In that these values were the lowest of the years, they are consistent with the fractionation hypothesis. However, basal outflow pH's during the second week in February, a period of base level outflow and stream discharge, were only marginally higher than the mid-February recordings. pH values of basal outflow during the mid-March outflow event, moreover, were appreciably above the mean and reached the seasonal high (6.49) for pan 2. Likewise, the March 20-22 and 26-27 outflow events were associated with pH values greater than the mean. The fractionation may have occurred early in the winter; by the time the snow was inundated with new percolating water in March it had already fractionated. The high pH's in April and May from pan 1 samples and the near-mean values from pan 2 support this contention, as does evaluation of the stream chemistry.

NO₃ and SO₄ solute concentrations from the basal outflow were elevated slightly from the corresponding snowfall values (Tables 3, 4). The third highest NO₃ concentration was recorded on February 12 in one pan and the highest from the second pan³ on March 26. For the other major outflow events, both NO₃ and SO₄ concentrations approximated, or were lower than, the mean value. In both pans³, maximum SO₄ concentrations were recorded in May. Correlation between pH and NO₃ was relatively high and reached -0.63 for one melt pan.

Stream chemistry

Sixty-seven samples were collected between October 17, 1983 and July 31, 1984 at Lower Castle Creek; five of these were replicated to assess measurement error. The pH and alkalinity mean and median values were nearly identical, suggesting minimal skewness (Table 2). Wide variations between means and medians for SO₄ and NO₃ signal the possible presence of outliers; single observations for both NO₃ and SO₄ were twenty fold greater than the median values (Tables 3, 4). Sample standard deviations for pH and HCO₃ were much lower than the mean values, while the NO₃ standard deviation was about 50 percent of the replicated mean. Sulfate replicate variability was large, moreover, and approximated the group mean. The small number of replications limits the use of these error assessments.

pH values of stream water samples ranged between 6.0 and 7.38. The two lowest values, recorded on December 15 and March 20, were synchronous with basal outflow and stream discharge increases. The four other subminima below 6.35 were not apparently associated with any meteorologic events. Except for two observations, April through June pH's were above 6.70 and increased through the rest of the summer (Figure 3).

Buffer capacity of Lower Castle Creek water was low: 77 percent of the samples had alkalinities less than 180 µeq/l, with only 10 percent above 200 µeq/l. Before early March, alkalinity was generally above 150 µeq/l. The creek water was less alkaline through the end of June and reached a minimum during the last week in May. These values compare with numerous summer alkalinities at the level of <60 µeq/l recorded for alpine lakes in California (Melack *et al.*, 1983) and a mean alkalinity of 103 µeq/l for 10 subalpine lakes in the Sierra Nevada (Tonnessen and Harte, 1983).

NO₃ and SO₄ sample concentrations were not closely associated over time with each other or with pH. Although maximum concentrations for NO₃ and SO₄ both occurred well into the spring melt period, correlations between the two³ were low--less than 0.19 in absolute magnitude.

The Onion Creek tributary, sampled 38 times by the end of August, 1984, recorded a pH minimum (6.43) on December 13, again during a major rain-on-snow event. pH was not elevated during other periods of elevated creek discharge (Table 1) and pH recordings from mid-January through mid-June were tightly distributed between 7.0 and 7.3; elevated pH's during the spring melt period were not observed.

During the monitoring period, Onion Creek had a greater buffering capacity than Lower Castle Creek. Except for the 6-week period in October and early November, alkalinities were consistently in the range of 200 to 300 $\mu\text{eq/l}$ and reached a maximum of 420. Correlations between Onion Creek pH, nitrate and sulfate values were low and influenced strongly by one or two nitrate and sulfate outliers valued between 4 and 20 fold greater than the associated medians.

Snowpack layer chemistry

Between January 6 and May 14, 1984, we sampled 12 layers each week at the CSSL snowpit and collected 189 samples from a snowpack that deepened from 197 cm on January 6, to 297 cm on March 17. The seven sample collections after March 17 were from an ablating pack. Layer thicknesses and densities varied and depended upon precipitation amount and densification of the snowpack.

Except for a pH minimum on January 17 in all layers, few patterns were obvious in the layer pH data. The lower five layers initially had relatively high pH's during January followed by subminima in mid-February and consistent values through the rest of the season (Figure 4). The January 17 minima were probably due to measurement error; neither basal outflow nor stream discharge increased in mid-January nor did any meteorological activity occur that might account for the January 17 minima.

Figure 2. pH of basal outflow, Central Sierra Snow Laboratory, 1983-1984, northern California.

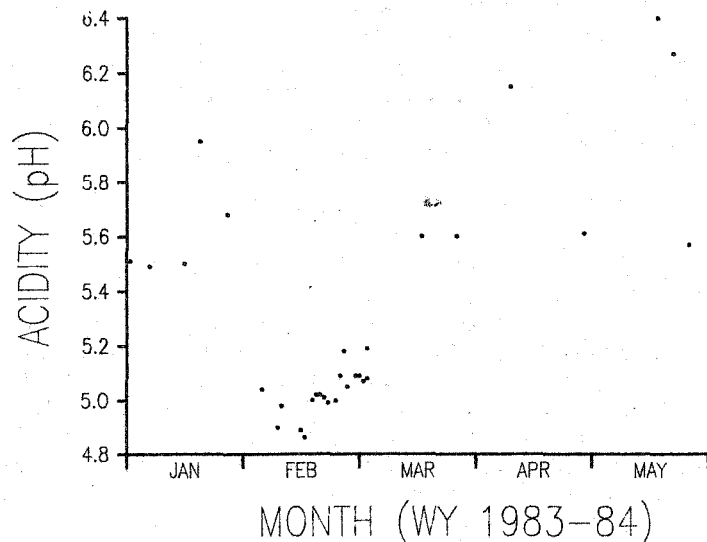


Figure 3. pH of Lower Castle Creek, 1983-1984, northern California.

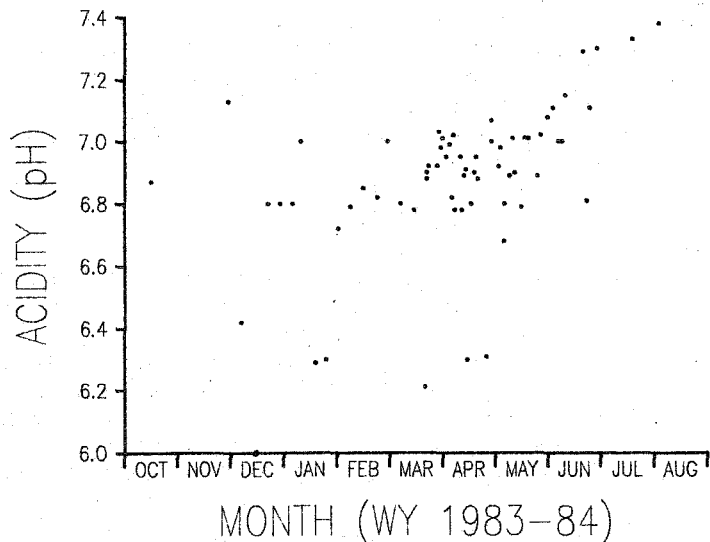
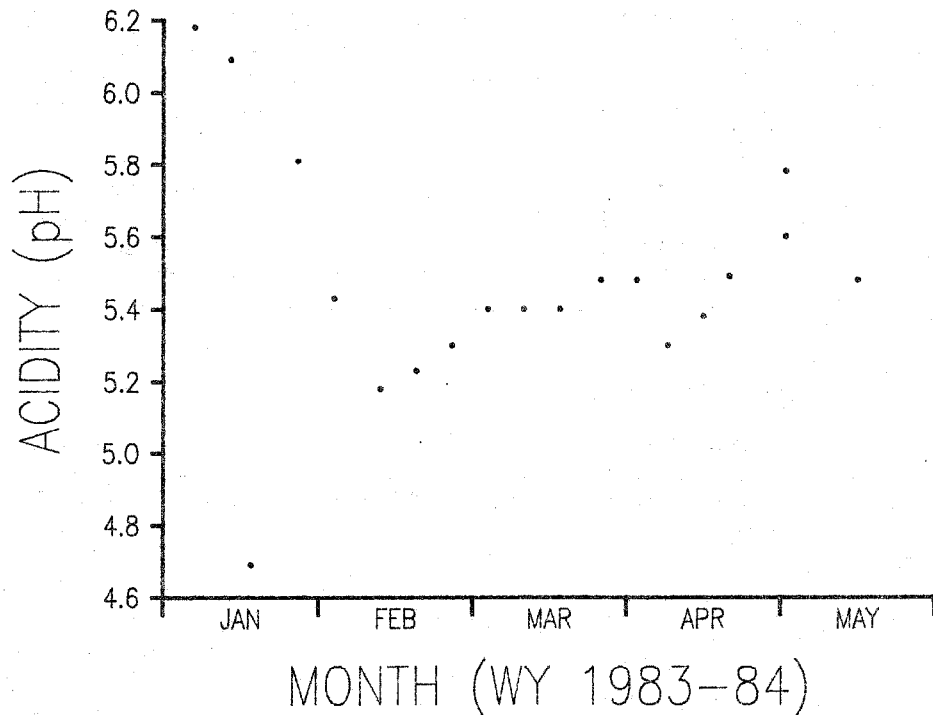


Figure 4. pH of snow layer originally deposited at 109 cm above soil surface



The layer closest to the ground had the highest mean pH value: 5.62. Means for the other layers varied between 5.37 and 5.49, with most between 5.42 and 5.48. These means were not significantly higher from a statistical viewpoint than the overall precipitation mean of 5.30. Variability within layers over time was low; standard deviations varied from 0.10 to 0.33 and were generally lower for layers near the snow surface. pH correlated highly between layers, with correlation coefficient values ranging from 0.77 to 0.97.

Layers were sampled once in February and once in March at times synchronous with outflow/stream discharge events. The February sub-minima occurred on the 11th, and coincided with the beginning of elevated basal outflow. Except for the January 17 measurement, in 75 percent of the layers the lowest recorded pH of the year occurred on February 11. These observations suggest the presence of a pulse of acidified flow during this period. On March 25, when the layers were sampled coincident with an outflow event, pH values were slightly greater than the seasonal mean. Other pulses of acidified flow through the layers may have occurred, but they may have been missed by the systematic weekly sampling schedule. During the main spring melt, a period originally expected to show elevated acidity, pH values did not decrease, and in fact a slight trend toward reduced acidities was evident.

Through time pH did not correlate well with either NO_3 or SO_4 in any of the layers. The correlation coefficient was typically in the -0.1 to 0.3 range. At any one sampling, NO_3 concentrations correlated moderately highly between layers, and reached a maximum of 0.84; correlations of SO_4 concentrations between layers were appreciably lower, again highlighting the high variability in sulfate. Similar to the basal outflow situation, layer SO_4 and NO_3 mean and median concentrations approximated those of mixed rain and snowfall and snow precipitation.

SUMMARY AND CONCLUSIONS

- During the main spring melt period, we found no evidence for acidification of stream waters or meltwater from the base of the snowpack at the Central Sierra Snow Laboratory.
- Fractionation may be occurring prior to the spring melt. Elevated acidities of stream and basal outflow water were synchronous with rain or mixed rain and snowfall events during early- and mid-winter when streamflow and basal outflow volumes increased.
- Stream waters had low buffering capacity (mean alkalinity between 150 and 240 $\mu\text{eq/l}$).
- Precipitation pH varied with precipitation type and was lowest at the sampled site for hail and graupel (mean = 4.7), followed by rain (mean = 4.9), snow (mean = 5.3) and mixed rain and snow (mean = 5.4). Standard deviations were 0.6, 0.3, 0.2, and 0.6 pH units, respectively, for the four types.

- The chemistry of snowpack layers remained relatively constant through time. Although mean pH's approximated 5.5 for both basal outflow and snowpack layers, pH was less variable in the layers than in basal outflow. Pulses of acidified water may have moved through the pack but little evidence of their chemical signature remained several days after such an event. A better understanding of the dynamics of water movement through the snowpack is needed.
- Mean nitrate and sulfate concentrations were in the range of 0.5 to 1.0 and 4 to 5 $\mu\text{eq/l}$ for mixed rain and snowfall and snow precipitation, respectively. Rainfall and hail and graupel had concentrations elevated appreciably above these levels while nitrate was less plentiful in the streams sampled. Sulfate and nitrate in the sampled basal snowpack outflow and snowpack layers approximated the mean concentrations of snow precipitation.
- Correlation between pH and nitrate and sulfate was poor. This may have been due partially to the existence of a small number of outliers, often up to one order of magnitude greater than the median nitrate or sulfate concentrations. Nitrate and sulfate data were not as useful as pH data because of their high variability.
- The ratio of median sulfate to median nitrate concentrations varied from 2.6 to 3.8 for the 4 precipitation types, and from 2.3 to 2.8 for basal outflow. The ratio was slightly higher for snowpack layers and increased dramatically, to the 20 to 30 range, for stream waters.

Future studies on the disposition of acidic pollutants in the snowpack should emphasize monitoring of precipitation chemistry by type. Flow-proportional sampling of basal outflow and stream water is recommended to identify chemical changes associated with short-term precipitation events, like rainfall onto the snow surface, which may trigger basal outflow. Layer or snowpack core sampling should be undertaken as well during rain or wet snowfall to provide the optimum means of identifying chemical fractionation signatures. Mesoscale measurements need to be made as well, to determine variability in precipitation and stream and lake chemistries on a basin scale.

ACKNOWLEDGMENTS

This research was partially supported by the Division of Atmospheric Resources Research, Bureau of Reclamation, U.S. Department of the Interior. We thank Kathy Tonnessen, Danny Marks, John Melack, and Dan Dawson for their critical evaluations of review drafts of the manuscript. Without the attention to detail and careful sample handling and analysis procedures followed by Randy Osterhuber, Todd Mihevc, and Richard Kattelmann, this study would not have been successfully completed.

REFERENCES

- American Public Health Association, 1975: Standard Methods for the Examination of Water and Wastewater, 14th ed. APHA, New York. 769 p.
- Berg, N.H., 1982: Layer and Crust Development in a Central Sierra Nevada Snowpack: Some Preliminary Observations, Proceedings of the 50th Western Snow Conference, Reno, Nevada, p. 180-183.
- _____, 1985: Unpublished data on file at the Pacific Southwest Forest and Range Experiment Station, USDA Forest Service, Berkeley, California.
- _____ and S. Woo., 1983: Snow Meltwater Chemistry Changes, Trans. Amer. Geophys. Union, (EOS), 64(45):710 (abstract).
- Brown, J.C. and C.M. Skau, 1975: Chemical Composition of Snow in the East Central Sierra Nevada. Center Wat. Resour. Res., Desert Res. Inst., Reno, Nevada, . Rept. AG-1, 13 p.
- California Air Resources Board, 1984: Second Annual Report to the Governor and the Legislature on the Air Resources Board's Acid Deposition Research and Monitoring Program, Air Resources Board, December, 1984. 85 p. + append.
- Colbeck, S.C., 1981: A Simulation of the Enrichment of Atmospheric Pollutants in Snow Cover Runoff, Water Resources Research, 17(5):1383-1388.

- Galloway, J.N., C.L.Schofield, G.R. Hendrey, N.E. Peters and A.H. Johannes., 1980: Sources of Acidity in Three Lakes Acidified During Snowmelt, p. 264-265 In Ecological Impact of Acid Precipitation. D. Drablos and A. Tollan (eds). Proc. Internat'l. Conf., Sandefjord, Norway, March 11-14, 1980. SNSF Proj. Rept. FA 65/80. As, Norway, 383 p.
- Johannes, A.H., J.N. Galloway and D.E. Troutman., 1980: Snow Pack Storage and Ion Release, p. 260-261 In Ecological Impact of Acid Precipitation. D. Drablos and A. Tollan (eds). Proc. Internat'l. Conf., Sandefjord, Norway, March 11-14, 1980. SNSF Project Rept. FA 65/80. As, Norway. 383 p.
- Johannessen, M. and A. Henriksen, 1978: Chemistry of Snow Meltwater: Changes in Concentration During Melting, Water Resources Research, 14(4):615-619.
- _____, M., A. Skartveit and R.F. Wright, 1980: Streamwater Chemistry Before, During and After Snowmelt, p. 224-225 In Ecological Impact of Acid Precipitation. D. Drablos and A. Tollan (eds). Proc. Internat'l. Conf., Sandefjord, Norway, March 11-14, 1980. SNSF Project Rept. FA 65/80. As, Norway. 383 p.
- Kattelman, R.C., 1985: Macropores in Snowpacks of the Sierra Nevada, Annals of Glaciology, In press.
- Kling, G.W., and M.C. Grant, 1984: Acid Precipitation in the Colorado Front Range: An Overview with Time Predictions for Significant Effects, Arctic and Alpine Research, 16(3):321-329.
- Leivestad, H. and I.P. Muniz, 1976: Fish Kill at Low pH in a Norwegian River, Nature, 259:391-392.
- McColl, J.G., L.K. Monette, and D.S. Bush, 1982: Chemical Characteristics of Wet and Dry Atmospheric Fallout in Northern California, Journal of Environmental Quality, 11(4):585-590.
- Melack, J.M., J.L. Stoddard and D.R. Dawson, 1983: Acid Precipitation and Buffer Capacity of Lakes in the Sierra Nevada, California, p. 465-472 In Internat'l Symp. on Hydrometeor., A.I. Johnson and R.A. Clark (eds.), Amer. Wat. Resour. Assoc., Bethesda.
- _____, J.M., J.L. Stoddard and C.A. Ochs, 1985: Major Ion Chemistry and Sensitivity to Acid Precipitation of Sierra Nevada Lakes, Wat. Resour. Res., 21. In press.
- Pough, F.H., 1976: Acid Precipitation and Embryonic Mortality of Spotted Salamanders, Ambystoma maculatum, Science, (4235):68-70.
- Seip, H.M., 1980: Acid Snow - Snowpack Chemistry and Snowmelt, In Huchinson, T.C. and M. Haras (eds). Effects of Acid Precipitation on Terrestrial Ecosystems, Plenum Press, N.Y. 654 p.
- Siegel, D.I., 1981: Effect of Snowmelt on the Quality of Filson Creek and Omaday Lake, Northeastern Minnesota, USDI, Geological Survey, Water-Resources Investigations 81-66. 81 p.
- Smith, J.L., 1982: The Historical Climatic Regime and the Project Impact of Weather Modification upon Precipitation and Temperature at Central Sierra Snow Laboratory, In The Sierra Ecology Project Volume 3. USDI, Bureau of Reclamation, Off. Atmos. Resour. Res. Denver, Colorado. 43 p.
- Smith, J.L. and N.H. Berg, 1982: Historical Snowpack Characteristics at the Central Sierra Snow Laboratory, a Representative Sierra Nevada Location, In The Sierra Ecology Project Volume 3. USDI, Bureau of Reclamation, Off. Atmos. Resour. Res. Denver, Colorado. 44 p.
- Suzuki, K., 1982: Chemical Changes of Snow Cover by Melting, Japanese Journal of Limnology, 43(2):102-112.
- Tonnessen, K.A. and J. Harte, 1983: Potential for Acid Precipitation Damage to Lakes of the Sierra Nevada, California, p. 505-509 In Internat'l Symp. on Hydrometeor., A.I. Johnson and R.A. Clark (eds.), Amer. Wat. Resour. Assoc., Bethesda, Maryland.