Solute Chemistry of Snowmelt and Runoff in an Alpine Basin, Sierra Nevada

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Snowpack runoff contributions to the hydrochemistry of an alpine catchment in the Sierra Nevada were evaluated in 1986 and 1987 by analyzing snowpack, meltwater, and stream water samples for major inorganic ions, conductance, acid neutralizing capacity (ANC), and silicate. An ionic pulse in meltwater with initial concentrations twofold to twelvefold greater than the snowpack average, varying with site and with ion, was measured in lysimeters placed at the base of the snowpack. Maximum concentrations of ions in meltwater were inversely related to the rate of snowmelt; melt-freeze cycles increased the concentration of solutes in meltwater. Hydrogen concentration in meltwater was buffered by ANC produced in part by the dissolution of particulates. The anionic pulse in meltwater was observed in stream waters during the first 30 days of snowpack runoff, with NO_3 concentrations in stream waters at this time about 1.6-fold greater than the average NO3 concentration for the time period of snowpack runoff, Cl^- about 1.5-fold greater and SO_4^{2-} about 1.3-fold greater. Maximum H⁺ concentration during snowpack runoff (increase of 170% over winter concentrations) occurred near maximum discharge. ANC minima occurred at maximum discharge as a result of dilution, with a decrease from winter concentrations of 70% in 1986 and 60% in 1987. Interactions between snowpack runoff and soils were important to the chemistry of stream water. Eighty to ninety percent of the H + stored in the snowpack was consumed before it reached the base of the catchment. Soils were a sink for NH4⁺ from snowpack meltwater, with less than 1% of the NH4⁺ released from snowpack storage exported from the basin as NH4⁺. Sulfate concentrations in stream waters were less variable than NO₃⁻ or Cl⁻ concentrations; sorption processes in soils were a likely cause for the regulation of SO_4^{2-} concentrations.

INTRODUCTION

Field and laboratory experiments have demonstrated that initial stages of snowmelt often have ionic concentrations many times higher than averages for the whole snowpack, an ionic pulse [e.g., Johannessen and Henriksen, 1978; Colbeck, 1981]. Physical and chemical processes that determine the occurrence, magnitude, and extent of an ionic pulse are not sufficiently understood to predict the ionic concentrations of snowpack meltwater at a point in time. Research to date on the chemistry of snow in the Sierra Nevada has shown no evidence of an ionic pulse in snowpack meltwater [Berg, 1986; Stoddard, 1987].

Acidification of lake and stream waters during spring snowmelt has been reported in the United States (e.g., in New York by Galloway et al. [1987] and in Michigan by Cadle et al. [1984]), in Canada [Jeffries et al., 1979], in Norway [Skartveit and Gjessing, 1979], and in Sweden [Dickson, 1980]. The differential release of ionic solutes in the first fractions of snowpack runoff is often considered to be the main cause of the acidification. Interactions between snowpack runoff and soils, which can modify the solute concentrations of snowpack runoff, are generally considered negligible in alpine areas underlain by granitic bedrock [e.g., Drever and Hurcomb, 1986]. Lakes in the Sierra Nevada have the lowest ionic concentrations in the United States [Landers et al., 1987], and catchments in the Sierra Nevada have a limited capacity to neutralize acids [Melack et al., 1985; Sickman and Melack, 1989]. An important question is how will snowpack runoff affect the hydrochemistry of high-altitude stream and lake waters in the Sierra Nevada.

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Paper number 90WR02774. 0043-1397/91/90WR-02774\$05.00 Here we report snowpack runoff contributions to the hydrochemistry of a headwater alpine catchment in the Sierra Nevada in 1986 and 1987 and discuss four questions. First, we determine whether the dilute snowpack of the Sierra Nevada does produce an ionic pulse. Second, we investigate the chemical and physical processes that determine the magnitude and extent of an ionic pulse in a natural snowpack. Third, we determine if the main effect of snowpack runoff is to dilute the ionic concentrations of stream and lake waters. Fourth, we discuss the hypothesis that interactions between snowpack runoff and soils can be neglected in alpine basins characterized by poorly developed soils.

SITE DESCRIPTION

The Emerald Lake watershed (ELW) is a north-facing glacial cirque, located on the upper Marble Fork of the Kaweah River drainage, in the southern Sierra Nevada of California (36°35'49"N, 118°40'30"W). The basin surface area is 120 ha, elevation ranges from 2800 m to 3416 m, and topography is steep and rugged, with a median slope of 31°. Exposed rocks comprise 33% of the surface area of the basin, unconsolidated clays, sand, gravels, and talus comprise about 47%. Bedrock in the basin is composed mainly of granite and granodiorite with minor mafic intrusions, aplite dikes, and pegmatite veins [Sisson and Moore, 1984; Clow, 1987]. Conversion of plagioclase to kaolinite is the predominant weathering reaction in the basin [Clow, 1987]. Poorly developed soils cover about 20% of the basin, and these are acidic and weakly buffered [Huntington and Akeson, 1986; Brown et al., 1990]. The primary clay minerals are kaolinite, illite, and several types of vermiculite [Weintraub, 1986]. Vegetation is sparse, including only scattered coniferous trees, although low woody shrubs are often abundant where soils occur [Rundel et al., 1989].



Fig. 1. Topographic map of the Emerald Lake watershed and location of snowpit sites: 1, tower; 2, inlet; 3, bench; 4, ridge; 5, ramp; 6, pond; 7, hole; 8, circue. Snowpit locations in 1986 were at 1, 2, 4, and 6; snowpit locations in 1987 were at 2, 3, 5, 6, 7, and 8. Subbasins are as follows: A, east joint; B, southeast gully; C, inflow 1; C+D, inflows 1 and 2; D, inflow 2; E, inflow 3; F, inflow 4; G, west joint.

Emerald Lake is a 2.7-ha cirque lake that is fed by 2-8 inflows, depending on the season, and is continuously drained by a single outflow. There are no known groundwater seeps into or out of the lake [Kattelmann, 1989]. The lake has a mean depth of 5.9 m, a maximum depth of 10.5 m, and is ice covered from November through May to July. Emerald Lake and the streams in its catchment are weakly buffered, calcium-bicarbonate waters [Melack et al., 1989] which are typical of high-altitude Sierran lakes [Melack et al., 1985; Melack and Stoddard, 1991]. Tonnessen [this issue] provides a more detailed site description.

METHODS

Sample Collection

Integrated samples of the entire snowpack were obtained by digging pits to the ground and collecting duplicate, contiguous, vertical cores in increments of about 40 cm. Snowpack samples were collected from the time period of maximum snow accumulation through the snowmelt season, at approximately weekly intervals in 1987 and less frequently in 1986. The snow 5–10 cm above the ground was not sampled to eliminate the possibility of contamination from soils or overland flow. The snow cores were transferred into polyethylene bags and kept frozen while in transit to our laboratory. Snow water equivalence (SWE) measurements were made using a 1-L stainless steel cutter [*Elder et al.*, this issue]. Temperature of the snowpack was measured every 10 cm with digital thermometers, calibrated to $\pm 0.2^{\circ}C$. Snowpits in 1986 were located at the inlet, tower, pond, and ridge; snowpits in 1987 were located at the bench, cirque, hole, inlet, pond, and ramp (Figure 1). Snowpit locations in 1987 were selected to represent the major elevational, slope, and radiation classes of the basin [*Elder et al.*, this issue].

Meltwater draining from the snowpack in 1987 was collected in lysimeters before contact with the ground. Locations of meltwater sites in 1987 were the same as snowpli sites: the bench, cirque, hole, inlet, pond, and ramp. We collected meltwater samples in an open, acid-washed, polyethylene container with dimensions of $10 \times 10 \times 50$ cm, a surface area of 0.05 m^2 , and a volume of 5 L. The lysimeter was placed in a 20-cm-tall snowcave excavated at the bottom of the snowpack on a thin (usually less than 5 cm thick) ice crust. Sample containers were situated so as to prevent surface runoff from flowing into the containers. The sampling interval was approximately weekly; on occasion samples were collected more frequently.

Solutes in rain were collected with a wet-only Aerochem Metrics model 301 sampler, located at the inlet. Sampling sites for water chemistry were located immediately above the lake for all inflows and immediately below the lake for the outflow (Figure 1). Stream water samples were collected at about weekly intervals during snowpack runoff and a intervals of 4–6 weeks from November through March in acid-washed, linear polyethylene bottles that were copiously rinsed with deionized water and then rinsed again with sample water.

Sample Storage and Analysis

Snow samples were stored frozen (-20°C) for 3-9 months until analysis. Snow samples were placed in covered polyethylene buckets and melted at room temperature in 1986 and at 4°C in 1987. Subsamples were filtered through prerinsed, 47-mm filters with about $1-\mu m$ pore size (Gelman A/E glass fiber in 1986 and the first part of 1987; Nuclepore polycarbonate filters in the remainder of 1987). Filtered samples were stored in the dark at 4°C for subsequent cation and anion analyses. Meltwater and stream water samples were subsampled in the field into unfiltered and filtered (Gelman A/E glass fiber, prerinsed with a minimum of 300 ml, 47-mm, 1.0-µm pore size) aliquots. Conductance and pH were analyzed on unfiltered samples, NH_4^+ and PO_4^{3-} were analyzed on filtered samples, and ANC was analyzed on unfiltered stream water, snowpack meltwater, and occasional snowpack samples using the Gran titration method.

The pH measurements were made with combination electrodes suitable for use in dilute waters (Sargent Welch S-30072-15 or Ross 8104) and a Fisher Acumet 805 pH meter. For each series of measurements the electrode was calibrated with pH 7.00 and pH 4.00 reference buffers and washed twice for 3 min with stirred deionized water. The pH calibration was then verified with low ionic strength solutions of HCl $(10^{-5} \text{ and } 10^{-4} \text{ N})$; calibration was repeated if the measured pH values of these solutions differed from the expected values by more than 0.1 units. The electrode was rinsed with an aliquot of sample, and the temperature compensated pH determination made on a fresh, quiescent sample after 5 min. Conductance was measured with a Yellow Springs Instruments Model 32 and a glass electrode with a 0.1 cell constant. Simultaneous temperature measurements were made, and conductivity was standardized to 25°C using a coefficient of 2% per °C. The conductivity cell was calibrated with dilute solutions of KCl.

Ammonium and phosphate were determined spectrophotometrically by the indophenol-blue and molybdenum-blue methods, silicate by the silic-molybdate method [Strickland and Parsons, 1972]. Calcium, magnesium, sodium, and potassium were analyzed with a Varian AA6 atomic absorption spectrophotometer. An air-acetylene flame was used; addition of lanthanum chloride suppressed chemical and ionization interferences during calcium and magnesium determinations. Especially dilute samples were also analyzed with a graphite furnace and manual 20 μ L injections. Chloride, nitrate, and sulfate were measured by ion chromatography (Dionex Model 2010i), employing chemical ion suppression and conductivity detection. Overall agreement of measured values of cations and anions with National Bureau of Standards certified controls warranted no corrections. Additional information on quality control and accuracy for snow and meltwater chemistry is in the papers by Williams and Melack [this issue] and Dozier et al. [1989]. Information for stream water chemistry is in the paper by Melack et al. [1989].

RESULTS

Water years 1986 and 1987 differed in several important ways. The peak accumulation of snow for the 1986 water year was 2000 mm SWE, about twice the 50-year mean, and peak accumulation for 1987 was 670 mm, about half the 50-year mean [*Elder et al.*, this issue]. Mean depth of snow over the basin at maximum accumulation was 3840 mm in

1986 and 1400 mm in 1987. The snow-covered area of the basin was about 95% on May 15, 1986 and 55% on the same date in 1987. Snow deposition in the two water years bracketed the snow conditions in the Sierra Nevada over the last 50 years. The volume-weighted mean ionic concentrations for each ion, for all snowpits on all dates, never exceeded 5.0 μ eq L⁻¹ in either year. Temperatures during the 1986 winter were relatively mild, with snow temperatures generally above -5° C; the ground and soils did not freeze. The winter of 1987 was relatively cold, with snow temperatures often below -5° C; extensive freezing of the ground and soil occurred before snow began accumulating. Sheets of anchor ice in streams were common in 1987 but not in 1986. Ice and snow cover on Emerald Lake in 1986 was about 6 m in thickness and persisted into late July; in 1987, ice and snow cover was about 1 m in thickness and was gone by early May.

Snowpack Meltwater

The enhancement of ionic concentrations in meltwater was assessed using two different techniques. In 1986 the ratio of the ionic concentration of meltwater to the snowpack was calculated indirectly from losses of the ionic loads and SWE in snow cover during the period of snowpack runoff. Anions and base cations were concentrated threefold to fourfold, while there was no enhanced loss of H⁺ [Williams and Melack, 1989]. Wet deposition during the period of snowpack runoff in 1986 added less than 1% of the amount of ions and water stored in the snowpack. In 1987, meltwater draining from the snowpack was collected in snow lysimeters before contact with the ground. Concentrations of inorganic ions in 1987 were high in the initial stages of snowpack meltwater relative to bulk snowpack concentrations, then generally declined with time except for H⁺ (Figures 2 and 3). Ionic concentrations in meltwater increased noticeably after sporadic spring precipitation, which began on April 27. Charge balance in meltwater in 1987 was maintained by the presence of acid neutralizing capacity (ANC) (Figure 4). Snowpack measurements and calculations of carbonate equilibrium reactions show that ANC concentrations in the snowpack were always less than 1 μ eq L⁻¹. Silicate and PO_4^{3-} concentrations in meltwater were generally near detection limits and always less than 1 μ mol L⁻¹ and 1 μ eq L⁻¹, respectively.

Solutes moved from the top of the snowpack toward the bottom of the snowpack as snowpack temperatures increased toward 0°C. Prior to the initiation of snowpack runoff at the cirque on April 17, 1987, NO₃⁻ and SO₄²⁻ concentrations in the upper portion of the snowpack decreased, while NO₃⁻ and SO₄²⁻ concentrations in the lower portion of the snowpack increased (Figure 5). After the initiation of snowpack runoff the upper portion of the snowpack continued to lose NO₃⁻ and SO₄²⁻, as did the lowest layer of the snowpack. The increase in concentrations of NO₃⁻ and SO₄²⁻ in the layer from 90 to 40 cm above the ground on April 23 indicates that lateral flow of meltwater may have occurred.

Ionic concentrations increased in meltwater after several melt-freeze cycles between April 18 and April 22, 1987. At the inlet site, Ca^{2+} and Mg^{2+} showed a several-fold increase in concentration at this time, matched by an increase in ANC concentration (Figure 4). All other ions except H⁺ also increased in concentration but to a lesser extent. Similarly,



Fig. 2. Snow water equivalence and the concentration of selected ions in the snowpack (open boxes) and in snowpack meltwater (solid boxes) at the bench in 1987. Solute concentrations in the initial fraction of meltwater were higher than bulk snowpack concentrations, then decreased with time. The increase in meltwater concentrations on April 29 was due to rainfall.

at the cirque site all ions except H⁺ increased in concentration over the same time period (Figure 3). Acid neutralizing capacity at the cirque increased from 7.5 μ eq L⁻¹ to 15.3 μ eq L⁻¹ at this time. Ionic concentrations at the bench site followed a similar pattern but with a smaller change in concentration (Figure 2). At the inlet site the strong acid anions Na⁺, Mg²⁺, and NH₄⁺ were highly correlated (r for all combinations ranging from 0.83 to 0.99), while ANC was highly correlated with Ca²⁺ and Mg²⁺ (r = 0.83 and 0.96). Hydrogen at the same site was inversely correlated with Ca²⁺, Mg²⁺, and ANC (r = -0.70 to -0.76) and not correlated with other ions. After rain events on April 27 the concentration of ANC in snowpack meltwater was near zero at all sites.

The larger the melt rate the lower the enhancement of ionic concentration in meltwater (C_m) relative to bulk snow concentration (C_p) . For example, at the inlet after 9 days of melt, SWE was reduced 31%, and C_m/C_p for NO₃⁻, SO₄²⁻, and Cl⁻ was 2 or less (Figure 6). In contrast, after 8 days of melt at the cirque, SWE was reduced about 11%, and C_m/C_p for the three ions was about 3-4. Comparing the C_m/C_p ratios at equal melt fractions of 0.08, SO₄²⁻ was 10.9 at the cirque and 2.9 at the inlet, while NO₃⁻ was 6.6 and 2.7, respectively. Sulfate had a greater enrichment in the initial fraction of meltwater at the bench and cirque sites than did

Fig. 3. SWE and the concentration of selected ions in the snowpack (open boxes) and in snowpack meltwater (solid boxes) at the cirque in 1987. Solute concentrations in the initial fraction of meltwater were higher than bulk snowpack concentrations. Solute in meltwater increased in concentration on April 23, after a series of melt-freeze events. The increase in meltwater concentrations on and after April 29 was due to rainfall.

NH₄¹

Ca2.

Na⁺

13 22

Mav

29

April

NO₃ or Cl⁻. The NO₃ and SO₄² values of C_m/C_p decreased to 1 or lower after the first 30% of melt at the inlet and bench sites, while Cl⁻ values remained greater than 1 after 30% of melt. Chloride enhancement in the first fraction of snowpack meltwater was lower than NO₃ or SO₄², except in the first fraction of meltwater at the inlet.

Spatial variability in the rate and timing of snowpack runoff produced differences in the timing of ionic pulses a individual sites. For example, on April 23, 1987, N0₃ concentrations at the cirque (24 μ eq L⁻¹) were eightfold higher than at the bench (3 μ eq L⁻¹). In turn, the spatial variation in the chemistry of meltwater caused spatial variation in the ionic loading from snowpack meltwater to soil and rock surfaces. For the date above, NO₃⁻ loading from snowpack meltwater was 330 μ eq m⁻² at the bench, 3.5 μ et m⁻² at the inlet, and 1,540 μ eq m⁻² at the cirque.

Water and ionic loading from wet deposition during the period of snowpack runoff in 1987 were important inputs to the hydrology and chemistry of snowpack runoff (Table 1). Precipitation during spring runoff (April 27 to June 8) deposited about 2.2×10^3 eq of H⁺ to the basin, compared to the 1.6×10^3 eq of H⁺ stored in the snowpack on April 27. The combination o high ionic concentrations and a large amount of water in sprint precipitation resulted in more ionic loading from spring snow



Fig. 4. Time series of major inorganic ions in snowpack meltwater at the inlet, 1987. Calcium, Mg^{2+} , and acid neutralizing capacity increased in concentration after a series of melt-freeze cycles from April 18 to 22, while the concentration of H⁺ decreased at this time. The increase in meltwater concentrations on and after April 29 was due to rainfall.

fall and rainfall than from winter snowfall for NO₃, SO₄²⁻, NH₄⁺, Na⁺, and Mg²⁺ in water year 1987. After April 27 the chemistry of snowpack runoff in 1987 was therefore a combination of snowpack meltwater and spring precipitation.

Chemistry of Stream Water

Discharge of inflowing streams in 1986 increased because of snowpack runoff beginning in early April, peaked in early May, followed by a decrease due to a cold spell, and remained large through the month of June (Figure 7). Snowpack runoff in 1987 also started in early April, with discharge generally high until a cold spell at the end of May. Discharge then increased after rainstorms in early June, and by the end of June discharge was near presnowpack runoff amounts. Discharge from the basin during snowpack runoff in 1986 was threefold greater than in 1987, and snowpack runoff lasted about 2 months longer in 1986 than in 1987.

Silicate concentrations of inflowing streams in both years decreased from a winter concentration of about 55 μ mol L⁻¹ to a minimum of about 20 μ mol L⁻¹ (Figure 7). The sum of basic cations ($C_b = Ca^{2+} + Mg^{2+} + Na^+ + K^+$) in 1986 also decreased from a winter concentration of about 55 μ eq L⁻¹ to a minimum of about 20 μ eq L⁻¹. In 1987, C_b followed a similar pattern, except that values at all times were slightly higher than in 1986. Ammonium concentrations in both years were generally at or below detection limits and never exceeded 2 μ eq L⁻¹ (not shown). The sum of strong acid anions ($C_a = NO_3^- + SO_4^{2-} + CI^-$) in 1986 increased during the first part of snowpack runoff and then decreased with time, and in 1987, concentrations were more variable as a result of spring precipitation.

Temporal differences in the initiation of snowmelt within the ELW caused a spatial difference in the NO_3^- and SO_4^{2-} concentration of streams flowing into Emerald Lake in 1986 (Figure 8). Snowmelt started in a southeast-facing basin (east joint), then progressed temporally to more north-facing basins [Williams and Melack, 1989]. The initiation of snowmelt in the subbasins of the ELW spanned about 20 days, from April 14 at the east joint and inflow 1 to May 5 at inflow 4. Nitrate and SO_4^{2-} concentrations in streams were highest at the initiation of snowmelt in each subbasin, then decreased as the amount of snowmelt increased. For example, on May 18, 1986, NO₃⁻ concentration in the east joint, inflow 1, inflow 2, inflow 4, and the outflow was 0 μ eq L⁻¹, 6.1 μ eq L⁻¹, 10.3 μ eq L⁻¹, 18.0 μ eq L⁻¹, and 10.3 μ eq L⁻¹, respectively. Nitrate and SO_4^{2-} concentrations in the outflow remained elevated for a longer time period than any of the inflows to the lake. Logistical problems caused by the 3to 6-m deep snowpack prevented collection of stream samples from most inflowing streams before May 1. In 1987 the pattern of NO_3^- and SO_4^{2-} concentrations in inflowing streams and the outflow was similar to that in 1986, until the advent of precipitation on and after April 27.

Discharge in the outflow followed a similar pattern to that of the inflowing streams (Figure 9). The increased discharge in the outflow in February and March 1986 was due to avalanches and snowfall forcing water out of the lake. The strong acid anions $(NO_3^-, SO_4^{2-}, and Cl^-)$ in the outflow increased in concentration during the first 30 days of snowpack runoff in 1986, then decreased in concentration to below winter levels at maximum discharge (Figure 9). In 1987 the strong acid anions also increased in concentration in the first 30 days of snowpack runoff. However, in contrast to 1986, concentrations remained elevated through the period of maximum discharge, which coincided with the period of spring precipitation in 1987.

Silicate concentration in the outflow in 1986 decreased steadily from a winter concentration of 60 μ mol L⁻¹ to a minimum of 20 μ mol L⁻¹ toward the end of snowpack runoff (Figure 9). In 1987, silicate concentration increased from a



Fig. 5. A time series at the cirque in 1987 of NO_3^- and SO_4^{2-} concentrations with snowpack depth prior to (March 31 and April 9) and after (April 23) the initiation of snowpack runoff on April 17. The depth of the snowpack decreased with time. As the temperature of the snowpack increased with time to 0°C, solute concentrations near the top of the snowpack decreased while solute concentrations near the bottom of the snowpack increased.

winter concentration of 26 μ mol L⁻¹ to 40 μ mol L⁻¹ at the beginning of runoff, then decreased to 20 μ mol L⁻¹ in early June. Minimum ANC concentrations occurred at maximum discharge, with ANC decreasing from a winter concentration of about 40 μ eq L⁻¹ to 12 μ eq L⁻¹ in 1986 and to 16 μ eq L⁻¹ in 1987, decreases of 70 and 60%, respectively (Figure 9). After maximum discharge, ANC concentration in both water years increased steadily toward presnowpack runoff concentration. Hydrogen ion concentration in both water years peaked near the time of maximum discharge (Figure 9). Maximum concentration of H⁺ in the outflow for both water years was about 2 μ eq L⁻¹, an increase of 170% over the winter concentration of 0.7 μ eq L⁻¹. The C_b in the outflow remained near winter values (50 to 60 μ eq L⁻¹) during the first 30 days of snowpack runoff in 1986, then decreased consistently during the remainder of snowpack runoff to a minima of 23 μ eq L⁻¹ (Figure 9). In 1987, C_b increased from 45 μ eq L⁻¹ to 60 μ eq L⁻¹ during the first 30 days of snowpack runoff and then decreased to slightly below the winter concentration during the remainder of snowpack runoff. Ammonium concentrations were generally at or below detection limit in the outflow and never exceeded 1



Fig. 6. Ratio of meltwater concentrations (C_m) to average bulk snow concentration at the start of snowpack runoff (C_p) , as a function of snowmelt, for SO_4^{2-} , NO_3^- , and Cl^- at the bench, inlet, and cirque sites in 1987. The lower right panel is a time series of the fraction of snowmelt at each of these sites. The C_m/C_p ratios increased as the rate of snowmelt decreased.

	April	Мау				June	
	27	5	12	19	26	6	8
Water, mm	8	32	27	17	29	12	14
pН	4.48	4.94	4.87	5.13	5.04	5.06	4.55
Conductance, $\mu S \text{ cm}^{-1}$	25.0	16.7	12.5	13.4	29.7	13.2	19.2
н'	33.1	11.5	13.5	7.4	9.1	8.7	28.2
NH₄ [†]	24.4	48.2	32.2	45.5	133.1	30.9	44.8
Ca ²⁷	28.4	43.9	14.5	19.5	23.5	6.4	8.7
Mg ²⁺	4.9	5.8	3.3	4.9	9.1	1.4	2.6
Na ⁺	6.1	10.0	2.2	4.4	27.0	53.3	38.1
К *	3.3	2.8	3.8	6.9	3.6	1.4	1.4
NO ₁	43.1	45.2	21.9	39.2	95.5	14.9	41.1
SO ²⁻	38.9	47.7	31.2	29.4	74.1	16.9	33.1
CI	5.6	6.5	4.8	4.5	18.9	5.2	3.9

TABLE 1. Rainfall Chemistry During Spring Runoff, 1987

 μ eq L⁻¹ (not shown). Within-lake processes (dilution and/or nutrient cycling) may have been responsible for the increase in silicate and C_b concentrations of the outflow during the first part of snowpack runoff in 1987, due to an increase in lake residence time of about tenfold during the winter of 1987 compared to the winter of 1986. The longer residence time in 1987 was primarily the result of a larger lake volume due to a thinner ice cover in 1987 compared to 1986.

Mass Balance Calculations

Biogeochemical interactions between the basin's terrestrial components and snowpack runoff can be partially determined by comparing the loading of ions stored in the snowpack to that in streams flowing into Emerald Lake (Table 2). Streams flowing into the lake, rather than the lake outflow, were used for the loading calculations so as not to confound mass balance calculations with ionic sources or sinks within the lake. Ionic storage in the snowpack was calculated as the ionic volume-weighted mean concentration of snow-covered area times snow water equivalent and includes spring rain and snow events. Stream loading was calculated as discharge (measured every 15 min) times concentration (sampled about weekly) during the period of snowpack runoff (April 1 through July 30, 1986, and April 1 through June 30, 1987). Calculations and error analysis for ionic loading in the snowpack are described by *Williams and Melack* [this issue]; calculations and error analysis for discharge measurements are described by *Kattelmann and Elder* [this issue]. Sampling protocol and error analysis for the sampling of stream water are described by *Melack et al.* [1989].

Hydrogen showed a similar pattern for both years, with more H⁺ released from the snowpack than reaching Emerald Lake (Table 2). Seventy-seven percent of the H⁺ released from the snowpack was consumed before it reached the lake in 1986, and 89% was consumed in 1987. The basin was a source of about 20% of the NO₃⁻ in stream waters in 1987, and a large sink (40%) for the NO₃⁻ in wet deposition in 1987. Sulfate showed the same pattern as NO₃⁻, with much more SO₄²⁻ in stream water than stored in the snowpack in 1986 and with basin retention of the SO₄²⁻ in wet deposition in 1987. Chloride in 1987 acted conservatively



Fig. 7. Discharge, silicate, C_b , and C_a of inflows prior to and during the period of snowpack runoff in 1986 and 1987.



Fig. 8. Nitrate and SO_4^{2-} concentrations of inflowing streams to Emerald Lake in 1986 (and its outflow) compared to the percentage of snowmelt in their respective subbasins. Concentrations in inflowing streams were highest at the initiation of snowmelt, then decreased with time (adapted from *Williams and Melack* [1989]).

during the time period of snowpack runoff. The small amount of Cl⁻ retention (12%) indicated by the mass balance calculations is within the error of analytical precision for Cl⁻ (13%). Little of the NH₄⁺ released from storage in the snowpack reached Emerald Lake as NH₄⁺.

DISCUSSION

Chemistry of Snowpack Meltwater

Snowpack meltwater in the ELW was ionically concentrated relative to bulk snowpack concentrations. *Stoddard* [1987] has conducted the only other investigation on the chemistry of snowpack and snowpack meltwater at a highelevation site in the Sierra Nevada. At the Gem Lake catchment (elevation 3,341 m), Stoddard reports no evidence for an ionic pulse in snowpack meltwaters. Stoddard collected free water by spinning snow samples in a plastic centrifuge, sampled at the base of the isothermal layer of the snowpack. His centrifuge may have removed snow as well as free water from the snowpack. Furthermore, Stoddard sampled only during one 2-day period when part of the snowpack was 0°C and a portion of the snowpack was below 0°C, which may not have been adequate to test whether

meltwater concentrations were higher than bulk snowpack concentrations. Methodological and timing differences between our sampling protocol and that of Stoddard may explain why an ionic pulse is reported for ELW but not for the Gem Lake catchment.

Our research in a natural snowpack supports the laboratory experiments of Bales et al. [1989] and Colbeck [1981] that melt-freeze cycles enhance the concentrations of solutes in snowpack meltwater. Bales et al. [1989] report that in laboratory studies, larger initial peaks occurred in the solute concentration of meltwater in snow subjected to melt-freeze cycles, when compared with replicates not subject to meltfreeze action. They attributed the enhancement of ionic concentrations in meltwater by melt-freeze cycles to the ionic enrichment of residual liquid in grain clusters, as the area of grain bonds grows during freezing. Colbeck [1981] has also reported that in laboratory experiments, multiple melt-freeze actions enrich the first fraction of meltwater. At the ELW, areas with rapid melt had the lowest maximum concentrations of solutes in meltwater (bench); areas with lower rates of snowmelt had higher maximum concentrations of solutes in meltwater (cirque). Furthermore, after a series of melt-freeze cycles, from April 18 to April 22, 1987, the ionic concentration in meltwater increased at both the inlet and cirque.

The occurrence of melt-freeze cycles and the rate of snowmelt may be more important factors in determining the C_m/C_p ratio than the initial bulk concentrations of ions in the snowpack. The C_m/C_p ratio at the ELW is comparable to that from natural snowpacks where the initial bulk concentrations were as much as thirtyfold higher [e.g., Johannessen and Henriksen, 1978] than at the ELW. This relationship suggests that the C_m/C_p ratio in meltwater may be independent of the bulk ionic concentration of the snowpack.

Preferential release of one ionic species over another, from the snowpack to meltwater, has been reported by several researchers [Davies et al., 1982; Tsiouris et al., 1985; Tranter et al., 1986, 1987]. The ionic sequences generally have SO_4^2 and NO_3 eluted before Cl [Brimblecombe el al., 1985]. Physicochemical reasons for this phenomenon are unknown. Different distributions of ionic species on the scale of individual crystals have been hypothesized to be the main cause of preferential elution, with condensation nuclei (e.g., Cl⁻ in sea salt aerosols) being retained within the crystal and species scavenged during snowfall (e.g., SO4 and NO₃) being eluted first [Tsiouris et al., 1985; Tranter el al., 1986]. Anion exclusion has also been proposed as one mechanism to explain preferential elution [Bales, 1991]. Our meltwater samples indicate that preferential elution may occur among the strong acid anions at the ELW, with SO_4^{4-1} eluted before NO₃⁻ and Cl⁻ eluted last. The slower the rate of snowmelt, the greater the effect of preferential elution. The sequence of ion elution from the snowpack at the ELW is consistent with the condensation nuclei hypothesis, as well as anion exclusion.

Hydrogen did not act conservatively in snowpack meltwater. The decrease of H^+ in meltwater relative to the other major inorganic ions is similar to that reported by *Hornbeck et al.* [1977], *Jones and Sochanska* [1985], and *Cadle et al.* [1987]. Contamination from soil water is a potential source of H^+ buffering, but silicate measurements indicate that there was little or no soil water in the snow lysimeters. Clay and dust particulates in the snowpack are a potential source of H^+ buffering. Calcium and magnesium-containing particl-



Fig. 9. Discharge, NO_3^{-1} , SO_4^2 , Cl⁻¹, silicate, ANC, H⁺, and C_b in the outflow, during the time period of snowpack runoff in 1986 and 1987.

lates that dissolve in snowpack meltwater can react with atmospheric CO₂ to form HCO₃⁻ and Ca²⁺ or Mg²⁺ or dissociate to cations and HCO₃⁻ if the particulates are in the form of carbonates. Either process would result in increased Ca²⁺, Mg²⁺, and ANC concentrations and decreased H⁺ concentration in meltwater. This hypothesis is supported by the increase in ANC, Ca²⁺, and Mg²⁺ concentrations and decrease of H⁺ concentration at the inlet and cirque sites in meltwater on April 23, 1987. Furthermore, ANC, Ca²⁺, and Mg^{2+} were highly correlated with each other and negatively correlated with H^+ .

The role of particulates in buffering the H⁺ in snowpack meltwater was further investigated in 1989. Snow collected in the central Sierra Nevada was melted, and particulates were filtered onto $100-\mu m$ and then $0.4-\mu m$ pore size filters. The two size fractions of particulates were then leached in 5°C snowpack meltwater for 7 days. Results from this experiment showed a significant increase at the 95% confi-

 TABLE 2. Ion Loading (10³ eq) in the Snowpack and Stream Inflows to Emerald Lake, Spring Runoff 1986 and 1987

Ion	Snowpack		Streams		Fraction*	
	1986	1987	1986	1987	1986	1987
		()	2.6	0.5	0.23	0.11
H ⁺	11.4	6.0 11.2	2.0	6.4	1.21	0.57
NO3 50 ²⁻	0.0	95	9.1	4.6	1.87	0.49
	4.7	2.5	4.4	2.2	•••	0.87
NH ⁺	5.9	12.9	•••	•••	0.03	<0.01

*Fraction is the ratio of loading in streams to loading in the snowpack.

dence level in the alkalinity of meltwater with particulates greater than 100 μ m, compared to controls [Murphy, 1990].

Chemistry of Stream Water

Nitrogen. Nitrate had the highest concentrations of the strong acid anions in surface waters of the ELW during the time period of spring runoff. The source of the elevated NO_3^- concentrations in stream water during the initial increase in discharge may be from (1) the high NO_3^- concentrations in the ionic pulse of snowpack meltwater, (2) mineralization and nitrification processes in soils and subsequent transport by meltwater percolating through the soils, (3) oxidation of NH_4^+ released from the snowpack to NO_3^- , or (4) combinations of 1, 2, and 3.

Maximum NO₃⁻ concentrations measured in snowpack meltwater (26 μ eq L⁻¹) were of sufficient magnitude to account for the maximum NO₃⁻ concentrations measured in stream waters (19 μ eq L⁻¹). If the measured NO₃ pulse in stream waters was from snowpack runoff, the amount of NO₃⁻ released from the snowpack should be equal to or greater than the amount of NO₃⁻ that entered Emerald Lake from its inflowing streams. More NO₃⁻ was deposited to the basin by winter snowfall and spring precipitation than was in streamflow in 1987, supporting this hypothesis. However, the stream to snowpack ratio in 1986 of 1.21 indicates that there was a source of NO₃⁻ in stream water in addition to the NO₃⁻ stored in the snowpack at maximum snow accumulation.

Nitrate concentrations in soil reservoirs at the start of snowpack runoff should be high enough to combine with the more dilute waters of snowpack runoff to produce the elevated NO₃⁻ concentrations observed in surface waters if mineralization and nitrification processes are the source of NO_3 in stream water. Soil lysimeter data collected by Brown et al. [1990] from a well-drained Lithic Cryumbrept at the ridge site, similar in elevation, aspect, and soil type to the cirque location, show that NO₃⁻ was below detection limits at the initiation of snowpeak runoff in 1987 (Figure 10). Nitrate concentrations then increased with time, reflecting inputs from snowpack meltwater and spring precipitation. Nitrate concentrations were about threefold greater at a depth of 10 cm compared to a depth of 30 cm, suggesting that hydrologic flow paths may be important to the chemistry of stream waters. At the bench site, NO_3^- concentrations in a well-developed Entic Cryumbrept soil, at depths of 10 and 30 cm, remained near 0 μ eq L⁻¹ throughout the period of snowpack runoff [Brown et al., 1990]. Mineralization and nitrification processes do not appear to have been an important source of NO₃⁻ during snowpack runoff.

Oxidation of NH₄⁺ in soils during the period of snowpack runoff may be an important source of NO₃⁻ in stream water. Nitrate concentrations (140 μ eq L⁻¹) at the ridge site at a soil depth of 10 cm in late May and early June 1987 (Figure 10) were greater than that of NO₃⁻ in rainfall (95 μ eq L⁻¹) but less than that of NO₃⁻ plus NH₄⁺ (230 μ eq L⁻¹). Interactions between snowpack runoff and soils determined NH₄⁺ concentration in stream waters. Ammonium in soils during snowpack runoff was generally near detection limits, increasing to about 10 μ eq L⁻¹ at the ridge only after rain events with NH₄⁺ concentrations near 130 μ eq L⁻¹ (Figure 10). Consequently, NH₄⁺ concentrations in inflowing water never exceeded 2 μ eq L⁻¹ during the snowmelt season and



Fig. 10. Concentrations of NO₃, NH₄⁺, and SO₄² from soil lysimeters at the ridge site during the period of snowmelt runoff in 1987 [from *Brown et al.*, 1990]. Nitrate and NH₄⁺ concentrations were near 0 μ eq L⁻¹ at the beginning of snowmelt runoff; NO₃⁻ concentrations then increased with time, reflecting inputs from snowpack meltwater and spring precipitation. Sulfate concentrations showed little variability with time.

generally were near or below detection limits. Furthermore, mass balance calculations show that in 1986 and 1987 more than 99% of the NH_4^+ in wet deposition was not exported from the basin as NH_4^+ . Retention of NH_4^+ on soils by cation exchange processes may also have been an important source of NH_4^+ removal from snowpack runoff.

Sulfate. The relative constancy of SO_4^2 concentration in stream waters compared to NO3 and Cl indicates that SO₄²⁻ concentrations were regulated. Concentration to log discharge relationships show that SO_4^{2-} concentration in the outflow was less sensitive to changes in discharge than either NO3 or Cl- (Figure 11). Maximum and minimum concentrations of SO_4^{2-} in the outflow during the period of snowpack runoff were less variable than those of NO_3^- and Cl^- . The ratio of each strong acid anion concentration (C_i) to its mean concentration (C_{avg}) in the outflow over the period of snowpack runoff further illustrates the relative stability of $SO_4^{2^-}$ concentration. The C_i/C_{avg} ratio for $SO_4^{2^-}$ was greater than that of NO_3^- or Cl^- at the beginning and end of the period of snowpack runoff and less than that of NO₃ and Cl⁻ at peak values during snowmelt runoff (Figure 12). The constancy of SO_4^{2-} concentrations in stream waters (range of 7.1 to 7.6 μ eq L⁻¹ in the outflow) following rain events (maximum concentrations are 74 μ eq L⁻¹) in the spring of 1987 also supports a regulatory mechanism.

Interactions between snowpack runoff and soils is a possible source of the SO_4^{2-} regulation in surface waters. Water collected from soil lysimeters in 1987 by *Brown et al.* [1990] show that SO_4^{2-} concentrations in soil waters changed very little during the period of snowpack runoff in 1987 with



Fig. 11. Concentration to log discharge relationships for the strong acid anions, C_b , silicate, and ANC in the outflow during snowpack runoff in 1986 and 1987. Sulfate concentrations were less variable than concentrations of NO₃⁻ and Cl₁. ANC and C_b concentrations changed in a like manner.

respect to concentrations of SO_4^{2-} in snowpack meltwater and rain (Figure 10). Absorption-desorption by the clay minerals of the basin is one potential source of this SO_4^{2-} attenuation. Export of SO_4^{2-} from the basin in a year (1986) when atmospheric deposition of SO_4^{2-} was lower than stream water concentrations and retention of SO_4^{2-} by the basin when atmospheric deposition was higher than stream water concentrations (1987) supports this hypothesis. Sulfate appears to have been removed from solution by adsorption during periods when concentrations in precipitation were high (to 75 μ eq L⁻¹) and released to solution when



Fig. 12. Time series from 1986 and 1987 of the ratio of each strong acid anion concentration (C_i) to its average concentration (C_{avg}) in the outflow over the time period of snowpack runoff. Sulfate concentrations were less variable with time than were NO₃⁻ or Cl⁻.

incoming snowmelt water was low in SO_4^{2-} (<1 μ eq L⁻¹ [Dozier et al., 1987]).

Weathering of sulfide minerals in the basin is another potential source of SO_4^{2-} in stream and soil waters. Geologic investigations do not report any sulfur-bearing minerals in the ELW basin [*Clow*, 1987]. However, such minerals need be present in only small amounts to effect the concentration of SO_4^{2-} in stream and soil waters. Discrimination of sulfatesorption mechanisms in soils from weathering of sulfide minerals needs further research.

Alkalinity. Dilution of C_b was the main cause of the decrease in the alkalinity of stream waters at the time of ANC minima. The relationship between C_b , C_a , and alkalinity can be expressed as

$$ALK = C_b - C_a = [HCO_3^-] + [CO_3^2^-] + [OH^-] - [H^+]$$

where

$$C_b = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+]$$

 $C_a = [NO_3^-] + [SO_4^{2-}] + [Cl^-]$

(all concentrations are expressed as $\mu eq L^{-1}$).

Ammonium and aluminum concentrations must also be considered when calculating C_b , but in stream waters of the ELW their concentrations are negligible [Melack et al., 1989]. Decreases in alkalinity during spring snowmelt can be caused by decreases in C_b or increases in C_a or a combination of the two. The relationships of concentration to log show that ANC and C_b both decreased in a similar manner as discharge increased in 1986 and 1987 (Figure 11). Regression analysis during the rising limb of the outflow hydrograph in 1986 and 1987 indicates that ANC was significantly correlated with C_b at the 95% confidence level ($r^2 = 0.72$;



Fig. 13. Alkalinity (ALK = $C_b - C_a$), C_b , and strong acid anion (C_a) concentrations of inflow 2 in 1986. A representative sample of water collected prior to snowpack runoff (January 7) is compared to samples collected during elevated anion concentrations (May 1) and during the dilution period of snowpack runoff (June 10). The decrease in alkalinity on May 1 relative to January 7 was due primarily to increases in C_a (80%) and secondarily to dilution of C_b (20%).

P < 0.0001; n = 21) and not significantly correlated with C_a ($r^2 = 0.10; P = 0.16; n = 21$). Dilution of ANC by snowpack runoff is consistent with similar findings by *Stoddard* [1987] at Gem Lake and by *Loranger and Brakke* [1988] in the Cascades.

However, during the first part of snowmelt, runoff alkalinity declined due to the increase in concentration of strong acid anions. To illustrate, a representative sample of water collected at inflow 2 before snowmelt (January 7) is compared to samples collected during elevated anion concentrations (May 1) and during the dilution period of snowpack runoff (June 10) (Figure 13). Dilution by snowpack runoff decreased ALK by 4 μ eq L⁻¹ on May 1, relative to winter concentrations on January 7. Increases in the strong acid anions decreased ALK by another 15 μ eq L⁻¹ on May 1 relative to January 7. The increase in concentration of C_a accounted for 80% of the decrease in ALK on May 1 relative to January 7, and the decrease in C_b accounted for 20% of the decrease in ALK. On June 10 the C_b decreased by 26 μ eq L⁻¹, C_a by 22 μ eq L⁻¹, and ALK by 4 μ eq L⁻¹ relative to May 1.

The relative importance of changes in C_a and C_b to changes in ALK during the period of spring runoff is further illustrated by comparing ALK to the ratio of C_{μ} to C_{k} (Figure 14). At inflow 2 in 1986 the decrease in ALK in early May was the result of an increase in the ratio of C_a to C_b . ALK then increased in concentration due to a decrease in the C_a to C_b ratio. During the remainder of spring runoff, ALK decreased as the ratio of C_a to C_b remained relatively constant and both C_a and C_b decreased in concentration, Spring precipitation in 1987 resulted in the C_a to C_b ratio of inflow 1 increasing through the month of May as ALK decreased. The rain events in late May and early June caused a peak in the C_a to C_b ratio of 0.72, which corresponded with the ALK minimum. ALK then increased with time as the C_a to C_b ratio decreased toward presnowpack runoff concentrations. Alkalinity of the outflow followed a similar pattern in both years; however, the changes in C_{m}



Fig. 14. A time series in inflowing waters of ALK $(C_b - C_a)$ and the ratio of C_a to C_b during the period of snowpack runoff in 1986 and 1987. At inflow 2 in 1986 the decrease in ALK in early May was primarily from increases in C_a . At inflow 1 in 1987 the large increase in the C_a to C_b ratio and decrease in ALK in late May and early June was associated with spring precipitation.

Mass balance calculations and the low H⁺ concentrations in stream waters relative to H⁺ concentrations in the snowpack and in spring precipitation indicate that the H⁺ in snowpack runoff was neutralized before it reached Emerald Lake. Ion exchange, weathering, adsorption, titration of HCO₃⁻⁻, and protonation of anions of weak organic acids are all possible sources of H⁺ buffering during snowpack runoff. Discrimination of the various processes that may have neutralized the H⁺ in snowpack runoff is beyond the scope of this paper. The consumption of H⁺ does indicate that interactions of snowpack runoff with physical and chemical processes in the basin are an important factor in the chemistry of stream waters.

SUMMARY AND CONCLUSIONS

An ionic pulse in meltwater with initial concentrations twofold to twelvefold greater than the snowpack average, varying with site and with ion, was measured in lysimeters placed at the base of the snowpack. The C_m/C_p ratio is comparable to that from snowpacks where the initial bulk concentrations were as much as thirtyfold higher than at the ELW. This relationship suggests that the C_m/C_p ratio in meltwater may be independent of the bulk ionic concentration of the snowpack.

Solute concentrations in meltwater were higher when the rate of snowmelt decreased. A series of melt-freeze cycles, which occurred after the initiation of snowpack runoff, increased the concentration of solutes in meltwater relative to concentrations in meltwater prior to the melt-freeze cycles. Hydrogen concentration in meltwater was buffered by ANC produced in part by the dissolution of particulates. Our results indicate that anions were preferentially eluted from the snowpack, in the order $SO_4^{2-} > NO_3^{-} > Cl^{-}$. Sulfate and NO_3^{-} concentrations in meltwater decreased below the initial bulk concentrations after about 30% of the snowpack had melted, while Cl^{-} concentrations after 30% of the snowpack had melted.

Solute concentrations in the meltwater of the basin varied spatially by a factor of 10 or more at a point in time. The time span of the ionic pulse in meltwater, at a point, decreased as the rate of snowmelt increased. At a site with a relatively rapid rate of snowmelt the ionic pulse lasted about 2 days; at a site with a relatively slow rate of snowmelt the ionic pulse lasted about 10 days. Temporal differences in the initiation and magnitude of snowmelt within the ELW caused a spatial difference in the NO_3^- and SO_4^{2-} concentration of streams flowing into Emerald Lake.

The anionic pulse in meltwater was observed in stream waters during the first 30 days of snowpack runoff. Strong acid anion concentrations then decreased below winter concentrations in 1986 but remain elevated in 1987 due to inputs from spring precipitation. The ANC minima during snowpack runoff was primarily due to dilution. However, the increase in C_a of surface waters during the first part of snowpack runoff also resulted in a decrease in alkalinity that was not associated with a decrease in C_b .

Interactions between snowpack runoff and soils were important to the hydrochemistry of the basin. Soils were an apparent sink for NH_4^+ in snowpack runoff and in spring precipitation. Oxidation of NH_4^+ in soils may have contributed to the elevated NO_3^- concentrations in stream waters. Sulfate concentrations in stream waters were apparently regulated by soil processes. Eighty to ninety percent of the H^+ in snowpack runoff and spring precipitation was neutralized before it reached Emerald Lake.

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