

Hydrogeochemistry of Snowmelt at Rabbit Ears Pass, Rocky Mountains, Colorado

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ABSTRACT

The chemical composition of snowmelt from ridge-top lysimeters, groundwater along a hillslope transect, and streamwater at the basin outlet was monitored during the spring of 1991 and 1992 in a 2-km² sub-alpine catchment on the western flank of the Rocky Mountains near Steamboat Springs, Colorado. Most of the snowmelt occurred during two-month periods that began in mid May 1991 and mid April 1992. The solutes in the meltwater were differentially eluted from the snowpack in each year and the meltwater was dominated by Ca²⁺ and Mg²⁺ and the acid anions, SO₄²⁻ and NO₃⁻; the concentration sum of Ca²⁺ and Mg²⁺ was equal to the sum of SO₄²⁻ and NO₃⁻.

The composition of groundwater and streamwater was dominated by weathering products, such as Ca²⁺, HCO₃⁻ (measured as alkalinity), and dissolved SiO₂, and their concentrations decreased as snowmelt progressed. The SO₄²⁻ and NO₃⁻ concentrations of groundwater generally were higher than those of meltwater. In particular, groundwater from one well in the mid-slope position, which was at the highest elevation sampled, had extremely high NO₃⁻ concentrations during snowmelt in both years. These high NO₃⁻ concentrations were balanced by Ca²⁺ concentrations. As snowmelt progressed, NO₃⁻ and Ca²⁺ concentrations in groundwater decreased, consistent with dilution by meltwater from the snowpack.

Solute concentrations in streamwater also decreased as snowmelt progressed. The NO₃⁻ concentrations decreased more rapidly than did SO₄²⁻ concentrations. These results indicate that some of the SO₄²⁻ and NO₃⁻ in streamwater was derived from sources other than the snowpack, or that the meltwater composition in other drainage areas was more concentrated with respect to either constituents. Also, the relative changes in the SO₄²⁻ and NO₃⁻ concentrations of streamwater indicate that different processes control their mobility.

INTRODUCTION

Snow accumulation and melt are the dominant hydrologic processes that provide most of the water to ecosystems in the western mountain ranges of the United States. Hydrologic and hydrochemical processes occurring in the snowpack and to the meltwater as it travels through the landscape are not well understood and have a high potential for affecting ecosystems (Schindler, 1988; Carline et al., 1992; Murdoch et al., 1992). Solute in melting snow have been observed to fractionate, which produces the highest concentrations in meltwater at the onset of snowmelt (Johannessen and Hendrickson, 1978; Johannes et al., 1980; Williams and Melack, 1991; Berg, 1992). Consequently, either flow routing or the processes occurring along the hydrologic pathways can have a major effect on the chemical composition and transport of constituents during snowmelt.

Surface waters in the mountains of Colorado and other areas of the western U.S. are relatively dilute, having some of the lowest concentrations of commonly measured ions particularly when compared to those of mountainous areas in the eastern United States. These dilute waters have relatively low alkalinities and are sensitive to alteration and acidification by changes in atmospheric deposition (Turk and Adams, 1983; Turk and Campbell, 1987; Denning et al., 1991; Williams and Melack, 1991). The increasing development of the western United States, therefore, may affect the hydrology and hydrochemistry of these waters. The objective of the study was to evaluate factors affecting the hydrologic and hydrochemical response of a sub-alpine watershed in the Rocky Mountains to snowmelt. The purpose of this paper is to present a preliminary analysis of the hydrochemical aspects of the study. The sampling was most complete for the snowmelt in 1992 and the results presented herein focus on these data, with reference to 1991 where appropriate.

BACKGROUND AND METHODS

Site Description

The study site is located in the North Fork Walton Creek basin, near Rabbit Ears Pass, about 18 km southeast of Steamboat Springs, Colorado (Fig. 1). The site was established by the U.S. Geological Survey in 1988 to investigate the processes of snow accumulation and snowmelt and the effect of these processes on the hydrology of a sub-alpine basin in the Rocky Mountain region. The basin is 2 km² in area and has elevations ranging from 2910 to 3035 m a.m.s.l. The area is underlain predominantly by granitic rocks composed of quartz monzonite, granodiorite, and quartz diorite (Tweto, 1976). A small area near the mouth of the basin is overlain by shallow deposits of glacial drift. The basin is predominantly soil covered with only small areas of exposed bedrock. The upper meter of the soil profile ranges from a loam to sandy loam in texture.

The basin is about 30% forested which is dominated by coniferous vegetation, including engelmann spruce and lodgepole pine, with scattered stands of aspen. Forested areas are at the higher elevations of the basin and the remainder of the basin is predominantly covered by grass and shrubs. Thick stands of willows and willow brush are found along the stream channel, which is marked by a series of beaver dams.

Precipitation for the period 1988-92 averaged 922 mm, of which about 95% was snow. The predominant storm direction was from the southwest. Average

snowpack water equivalent during the first week of April ranged from 524 mm in 1992 to 828 mm in 1988. Precipitation during the summer months (June-September) for the same period averaged 45.4 mm. Average daily maximum air temperature ranged from 19.7°C in July to -3.9°C in January. Average daily minimum air temperature ranged from 7.9°C in August to -16.8°C in January. Runoff was dominated annually by one event associated with snowmelt and averaged 66% of the annual precipitation.

Hydrology and Water-Quality Sampling Methods

Streamflow was measured using a 1.2-m wide Parshall flume. Stage was recorded every 15 minutes by a digital datalogger using a shaft encoder attached to a float and counter-weight assembly in a well.

Snowmelt volume was measured using several large rectangular melt-collection lysimeters, constructed on the soil surface at the meteorological data-collection site at the ridge top of a western slope of the watershed (Fig. 1). Each lysimeter was 12 m² and had 20 cm high sides. The lysimeters were constructed from a heavy-duty nylon-reinforced hypalon material. The lysimeters had about a 5% slope and drained through a 5-cm diameter PVC pipe to a collection shelter 1.5 m below land surface. The snowmelt volume was measured by 850-ml tipping-bucket collectors and the tips were recorded by a digital datalogger. To minimize contamination from wind-blown debris the lysimeters were covered immediately after snowmelt from the previous year and the cover was removed about two weeks before snow accumulation. Water-quality samples were collected manually from the PVC pipes in the collection shelter using polyethylene sample bottles.

Shallow groundwater wells were installed in 1988 along a transect on the hillslope below the snowmelt lysimeter site to measure water levels and collect samples (Fig. 1). The sites were about 30 (U3A), 60 (U3B) and 110 m (U3C) from the stream along a 5.5° slope. Wells were drilled to refusal, which was typically about 4 m, with a 5-cm diameter flight auger using a trailer-mounted hydraulic rotary drill. The wells were cased with 5-cm diameter PVC pipe and screened at the bottom with a 60-cm length of slotted PVC screen. Each well was developed by alternately pumping and then forcing water down the casing several times over a 24-hour period. Water levels were recorded manually in each well in 1991 and every 15 minutes in 1992 by a digital datalogger using a shaft encoder attached to a float and counter-weight assembly. Water samples were collected from each well using a small-volume peristaltic pump and 6 m of silicon tubing. The mouth of the tubing was placed 20 cm above the bottom of the well and the well was pumped to purge at least one replacement volume of current storage in the well casing prior to sample collection.

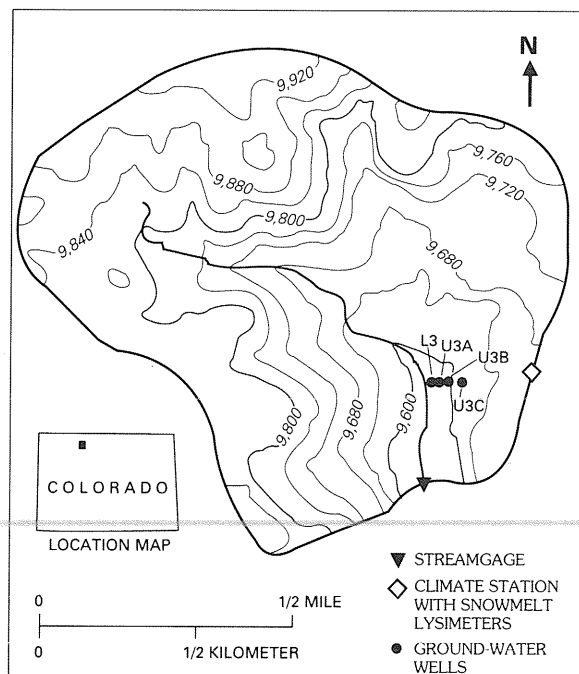


Figure 1. Map of the Rabbit Ears Pass watershed (REP) and data collection sites near Steamboat Springs, Colorado.

Meltwater, groundwater, and streamwater typically were sampled every two to three days as the snowmelt progressed, and several samples were collected from each site during each sampling day.

Water-Quality Analytical Methods

Water samples were analyzed in the laboratory in Atlanta for pH, specific conductance, alkalinity, and major solutes. The samples were shipped on ice to the laboratory and refrigerated until the time of analysis which was typically within two months of sample collection. Alkalinity was determined by a Gran titration. For the 1991 samples, the major solutes, which included cations, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ , and anions, Cl^- , NO_3^- , and SO_4^{2-} , were determined by ion chromatography (IC) and SiO_2 was determined colorimetrically through complexation with molybdate blue. For the 1992 samples, anions were determined by IC; a sample aliquot was passed through a $0.45 \mu\text{m}$ filter for the cation and SiO_2 determinations by an atomic emission spectrophotometric method, Direct Current Plasma; and NH_4^+ was determined colorimetrically on the unfiltered sample.

RESULTS AND DISCUSSION

Hydrology

Snowmelt began on 14 May 1991 and 10 April 1992 and continued at the lysimeter site for about one month in each year. The 15-minute snowmelt rates varied from 0 to 2.7 mm in 1991 and from 0 to 1.7 mm of water in 1992. The snowmelt rate was asymmetrical, increasing rapidly to a maximum at the onset of melt followed by an attenuated decrease (Fig. 2). In addition, the timing of melt shifted slightly as the melt progressed, which probably reflected a shift in the timing and intensity of the incident radiation. During the early snowmelt period, minimum melting occurred

from 0600 to 1000 and peak melt from 1430 and 1630, whereas in the latter part of the melt, minimum melting was at about 0900 and the maximum was at 1400.

Streamflow also varied diurnally and displayed a similar pattern to that of snowmelt, but the variations were much less marked (Fig. 2). The maximum amount of stream runoff for a 15-minute period was 0.4 and 0.25 mm in 1991 and 1992, respectively. On the day of the maximum 15-minute snowmelt rate, the total snowmelt for that day was 33.4 and 61.2 mm in 1991 and 1992, respectively; the baseflow transport was 23.8 and 7.2 mm; and the diurnal variation in streamflow contributed an additional 8.1 and 3.4 mm. The much larger contribution from snowmelt than observed in stream transport is attributed to the differential melting of the snowpack around the basin, most of which eventually contributes to streamflow. Streamflow peaked about 1-2 hours after the peak snowmelt and decreased to 60-70% of the peak flows about 18-19 hours later. Cumulative runoff from the beginning of snowmelt to the disappearance of the pack on 8 May was 40% of the cumulative meltwater transport (740 mm) recorded by the lysimeters in 1991 and 32% of that (390 mm) in 1992. Discharge was recorded through 11 July 1991 at which time 64% of the total meltwater released at the lysimeter site was transported out of the basin as streamflow. The discharge at that time, although on recession, could provide 2 mm of daily transport; whereas at the end of May 1992, 80% was transported and the discharge at that time could provide 7 mm of daily transport.

The water level in each of the wells rose rapidly in response to the onset of snowmelt, typically rising by more than 2-3 m in a few days, and remained high through the end of snowmelt. The water table responded daily in the wells, and in the lower elevations the water table typically was above land surface following the period of maximum melting (Figs. 2 & 3). Although the streamflow may have been

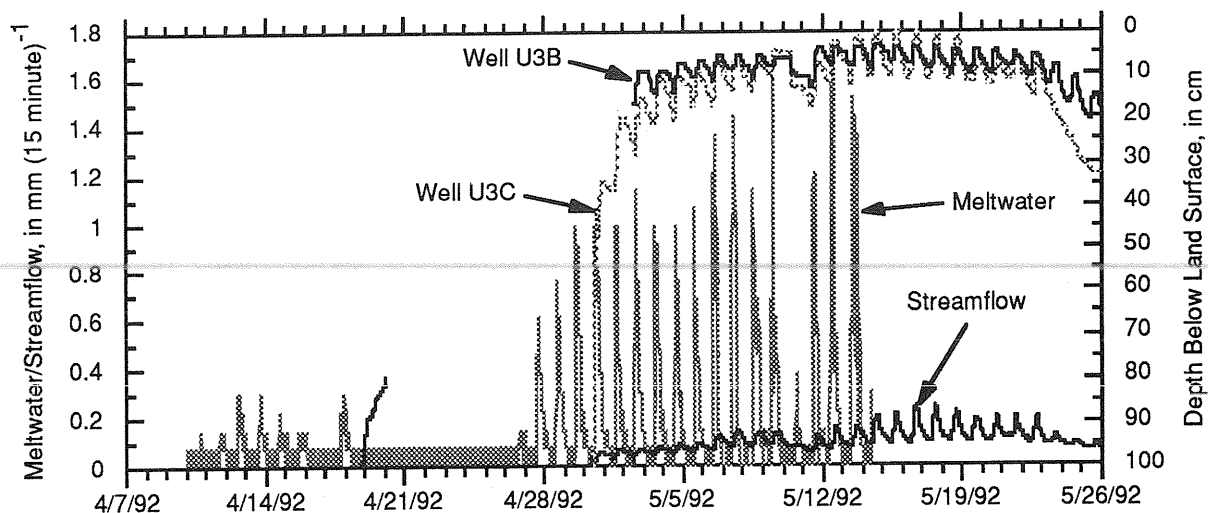


Figure 2. Meltwater rate, streamflow, and groundwater levels in two wells during snowmelt in 1992.

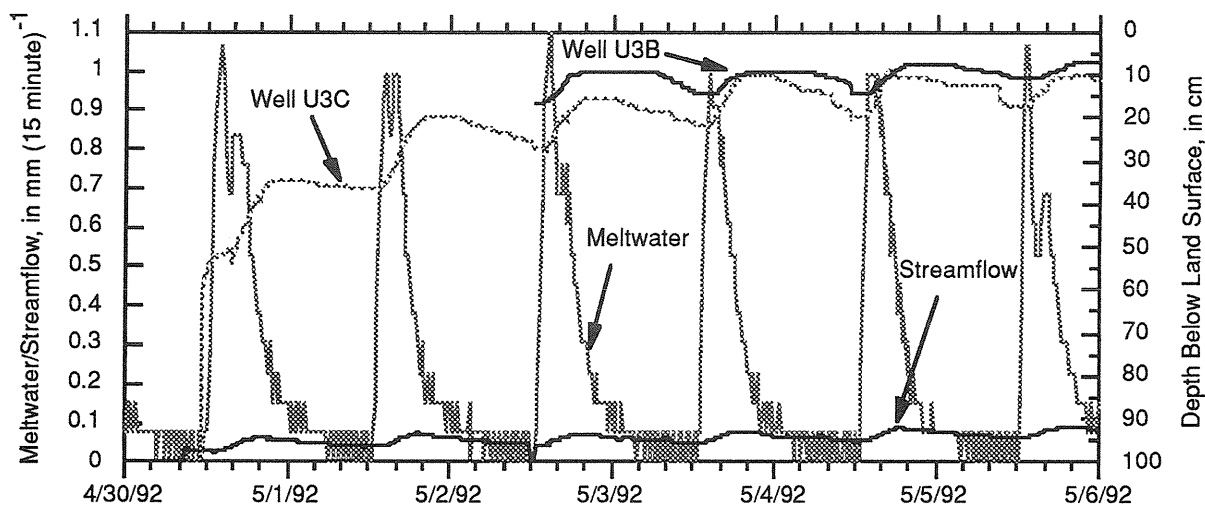


Figure 3. Meltwater rate, streamflow, and groundwater levels after the onset of the major snowmelt in 1992.

derived from saturated overland flow during the period of maximum melting, diurnal variations in the water levels of the upslope wells suggest that a large portion of the overland flow was derived from water that traveled through the surficial materials upslope. The diurnal variation in water levels was most pronounced at a lower elevation well (U3B) having a typical range of 12 cm in 1992 (Fig. 2). At the highest elevation well (U3C), the diurnal variation was about 6 cm. If the volumetric water content in the near surface groundwater zone was about 30%, then a minimum of 18 mm of water would have been transported daily through the ground at that upper elevation site and more than 36 mm at the lower elevation site. Groundwater levels remained high through the end of snowmelt, and the groundwater contributed to streamflow long after the snow had disappeared.

Hydrochemistry

Meltwater from the Snowpack

Meltwater from the snowpack for the entire snowmelt period was dominated by Ca^{2+} , NO_3^- , and SO_4^{2-} (Table 1). The pH ranged from 5.1 to 5.8, which was unexpected given the relatively high concentrations of acid anions, NO_3^- and SO_4^{2-} . In addition, the sum of Ca^{2+} and Mg^{2+} concentrations was linearly related to the sum of NO_3^- plus SO_4^{2-} ; for 1992, the r^2 was 0.94 and the slope was 1.0 (Fig. 4).

A comparison of the solute composition of the snowpack, which was sampled on 30 March 1992 prior to the onset of snowmelt (D.H. Campbell, 1993, pers. comm.), with the rate-weighted mean concentrations of the meltwater for the entire snowmelt period, suggests that the snowpack composition changed after the snow had melted. In particular, Ca^{2+} and Mg^{2+} were considerably enriched in meltwater compared to the snowpack and H^+ and SO_4^{2-} were depleted. Such

Table 1. Summary of the solute concentrations, in $\mu\text{eq l}^{-1}$, of the meltwater from the snowpack and a sample of the snowpack on 30 March 1992.

Solute	Meltwater Lysimeter (n=30)					Snow pack (n=1)
	Median (C_{med})	Rate- Weighted Mean (C_{mean})	Max. (C_{max})	$\frac{C_{max}}{C_{med}}$	$\frac{C_{max}}{C_{mean}}$	
H^+	2.1	3.0	7.9	3.8	2.6	10.7
NH_4^+	6.7	6.6	17.8	2.6	2.7	5.7
Na^+	2.4	1.5	4.0	1.6	2.7	0.8
K^+	2.0	2.2	6.6	3.3	3.0	2.5
Mg^{2+}	6.1	3.5	15.8	2.6	4.5	1.2
Ca^{2+}	16.7	14.9	79.4	4.8	5.3	4.0
Cl^-	3.0	1.5	8.2	2.7	5.5	2.8
NO_3^-	10.7	10.8	45.0	4.2	4.2	10.8
SO_4^{2-}	10.6	11.4	45.6	4.3	4.0	14.4

changes may have occurred through reactions with dry-deposited particles that had either accumulated in the snowpack or with the collector. The snowpack sample was collected and filtered as soon as the snow melted; whereas, the meltwater samples were stored for at least one month prior to filtration and analysis. Rate-weighted mean concentrations (Table 1) were determined by summing the product of the snowmelt rate from the lysimeter and the solute concentration, and dividing this by the sum of the snowmelt rates. The median concentrations were comparable to the rate-weighted means for most constituents.

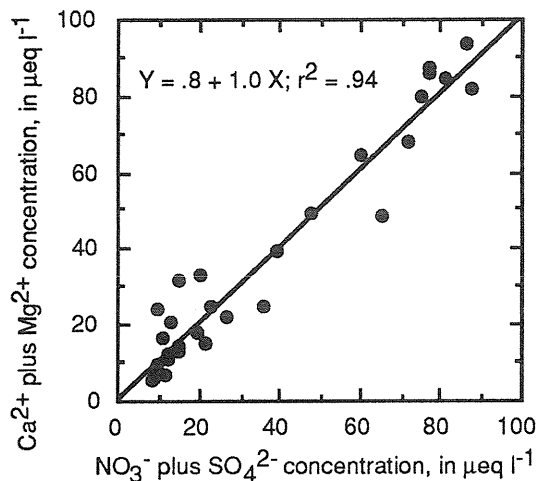


Figure 4. Relation between Ca^{2+} plus Mg^{2+} concentrations and NO_3^- plus SO_4^{2-} in 1992 meltwater.

The decrease in H^+ concentration and the increase in base cation concentrations, including Na^+ , in the meltwater compared to the snowpack were not accompanied by increases in dissolved SiO_2 . Although Ca^{2+} and Mg^{2+} may be weathered from aluminosilicate minerals without releasing SiO_2 , Na^+ cannot, which suggests an alternate source for the Na^+ . Other possible sources of the Ca^{2+} and Mg^{2+} include the reaction of H^+ with carbonate minerals, or exchange or release from organic material. The difference between the Ca^{2+} concentration of the meltwater and the snowpack alone is larger than that for H^+ , suggesting that some reaction had occurred with particulates or with the collector. It also has been suggested that small amounts of surface runoff or groundwater leakage into the lysimeter may have caused the difference.

In February 1990, following a distinct period of particle deposition to the snowpack, a snowpack sample was collected, melted, and passed through a

0.45 μm filter. An X-ray diffraction analysis of the residue indicated that the residue was composed predominantly of carbonate minerals, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). The underlying bedrock is granitic and therefore, is relatively devoid of these minerals. The suspected source of the carbonate minerals is upwind in the sedimentary rock basins to the west and southwest.

Carbonate minerals are relatively reactive compared to aluminosilicate minerals particularly in the presence of acid. Therefore, it is probable that the acid in the snowpack reacted with the eolian carbonate minerals during snowmelt producing high Ca^{2+} concentrations and high pH. On the other hand, the eolian material that was sampled in 1990 may not be representative of the materials typically transported into the basin (D.Clow, 1993, pers. comm.), so other scenarios are possible, including reaction with organic material (plant debris) that was observed to accumulate in the lysimeters to a minor extent.

An evaluation of the changes in meltwater solute concentrations suggests that solutes were both differentially (fractionated) and preferentially eluted from the snowpack. Concentrations of all solutes generally decreased as snowmelt progressed for the snowmelt period, as shown for Ca^{2+} , NO_3^- , SO_4^{2-} , and alkalinity in Fig. 5 and as observed elsewhere (Johannessen et al., 1975; Johannessen and Hendrickson, 1978; Tranter et al., 1986, 1987; Rascher et al., 1987; Peters and Driscoll, 1987, 1989; Williams and Melack, 1991; Berg, 1992). A similar pattern occurred on many of the sampling days with the highest concentrations associated with samples collected prior to the onset of the daily snowmelt, followed by a progressive decrease in concentration for successive samples.

Because the meltwater composition was different than the snowpack, concentration factors were computed by dividing the maximum concentration, which occurred at the beginning of snowmelt, by either

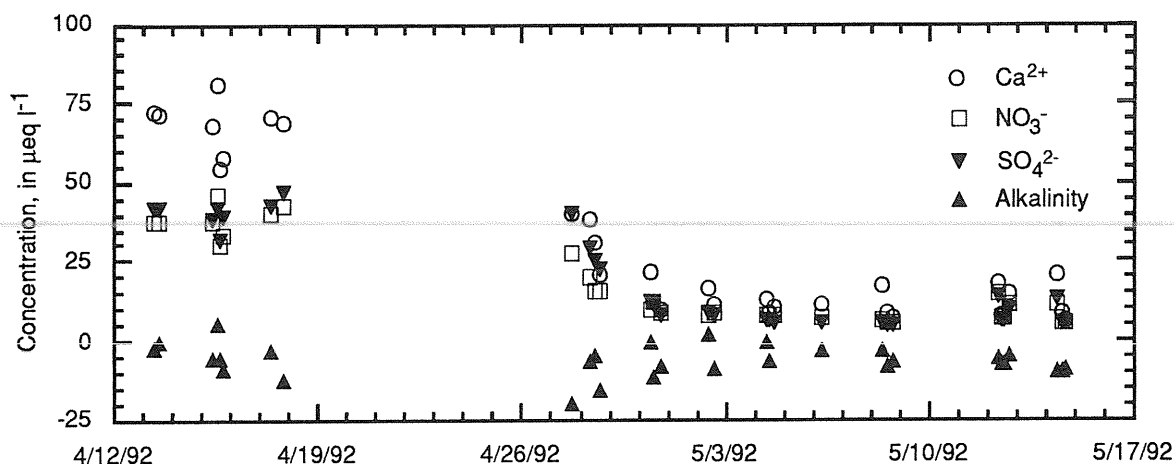


Figure 5. Concentrations of Ca^{2+} , NO_3^- , and SO_4^{2-} , and alkalinity in 1992 meltwater from the snowpack.

the median or rate-weighted mean for each major solute (see the two columns of italicized numbers in Table 1). Concentration factors for the individual constituents ranged from 2.6 to 5.5.

In addition to the general concentration decrease in meltwater for each constituent during the snowmelt period, relative variations in concentrations of solutes for the multiple collections on a given sampling day indicate that solutes were preferentially released from the snowpack. Samples with relatively high contributions of Cl^- to the sum of the anion equivalents for Cl^- , SO_4^{2-} , and NO_3^- , occurred at the end of meltwater recession from the previous days snowmelt and typically were the first sample collected on a given day prior to the onset of the daily snowmelt, i.e., before 1100. The pattern persists throughout the snowmelt period with a shift toward higher contributions of NO_3^- than SO_4^{2-} later in the melt. Solute were eluted in the order $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Cl}^-$, as reported for other snowpacks (Tranter et al., 1986; Peters and Driscoll, 1989; Williams and Melack, 1991).

Groundwater

The groundwater composition in each well was dominated by Ca^{2+} . Concentrations of most of the weathering products (SiO_2 , alkalinity, and base cations) increased down gradient, consistent with an increase in water residence time. However, extremely high Ca^{2+} concentrations were observed in the highest elevation well (U3C), which was unexpected (Fig. 6). The Ca^{2+} and NO_3^- concentrations on the day of the initial sampling were less than half that of the maximum which occurred two days later. Concentrations of most of the major ions decreased with time in this well, and although water levels fluctuated diurnally, the concentrations of most constituents remained relatively constant for any given day. The NO_3^- concentrations in the other two downslope wells were more than an order of magnitude lower at the onset of the snowmelt period than that of U3C, but they were

higher than those of meltwater and decreased as the snowmelt progressed.

The extremely high NO_3^- concentrations in the groundwater from well U3C indicate that biological processes, such as nitrification, may have produced large amounts of NO_3^- in the soils as was reported for a forested site in the northeastern United States (Rascher et al., 1987; Peters and Driscoll, 1987, 1989).

The lower elevation groundwater sites are in relatively open areas; but this high elevation site is adjacent to a small grove of conifers which may, in itself, have an impact on soil solutions and soil chemistry or may attract fauna, which likewise, could affect nitrogen cycling (Jones, 1991). The NO_3^- concentrations at well U3C were related to the Ca^{2+} plus Mg^{2+} concentrations; a linear regression of Ca^{2+} plus Mg^{2+} on NO_3^- had a slope of 0.80 with an r^2 of 0.94. Also, not only were the Ca^{2+} plus Mg^{2+} and NO_3^- concentrations comparable, but they were much higher than concentrations of other constituent in this groundwater. These results indicate that the processes generating the NO_3^- also either affected the Ca^{2+} and Mg^{2+} directly or if the process was nitrification, the H^+ generated by it was immediately neutralized, probably through cation exchange for Ca^{2+} and Mg^{2+} . Whereas, Ca^{2+} , Mg^{2+} , and NO_3^- increased and then decreased in well U3C, alkalinity decreased and then increased, which suggests that H^+ was generated (nitrification in overlying soils) causing the alkalinity decrease.

The SO_4^{2-} concentrations in groundwater ranged from 25 to 70 $\mu\text{eq l}^{-1}$ with the highest concentrations at the lowest elevations. The SO_4^{2-} concentrations at the two highest elevation wells (U3B and U3C) increased as the snowmelt progressed reaching a maximum several days after the maximum NO_3^- concentration and after most of the snow had melted. In contrast, the SO_4^{2-} concentration in the low elevation wells decreased throughout the melt period, but the lowest concentrations in well U3A were more than twice those of concurrent samples of streamwater (Fig. 7).

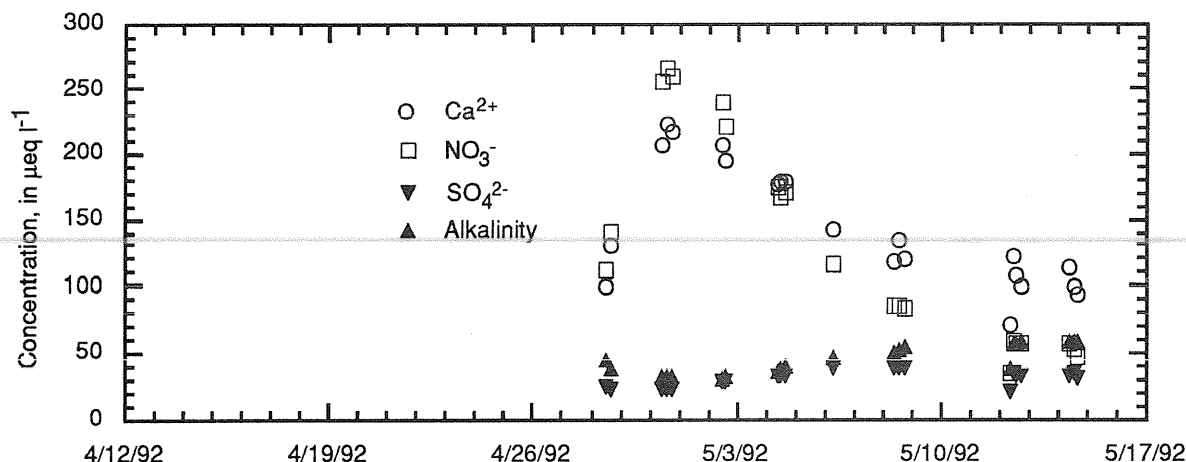


Figure 6. Concentrations of Ca^{2+} , NO_3^- , and SO_4^{2-} , and alkalinity in 1992 groundwater from well U3C.

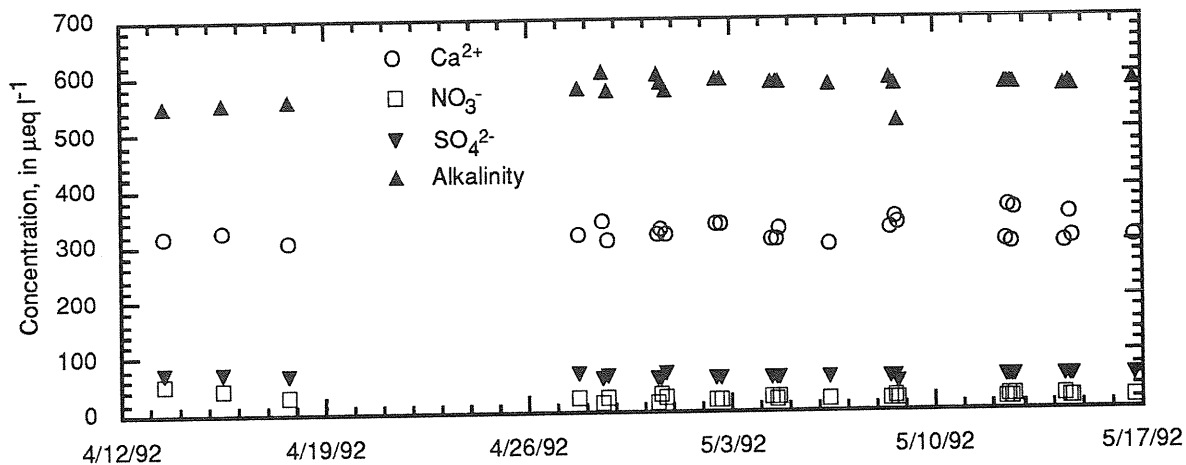


Figure 7. Concentrations of Ca^{2+} , NO_3^- , and SO_4^{2-} , and alkalinity in 1992 groundwater from well U3A

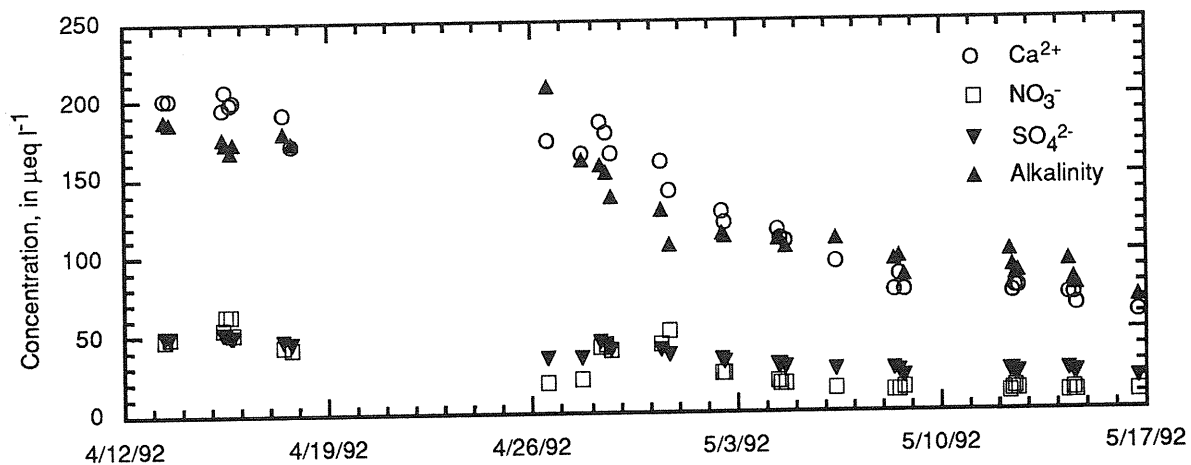


Figure 8. Concentrations of Ca^{2+} , NO_3^- , and SO_4^{2-} , and alkalinity in 1992 streamwater.

Streamwater

The streamwater composition was dominated by weathering products, primarily Ca^{2+} , SiO_2 , and alkalinity, which decreased as the snowmelt progressed (Fig. 8). Concentrations of these solutes varied diurnally, but the variations were less pronounced than those for solutes in the meltwater. The lowest concentrations corresponded with the highest streamflows, presumably a result of dilution by the daily meltwater. The NO_3^- concentrations in streamwater were: (1) less than those observed in the groundwater at the highest elevations; (2) higher than those of the meltwater and the groundwater at lower elevations; (3) increased to about $60 \mu\text{eq l}^{-1}$ on the second sampling day; and (4) generally decreased to less than $10 \mu\text{eq l}^{-1}$ at the end of the snowmelt period. The relatively high concentrations throughout the period and the high concentrations in groundwater indicate that the streamwater received NO_3^- from sources in addition to that released from the snowpack.

The SO_4^{2-} concentrations in streamwater were similar to those of NO_3^- at the beginning of the melt, and decreased later in the snowmelt period, but not as rapidly as the NO_3^- . The SO_4^{2-} concentrations of streamwater were: (1) less variable than NO_3^- ; (2) higher (median, $30.8 \mu\text{eq l}^{-1}$) than those observed in the meltwater (Table 1), particularly after the initial elution of SO_4^{2-} from the snowpack (Fig. 3); (3) considerably less than that of groundwater adjacent to the stream; and (4) comparable to those of groundwater from the upslope wells (U3B and U3C). These results suggest that most of the streamwater SO_4^{2-} was relatively well regulated when compared to NO_3^- . The SO_4^{2-} was derived from sources other than snowpack. The sources probably include wet and dry deposition after snowmelt, internal cycling (i.e., release from organic material), and release from some minerals in the basin. In particular, the high concentration of SO_4^{2-} at the onset of snowmelt may have resulted, in part, from the mobilization of SO_4^{2-} .

that had concentrated in the surficial materials by evaporation during the two months prior to snowpack accumulation.

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