

Composition of precipitation, bulk deposition, and runoff at a granitic bedrock catchment in the Loch Vale watershed, Colorado, USA

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Abstract The chemical composition of precipitation, bulk deposition, and runoff from a 30-m² granitic bedrock catchment in the Loch Vale Watershed in Rocky Mountain National Park was monitored over a 6-week period in the summer of 1994 to determine the importance of dry deposition in the alpine zone. Concentrations of acid anions and base cations were 1.1 to 4 times higher in bulk deposition than in precipitation. Concentrations of the same solutes were 3 to 10 times higher in runoff from the bedrock catchment than in bulk deposition, and during individual runoff events, the concentrations of most ions were highest in the initial runoff. Evaporation from the rock surface accounted for only a 15% increase in solute concentrations indicating that most of the dissolved load in bedrock runoff is derived from the dissolution of dry deposition that accumulates on the bedrock between storm events. These results indicate that dry deposition may be an important source of solutes to this alpine ecosystem.

INTRODUCTION

Atmospheric deposition, which includes wet and dry deposition, can be an important source of solutes to alpine catchments. Wet deposition occurs when particles and gases are removed from the atmosphere by precipitation. Dry deposition includes gases and particles which impact on natural surfaces in the absence of precipitation. Bulk deposition is a mixture of wet and dry deposition. Although adequate methods exist for estimating wet deposition fluxes to watersheds, measurement of dry deposition fluxes has remained problematic (Edgerton *et al.*, 1991). Two approaches have been used to estimate dry deposition fluxes. One involves using air quality data and meteorological measurements (Sheih *et al.*, 1979; Padro *et al.*, 1993), but the applicability of results to deposition fluxes on natural surfaces is uncertain (Sheih *et al.*, 1979; Hicks *et al.*, 1988). A second approach involves using natural and artificial surfaces to collect dry deposition (Shanley, 1989; Zobrist *et al.*, 1993). Direct measurement of dry deposition is possible by monitoring snowpack chemistry or collecting washings from natural surfaces such as throughfall or stemflow (Cadle, 1990; Peters, 1989). These techniques, however, suffer from problems of scale when the results from individual sites are extrapolated to entire watersheds, which have heterogeneous surface deposition characteristics. Surrogate surfaces have also been used to collect dry deposits, but there are doubts about the representativeness of artificial surfaces to the types of surfaces encountered in natural ecosystems (Peters, 1989).

The U.S. Geological Survey is conducting an investigation of Water, Energy, and Biogeochemical Budgets (WEBB) in the Loch Vale watershed, an alpine catchment in the Colorado Rocky Mountains (Lins, 1994). One goal of the study is to gain increased understanding of the processes affecting surface-water chemistry as the water flows through landscapes of increasing size and complexity. In much of the alpine zone of the Rocky Mountains, one of the first landscapes contacted by precipitation is bedrock or talus. These geologic materials can alter the chemistry of precipitation in a number of ways; rain and snow interact with dry deposition that accumulates on rock surfaces, lichens on rocks cycle nutrients, and bedrock surfaces weather chemically. The importance of these bedrock-related processes on the solute budget of the Loch Vale watershed are unknown. The purpose of this paper is to present results from the part of the WEBB study that was designed to characterize changes in the chemistry of rain as it passes over a bedrock surface, and in particular, to determine whether dry deposition fluxes to rock surfaces could be a substantial part of the solute budget for the Loch Vale watershed.

Site description and methods

The study was conducted in the Loch Vale Watershed, an alpine-subalpine watershed located in Rocky Mountain National Park, Colorado. The basin is 660 ha in size and ranges in elevation from 3050 m at the outlet to 4026 m at the western margin along the Continental Divide. Over 80% of the basin consists of bare rock and talus; 11% is alpine tundra; 3% is permanent snowfields and glaciers; and the lower 6% of the basin is covered by a subalpine spruce-fir forest. Bedrock in the basin consists of granite and gneiss of Precambrian age. Mean annual precipitation is 100 cm, and usually over 70% falls as snow. A detailed description of the basin can be found in Baron (1992).

Runoff was collected from a 30-m² granite outcrop over a 6-week period in the summer of 1994. The gently-sloping bedrock surface is above treeline at an elevation of 3300 m. Most of the rock surface is covered by lichens. A 5-cm-high plexiglass wing wall at the lower edge of the bedrock catchment was used to funnel runoff into a 28 by 26 cm polyethylene stage pond equipped with a V-notch weir. Discharge was calculated from stage, which was monitored continuously using a potentiometer and float-counter weight system connected to a data logger. Eighty-five runoff samples were collected with a stage-activated automatic sampler during nine storm events (Peters, 1989). Most storms were less than 1 h in duration, during which the sampler typically collected 5 to 10 samples. Weekly precipitation amount was measured using two rain gauges located on the outcrop. Bulk deposition samples were collected in a continuously open polyethylene funnel attached to a 2-l bottle. Runoff samples and bulk deposition samples were analyzed for major cations, anions, pH, and SiO₂. Ca²⁺, Mg²⁺, Na⁺, and SiO₂ were measured by inductively coupled plasma spectroscopy on filtered (0.45 μm) acidified aliquots. SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, and K⁺ were measured on filtered, chilled samples by ion chromatography. Acid-neutralizing capacity (ANC) and pH measurements were made on filtered aliquots in the laboratory within 48 hours of collection. ANC was measured by second-derivative titration, and pH was measured using a low-ionic strength electrode. Quality-assurance procedures included analysis of field blanks and duplicate samples (10%), and calculation of charge balance. There was a mean excess of cations of 13% (standard deviation, 8%), indicating that there was an

unmeasured anion species. The most likely unmeasured species is organic anions derived from organic acids.

Weekly wet deposition has been collected in Loch Vale since 1981 at an elevation of 3160 m. The site is part of the National Atmospheric Deposition Program/National Trend Network (NADP/NTN); collection and analytical procedures are given by Peden (1986).

RESULTS AND DISCUSSION

Chemistry of precipitation and bulk deposition

Both precipitation and bulk deposition were generally very dilute (Table 1). The major cations in precipitation were NH_4^+ and H^+ , and the major anions were NO_3^- and SO_4^{2-} . In bulk deposition, the major cations were Ca^{2+} and H^+ , and the major anions again were SO_4^{2-} and NO_3^- . Concentrations of all solutes except H^+ and NH_4^+ were higher in bulk deposition than in precipitation. Base cations were 1.4 to 4 times higher in bulk

Table 1 Volume-weighted mean concentrations ($\mu\text{eq l}^{-1}$) in precipitation, bulk deposition, and bedrock runoff in Loch Vale Watershed, Colorado for the period 7/5/94 to 8/19/94, except precipitation, which pertains to the period 7/5/94 to 8/16/94. Precipitation chemistry data from Loch Vale NADP/NTN site (NADP/NTN, 1994). na indicated not analyzed; SiO_2 is in $\mu\text{mol l}^{-1}$.

	ANC	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Cl^-	SO_4^{2-}	NO_3^-	SiO_2
Precipitation	na	14.9	8.5	1.9	2.0	0.6	16.8	2.8	17.9	21.0	nna
Bulk deposition	-13.7	14.0	23.0	9.3	2.8	2.6	9.5	3.4	22.0	23.7	<2.0
Bedrock runoff	2.9	4.5	101.7	24.7	8.6	5.4	9.9	6.6	76.3	49.5	10.9

deposition than in precipitation and SO_4^{2-} , NO_3^- , and Cl^- were 1.1 and 1.2 times higher in bulk deposition than in rain. Chloride was also 1.2 times higher in bulk deposition than in precipitation. The higher solute concentrations in bulk deposition compared to precipitation indicates that dry deposition to the funnel surface occurred. The lower concentrations of NH_4^+ in bulk deposition relative to precipitation suggest that uptake of NH_4^+ by biota may have occurred in the bulk collector.

In contrast to summer, bulk deposition chemistry in winter, inferred from snowpack samples, is not substantially different than winter precipitation chemistry measured at the NADP/NTN site (D. Campbell, personal communication; NADP/NTN, 1994) suggesting that dry deposition may be more important during snow-free periods of the year. This could be because there is less transport of particulates into the atmosphere in the winter when more of the ground is covered with snow and soils are generally wetter. Data from the National Dry Deposition Network indicate that concentrations of aerosols and particulates in the atmosphere typically are higher in summer than winter (Edgerton *et al.*, 1991). Another explanation for the lack of difference in chemistry between precipitation measured at the NADP/NTN site and the snowpack is that snow is a less efficient scavenger of gases and particles than soil, rocks, or vegetation.

Runoff chemistry and hydrology

Runoff samples were collected during nine rain events ranging in amount from 0.4 to 8.2 mm. Runoff from the bedrock surface during these events ranged from 0.092 to 0.281 m³ of water, and events ranged in duration from 10 min to 2 h. Total precipitation during the period of study was 5.16 cm, and total runoff was, 4.38 cm indicating approximately 15% of the precipitation evaporated from the rock surface. This estimate of evaporation concurs with other estimates of evaporation from bare rock surfaces in alpine areas (Carroll, 1990).

The dominant solutes in bedrock runoff were Ca²⁺, SO₄²⁻, and NO₃⁻, followed by Mg²⁺, SiO₂, and NH₄⁺. Concentrations of most solutes were much higher in bedrock runoff than in bulk deposition or precipitation (Table 1). Volume-weighted mean concentrations of NO₃⁻ and SO₄²⁻ in runoff from a bedrock catchment were 2 to 4 times higher than in precipitation, and base cations were 3 to 10 times higher in runoff than in precipitation (Fig. 1(a), (b)). The higher concentrations of solutes in runoff compared to precipitation cannot be explained solely by evaporation based on the water budget for the bedrock catchment, and probably were derived from dissolution of dry deposits that accumulated on the rock surface between storms. The higher concentrations in runoff from the bedrock relative to bulk precipitation suggest that the bedrock surface may be a more efficient collector of dry deposits than the plastic funnel used to collect bulk

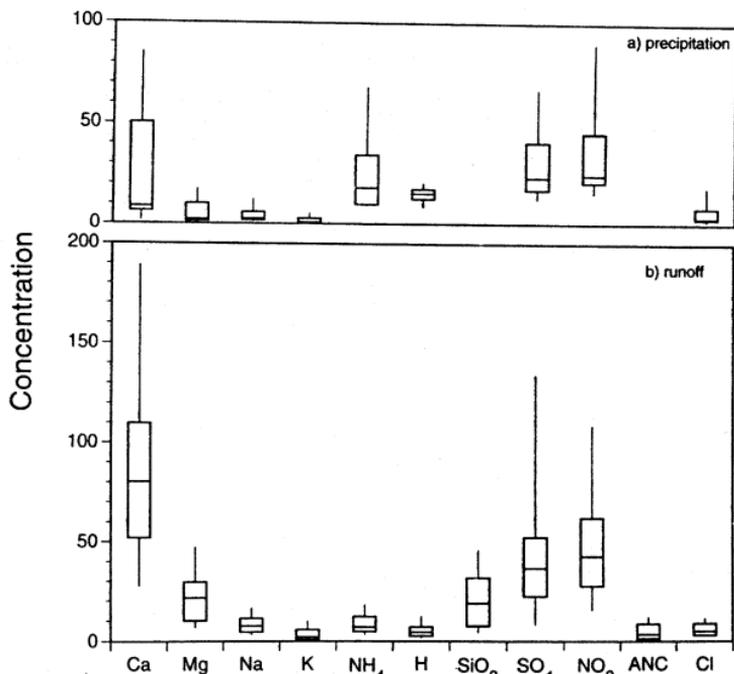


Fig. 1 Concentrations of major dissolved constituents in (a) precipitation samples collected at Loch Vale NADP/NTN site (NADP/NTN, 1994), and (b) runoff samples collected from bedrock catchment. All concentrations shown in $\mu\text{eq l}^{-1}$ except for SiO₂, which is in $\mu\text{mol l}^{-1}$. Boxes represent 1st to 3rd quartile ranges; median indicated by bar; whiskers indicate range.

deposition. Bedrock weathering may also contribute a small amount of solutes; however, the short contact time of water on the rock surface makes a large contribution unlikely.

During individual rain events, most solutes in runoff showed a consistent pattern of high concentrations at the beginning of the storm, followed by a rapid decrease in concentrations that leveled off toward the end of the event (Fig. 2(a), (b)). A notable exception was ANC, which often started out slightly negative and subsequently increased to slightly positive values. Peters (1989) identified similar trends in solute concentrations in runoff from a small granitic outcrop in Georgia during individual storm events. This kind of temporal trend in runoff chemistry could be due to wash-off of dry deposition from rock surfaces (Peters, 1989). Alternatively, trends in runoff chemistry may reflect changes in precipitation chemistry resulting from washout of particles and gases from the atmosphere during the initial stages of the storm event.

Runoff from the first measured event (23 July 1994) contained the highest solute concentrations of the season. This event was preceded by a 3-week dry period with precipitation of less than 1 cm. After the first event, rain fell more frequently, and measurable precipitation occurred approximately every 3 days. To test whether antecedent conditions or rainfall volume had a significant effect on runoff concentrations, volume-weighted mean concentrations in runoff were regressed against the antecedent dry period (ADP) using the Spearman correlation test, a nonparametric

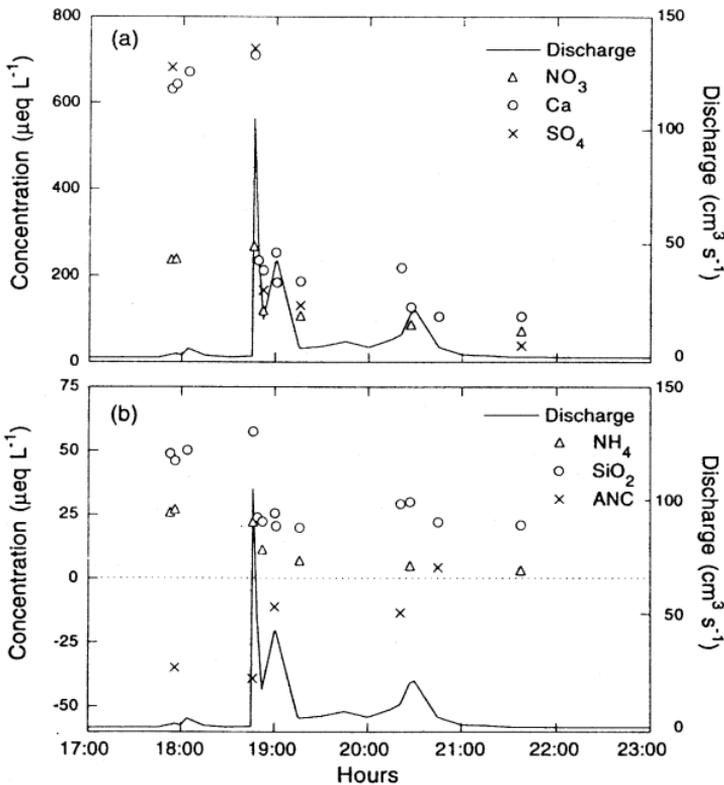


Fig. 2 Chemical composition and discharge of runoff from the bedrock catchment during a 4-mm storm on 23 July 1994; (a) NO₃⁻, Ca²⁺, and SO₄²⁻; (b) NH₄⁺, SiO₂, and alkalinity.

test that is insensitive to outliers and nonlinearity (Ott, 1993). None of the solutes in runoff was correlated with ADP at $p < 0.1$, but Ca^{2+} , Mg^{2+} , SiO_2 , Cl^- , and NO_3^- were correlated with ADP at $p < 0.2$. For those solutes, the amount of variance (r^2) in runoff concentrations explained by ADP was approximately 0.25. Rainfall amount during an event was negatively correlated with H^+ concentration in runoff at $p < 0.1$ ($r^2 = 0.38$), and positively with alkalinity at $p < 0.2$ ($r^2 = 0.25$). The correlations between solutes and ADP may be explained by wash-off and dissolution of dry deposition that accumulated on the rock surface over time. Longer antecedent dry periods allowed more dry deposits to accumulate. The cause of the decrease in H^+ and increase in alkalinity with increasing rainfall amount during an event may be related to wash-out of acidic components in the atmosphere. This is supported by the good inverse correlations between solute concentrations in weekly precipitation collected at the NADP/NTN station and weekly rainfall amount (p -values were less than 0.05 for all solutes except H^+). Spearman correlation coefficients for all solutes except H^+ , K^+ , and NH_4^+ were between -0.51 and -0.60 .

Processes affecting runoff chemistry

As noted above, the dominant anions in bedrock runoff were the strong acid anions, SO_4^{2-} and NO_3^- . It is unlikely that weathering of granitic bedrock released appreciable amounts of nitrogen or sulfur, due to the scarcity of those compounds in granitic rocks. While sulfur is not a major component of the biological cycle of lichen, nitrate probably is, and nitrogen fixation cannot be ruled out. Conversion of NH_4^+ to NO_3^- by lichen or bacteria is another possible explanation for the comparatively high NO_3^- concentrations in runoff. This is supported by the decrease in the ratio of NH_4^+ to all other solutes except H^+ in runoff compared to bulk precipitation.

A major difference between bedrock runoff and precipitation chemistry is the higher concentrations of base cations and SiO_2 . Weathering is the only reasonable source of SiO_2 . Weathering is the only reasonable source of SiO_2 , and its presence in runoff indicates that weathering reactions can occur very quickly. Whether the weathering source is bedrock minerals or wind-transported minerals is an unresolved question, but the high specific surface area of eolian material makes it the most likely contributor. The source of base cations, particularly Ca^{2+} , is less clear. Figure 3 shows that SO_4^{2-} and NO_3^- in runoff were strongly correlated with Ca^{2+} and Mg^{2+} . One possible explanation is that these cations are deposited directly on the rock surface as neutral SO_4^{2-} and NO_3^- salts. Alternatively, Ca^{2+} and Mg^{2+} may be derived from exchange reactions involving particulates and acids or other compounds in rain, such as HNO_3 , H_2SO_4 , NH_4NO_3 , or $(\text{NH}_4)_2\text{SO}_4$. In this case, eolian dust and locally derived soil particles that blow onto the catchment between rain events may provide a readily available source of exchangeable Ca^{2+} and other cations. A third possible source of base cations in bedrock runoff is dissolution of wind-blown or bedrock minerals.

Figure 3 shows that most solutes are at least moderately associated with each other with the exception of NH_4^+ and K^+ . Interestingly, NH_4^+ and K^+ are most strongly associated with each other, suggesting that their concentrations are partly controlled by a mutual process or source. Both elements are important nutrients for biota, and it seems likely that even in the supposedly unreactive environment of a bedrock catchment, biologic processes can exert important controls on water chemistry.

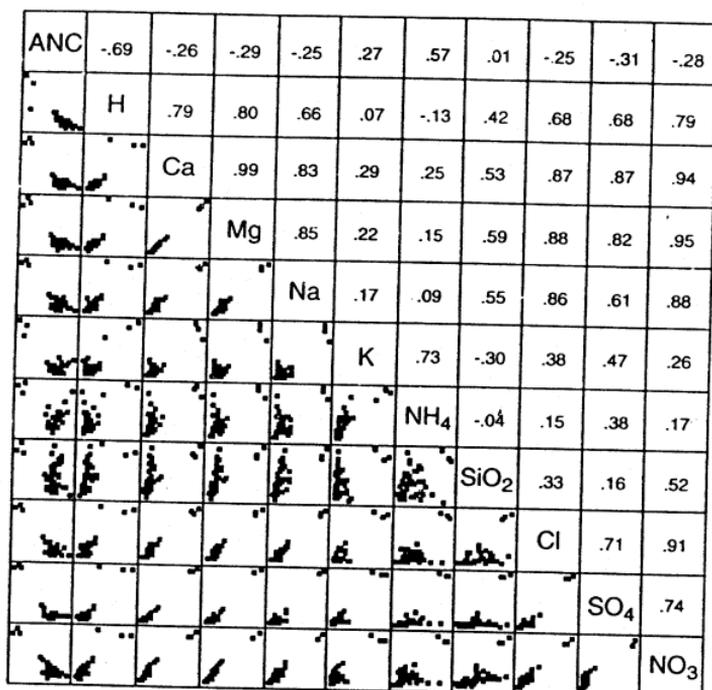


Fig. 3 Relations among major dissolved constituents in samples of bedrock runoff with the corresponding Pearson correlation coefficients. All concentrations in $\mu\text{eq l}^{-1}$, except SiO_2 which is in $\mu\text{mol l}^{-1}$.

CONCLUSIONS

Volume-weighted mean concentrations of NO_3^- and SO_4^{2-} in runoff from a bedrock catchment were 2 to 4 times higher than in precipitation, and base cations were 3 to 10 times higher. The increases in concentrations of these solutes between precipitation and runoff cannot be accounted for solely by evaporation. Dry deposition appears to be substantial part of the solute budget for the bedrock catchment, and because bedrock and talus account for a large percentage of the Loch Vale Watershed, dry deposition also could be an important component of the watershed solute budget.

Concentrations of all solutes in runoff except alkalinity are highest during the initial phase of individual storm events, and volume-weighted mean concentrations for individual storms are correlated with dry antecedent conditions. These results indicate that dry deposition accumulates on bedrock surfaces until appreciable rainfall occurs. The rainfall then washes dry deposits from the rock surface and provides a medium for interaction between strong acids derived from atmospheric deposition (both wet and dry) and geologic materials. The good correlation between strong acid anions and base cations and SiO_2 may be explained by cation exchange and strong acid weathering. Biologic reactions appear to have an effect on NH_4^+ and K^+ concentrations in runoff, and by implication may play a small role in regulating concentrations of other solutes in runoff.

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