

Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains

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Abstract. Time-intensive discharge and chemical data for two alpine streams in the Loch Vale watershed, Colorado, were used to identify sources of runoff, flow paths, and important biogeochemical processes during the 1992 snowmelt runoff season. In spite of the paucity of soil cover the chemical composition of the streams is regulated much as in typical forested watersheds. Soils and other shallow groundwater matrices such as boulder fields appear to be more important in controlling surface-water chemistry than their abundance would indicate. The chemical composition of the major source waters (usually thought of as end-members whose chemical composition is relatively constant over time) changes at the same time that their mixing ratio in streams changes, confounding use of end-member mixing models to describe stream-water chemistry. Changes in the chemical composition of these source waters are caused by the ionic pulse of solutes from the snowpack and the small size of the shallow groundwater reservoir compared to the volume of snowmelt passing through it. The brief hydrologic residence time in the shallow groundwater indicates that concentrations of most dissolved constituents of stream water were controlled by fast geochemical processes that occurred on timescales of hours to days, rather than slower processes such as weathering of primary minerals. Differences in the timing of snowmelt-related processes between different areas of the watershed also affect the stream-water chemical composition. Cirque lakes affect discharge and chemical composition of one of the streams; seasonal control on stream-water NO_3 and SiO_2 concentrations by diatom uptake in the lakes was inferred. Elution of acidic waters from the snowpack, along with dilution of base cations originating in shallow groundwater, caused episodes of decreased acid-neutralizing capacity in the streams, but the streams did not become acidic.

Introduction

Watersheds along the Continental Divide in Colorado and neighboring states are a major source of water not only in the Rocky Mountain region but in distant areas of the midwestern and western United States. The hydrologic cycle of these high-altitude watersheds is characterized by a snowpack accumulation period during late autumn, winter, and early spring; a snowmelt runoff period during late spring and early summer; and a period in late summer and early autumn, which is predominately base flow but has potential for storm flow from precipitation events. Although most of the annual streamflow occurs during the snowmelt runoff period, processes that control the release of solutes from the snowpack and their impact on surface waters are poorly understood. This lack of understanding is due in part to the fact that these streams have traditionally been thought of as pristine and unaffected by anthropogenic activity and in part to the difficulty of access to these watersheds during the runoff period.

Concern about effects of acid deposition focused attention on high-altitude watersheds of the western United States in the 1980s. Although chronic acidification is not believed to be a major problem in the Rocky Mountain region [Turk and Spahr, 1991], the chemistry of these systems during the runoff period

is not well known [Wigington *et al.*, 1990]. Concentrations of acid anions (NO_3 and SO_4) in the snowpack along the Continental Divide in northern Colorado were found to be twice the regional background level in 1991 and 1992 [Turk *et al.*, 1992], indicating strong potential for acidic meltwater in this area. Snowmelt also dilutes base cations which come from weathering, making these streams particularly susceptible to episodic acidification during the snowmelt runoff period. Episodic acidification of lakes and streams is well documented in areas known to be affected by acid deposition such as Scandinavia and the northeastern United States [Wigington *et al.*, 1990]. Although deposition rates are much lower in the western United States, many high-altitude lakes and streams have little natural buffering capacity and are at risk to acidification from even small amounts of acid deposition. The risk of episodic acidification during snowmelt is exacerbated by the ionic pulse effect that causes elevated concentrations of chemical constituents to be eluted from the snowpack during early snowmelt [Johannessen and Henriksen, 1978].

A number of studies have examined chemical processes that occur during snowmelt in the western United States. At Gem Lake in the Sierra Nevada Mountains of California, dilution was found to be the primary effect of snowmelt on surface waters; the absence of significant acidification may have been caused by relatively low concentrations of acid anions in the snowpack [Stoddard, 1987]. Similar results were observed in the North Cascades area of Washington [Loranger and Brakke,

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Paper number 95WR02037.

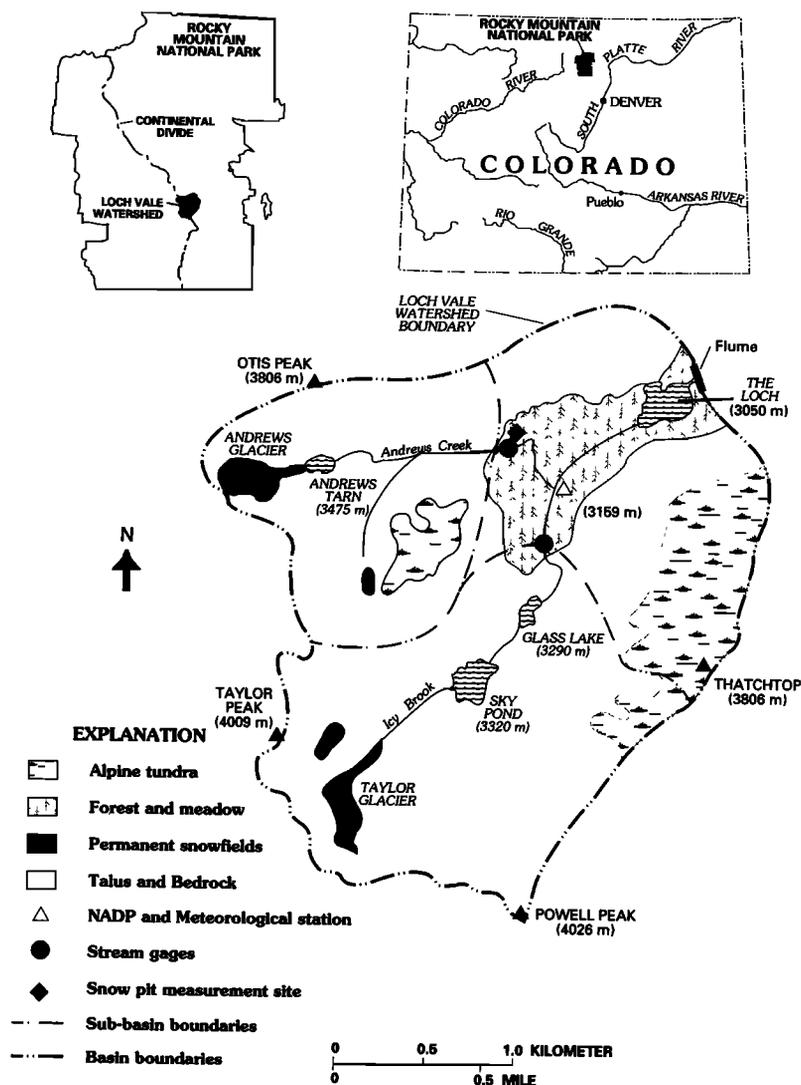


Figure 1. Location of the Loch Vale watershed.

1988]. However, at Emerald Lake in the Sierra Nevada [Williams *et al.*, 1993], snowpack concentrations of NO_3 and SO_4 were much larger, and acidification from snowmelt caused a loss of buffering capacity in addition to the dilution effect.

Investigations in the Snowy Range of Wyoming demonstrated a strong ionic pulse effect in snow meltwater [Bales *et al.*, 1990]. In other work in the Front Range, soil reactions [Finley and Drever, 1992] and nitrogen saturation [Williams and Caine, 1992] have been suggested as important processes controlling release of solutes during snowmelt.

An earlier investigation of snowmelt effects on the entire Loch Vale watershed [Denning *et al.*, 1991] indicated that during the early part of snowmelt, stream water was affected by inputs of soil water with high concentrations of NO_3 and organic acids. During low-flow periods, biogeochemical processes influenced stream chemistry, but during high flows of late spring and early summer the short residence times in the Loch Vale watershed minimized the importance of these processes [Baron, 1992].

In this paper we examine the chemical composition of snow and precipitation, the hydrologic and chemical processes that occur during snowmelt, and the seasonal variation in discharge

and chemical composition of two alpine streams which are tributaries to Loch Vale. Because concentrations of acidic anions in the snowpack are large and there is little soil in these watersheds to buffer the ionic pulse, it was hypothesized that these streams might be more sensitive to episodic acidification during snowmelt than streams and lakes which were the subject of previous studies. Stream discharge and chemical data collected daily during snowmelt are shown to be useful in evaluating sources of runoff, flow paths, and biogeochemical processes that control surface water chemistry.

Site Description

The Loch Vale watershed is located in Rocky Mountain National Park in the northern Front Range of Colorado (Figure 1) and has been the focus of ecosystem research by the National Park Service and a host of other investigators since 1981. A detailed description of the Loch Vale watershed is given by Baron and Mast [1992]. The Loch Vale watershed is 660 ha in area and ranges in elevation from 3050 to 4026 m. The work described in this paper consists of research on the

two major tributaries to the Loch: Icy Brook and Andrews Creek.

The entire Loch Vale watershed consists of 83% bare rock, boulder fields, snow, and ice; 11% alpine ridge (tundra); 5% forest; and 1% subalpine meadow [Baron *et al.*, 1992]. The area of the Andrews Creek and Icy Brook subbasins combined equals about 75% of the entire Loch Vale watershed. Less than 1% of the subbasin areas are forested; in the alpine ridge zone, only 10–15% of the area has significant soil development [Walthall, 1985]. Therefore only 5–15% of the area in the Andrews Creek and Icy Brook subbasins is covered by true soil. Even the true soils in Loch Vale are coarse textured and immature, having had a short time to develop in a cold climate. Total storage of soil water for the Loch Vale watershed was estimated to be less than 5% of the outflow at the Loch [Baron and Denning, 1992]. Deep groundwater storage was considered to be negligible [Baron and Denning, 1992].

In this paper the term “shallow groundwater” frequently is used. Since soil is thin and poorly developed, soils would not be expected to be as important as in lower-elevation forested watersheds where soil cover approaches 100%. Groundwater stored in aquifers is also scarce in these alpine watersheds. However, other shallow groundwater matrices exist, which may function similarly to soils. There are large fields of talus, the interstices of which may contain fine material that has weathered in situ or has been deposited by wind. Water from these areas is included along with water from true soils, saturated zones, and other types of subsurface materials when the influence of shallow groundwater is discussed.

Stream-water discharge and chemical composition were monitored at streamflow gaging stations on the two tributaries just below timberline (Figure 1). The catchments for the two streams are nearly entirely alpine, consisting of rock outcrops, talus slopes, and some tundra. Andrews Glacier drains into a small tarn in the headwaters of Andrews Creek, which flows down a steep channel and is joined by an unnamed tributary. The gaging station on Andrews Creek is located adjacent to a 2-ha wet meadow. The Icy Brook catchment begins at Taylor Glacier, which becomes a rock glacier just above Sky Pond. Sky Pond flows into Glass Lake, which discharges over Timberline Falls and flows through a small mixed forest/wet meadow area before reaching the Icy Brook stream gage.

The presence of larger areas of permanent snowfields and glaciers suggests a greater input of winter precipitation (primarily in the form of blowing snow) in the Andrews subbasin compared to the Icy subbasin. Less evaporation and sublimation are expected there also because of the narrower valley with more northerly aspects that limit solar heating during much of the year, greater albedo from year-round snow and ice, and less open-water surface to be evaporated by the strong winds blowing off the Continental Divide.

Methods

Snowpack chemical composition and snow-water equivalent samples were collected during a survey of the watershed that was conducted at the time of maximum snow accumulation in mid-April. Samples were depth-integrated snow cores collected in an aluminum Mt. Rose sampler and transferred to zip-lock plastic bags. The bags and all bottles and jars for snow and stream samples were triple rinsed with deionized water prior to use. Samples were transferred to polyethylene jars in the laboratory and allowed to melt at room temperature over-

night. Snow-water equivalent was calculated from density measurements of individual 10-cm strata collected at an index snow pit located in a meadow near the Andrews Creek sampling site. The snow pit was located to minimize effects of wind redistribution of snow.

National Atmospheric Deposition Program (NADP) data for the Rocky Mountain National Park-Loch Vale site also are presented. Precipitation was measured in a weighing bucket, and weekly samples of wetfall were collected (National Atmospheric Deposition Program (NRSP-3)/National Trends Network, NADP/NTN Coordination Office, National Resource Ecology Laboratory, Colorado State University, Fort Collins, 1993).

Stream-water samples were collected daily in polyethylene bottles by automatic sampler from mid-April (or beginning of streamflow) through early July; the sampling interval was increased gradually to weekly intervals by the end of September. Samples were retrieved at least once a week during snowmelt and at least once every 2 weeks later in the season. Grab samples were collected when automatic samples were retrieved. Stream stage was recorded at 15-min intervals at the stream-sampling sites, and discharge was measured once to twice per week during spring runoff to develop discharge rating curves. The discharge record was extended through the winter months using a logarithmic extrapolation of streamflow recession. Estimates of winter flow amounted to 0.5% of the total annual flow in Icy Brook and 7% in Andrews Creek; therefore any error in the extrapolation was considered insignificant to overall budget estimates.

Specific conductance, pH, and acid-neutralizing capacity (ANC) (automated Gran titration) were measured in the laboratory on unfiltered, unpreserved samples. HCO_3^- was considered equal to ANC. Filtered (0.45 μm), untreated aliquots were used to analyze Cl, NO_3^- , and SO_4^{2-} by ion chromatography (detection limits (2 standard deviations of blank samples) were 0.5, 0.3, and 0.4 $\mu\text{eq L}^{-1}$, respectively). Filtered aliquots preserved with nitric acid (pH less than 2) were used to analyze Ca, Mg, Na, and SiO_2 (detection limits were 0.4, 1.0, and 2.2 $\mu\text{eq L}^{-1}$ and 2.2 $\mu\text{mol L}^{-1}$, respectively) by inductively coupled plasma spectrophotometry and K by atomic absorption flame spectroscopy (detection limit was 0.8 $\mu\text{eq L}^{-1}$). Filtered aliquots preserved with mercuric chloride were used to analyze NH_4^+ colorimetrically (detection limit was 1 $\mu\text{eq L}^{-1}$). Methods for sulfur-isotope analyses are described by Turk *et al.* [1993].

Hydrologic budgets for Andrews Creek and Icy Brook, water year (WY) 1992, are presented in Table 1. Inputs were calculated as total precipitation at the NADP site. Estimating precipitation inputs to the Loch Vale watershed is difficult due to (1) spatial variability caused by orographic effects and wind redistribution of snow (including transport to and from areas outside the watershed boundary); and (2) inaccessibility of large areas in the watershed. Snow-water equivalent at maximum accumulation in the Andrews Creek watershed, calculated from 50 depth measurements, five density measurements, and aerial photographs of snow-covered area in 1994, was 56 cm, compared to 66 cm measured in a weighing-bucket precipitation gage located at the lowest elevation in the watershed, demonstrating the spatial heterogeneity of snow deposition and the difficulty with using simple models which account only for orographic effects. For this reason we chose to use the NADP precipitation as input, because it is located in an area that is dominated by neither scour nor deposition by wind and it has a historic record for comparison to long-term averages.

Table 1. Water Budget and Volume-Weighted Mean (VWM) Chemical Concentrations in the Snowpack (Seasonal), Precipitation (Seasonal and Annual), and Stream Water (Annual)

	Snowpack: Maximum Accumulation April 1992	Precipitation			Streams	
		NADP: October–March 1992	NADP: April–September 1992	NADP: WY1992	Andrews Creek: WY1992	Icy Brook: WY1992
Water, cm	44	47	43	90	85	64
Calcium, $\mu\text{eq L}^{-1}$	7	2	9	6	57	66
Magnesium, $\mu\text{eq L}^{-1}$	2	1	2	1	14	16
Sodium, $\mu\text{eq L}^{-1}$	2	2	3	2	18	18
Potassium, $\mu\text{eq L}^{-1}$	1	<1	1	<1	4	4
Hydrogen ion, $\mu\text{eq L}^{-1}$	5	6	7	6	<1	<1
Ammonium, $\mu\text{eq L}^{-1}$	6	4	10	7	1	1
Nitrate, $\mu\text{eq L}^{-1}$	10	8	14	11	23	21
Chloride, $\mu\text{eq L}^{-1}$	2	2	2	2	3	4
Sulfate, $\mu\text{eq L}^{-1}$	9	7	16	11	31	37
ANC, $\mu\text{eq L}^{-1}$	<1	<1	<1	<1	30	33
Silica, $\mu\text{mol L}^{-1}$	<2	<2	<2	<2	35	27

NADD is the National Atmospheric Deposition Program; WY1992 is water year 1992; ANC is the acid-neutralizing component.

Comparison with maximum snowpack water equivalent provides a check on point measurements of total precipitation during the winter, when collection efficiencies are poor in bucket-type collectors.

Results

Water Budget

Annual precipitation at the Loch Vale NADP site was 90 cm in WY1992, compared to an average of 100 cm for 1984–1992. Runoff was 85 cm in Andrews Creek and 64 cm in Icy Brook (Table 1). There was good agreement between the winter season (October–March) NADP precipitation amount total and the single measurement of total snowpack accumulation in April. Precipitation was evenly distributed between the winter (October–March) and summer (April–September) periods. The difference in runoff between the two subbasins may have been a combination of greater precipitation inputs and less evaporation in the Andrews Creek subbasin compared to the Icy Brook subbasin.

If precipitation at the NADP site is applied over the entire watershed and other outputs such as possible seepage to ground water are ignored, evaporation in Andrews Creek would be 9 cm, or 10%, and in Icy Brook 29 cm, or 31%. An estimate of 39% evaporation was made for the entire Loch Vale watershed, based on a modified Penman equation applied by land cover and season [Baron and Denning, 1992].

Annual Volume-Weighted Mean Chemical Concentrations

All chemical constituents (Table 1) are presented as volume-weighted mean (VWM) concentrations to facilitate comparison between the two streams while minimizing effects of uncertainty in the water budgets. For example, if precipitation was consistently underestimated by 20%, the calculated VWM concentrations would still be correct, while the input flux calculated from the same data would be underestimated by 20%. Cation concentrations in NADP precipitation were $\text{NH}_4 > \text{H} > \text{Ca}$, with small amounts of Mg, Na, and K. Anions in precipitation were predominately SO_4 and NO_3 , with small amounts of Cl. A comparison is presented of the NADP winter VWM chemical composition and the mean concentrations of snowpack samples collected in April. Dry deposition (which would be included in the snowpack but not the wet fall) ac-

counted for 0–33% of total deposition for most constituents during the snow accumulation period. Ca and Mg were substantially higher in the snowpack than in the winter NADP wet fall samples, probably indicating significant input in dry deposition. Sublimation of snow-water equivalent would cause uniformly higher concentrations in the snowpack compared to the wet fall (analogous to concentration by evapotranspiration); sublimation did not appear to be significant, based on Na and Cl values. In general, the precipitation inputs were typical of high-elevation sites in the region, except for higher amounts of the acid anions NO_3 and SO_4 [Turk et al., 1992]. Ca, Mg, Na, K, HCO_3 , and SiO_2 are all produced by mineral weathering in the watershed and were present in stream water at concentrations approximately 10 times those in precipitation.

SO_4 concentrations in stream water are approximately 3 times those in precipitation. While dry deposition contributes less than 25% of total deposition in winter (Table 1), the contribution from summer dry deposition is uncertain: A comparison of chemical composition of lakes and wet fall indicated no significant dry deposition of SO_4 in the Rocky Mountains [Turk and Spahr, 1991], while measurements of rainfall and runoff from a bedrock surface indicated dry deposition of sulfate equal to wet deposition during the summer months [Clow and Mast, 1995]. Unless dry deposition is equal to or greater than wet deposition, there would appear to be a watershed source that is equal to or slightly greater than the precipitation source. A watershed source of sulfate is supported by sulfur-isotope analyses of sulfate from the Loch outflow and bulk precipitation. During water year 1992, nine outflow samples had $\delta^{34}\text{S}$ values ranging from 1.2 to 2.0 per mil, compared to four bulk precipitation samples ranging from 4.7 to 6.2 per mil. The occurrence of sulfide-bearing minerals in the Loch Vale watershed may not be widespread, but their influence on the concentrations of SO_4 in surface water is significant in both Andrews Creek and Icy Brook. Only recently have sulfide-bearing minerals been identified in the Loch Vale watershed (J. Baron, National Biological Service, personal communication, 1993).

Cl concentrations in stream water are 1.5 to 2 times those in precipitation; at such low concentrations it is not possible to determine whether all of the Cl comes from precipitation, which is then concentrated by evapotranspiration, or whether there is a small watershed source of Cl contributing to the

stream-water concentrations. This ambiguity is unfortunate, because none of the major ions appear suitable for estimating the concentration effect of evaporation; that is, none are derived entirely from precipitation and behave conservatively in the watershed.

NO₃ export in the stream water is approximately equal to precipitation inputs of NO₃ plus NH₄, allowing for concentration by evaporation of 15–30%. Nitrogen concentrations in the snowpack of this part of the Front Range were among the highest measured in Colorado [Turk *et al.*, 1992]. Lakes in other high-elevation areas of Colorado usually have NO₃ concentrations below detection levels during summer [Eilers *et al.*, 1986; Landers *et al.*, 1986], whereas in the Loch Vale streams, concentrations were never less than 10 $\mu\text{eq L}^{-1}$.

Significant differences in mean concentrations of most major ions existed between the Andrews Creek and Icy Brook sub-basins. Annual VWM concentrations were typically larger in Icy Brook than in Andrews Creek: Ca and Mg by 15%, SO₄ by 19%, and ANC by 10%. Na and K were roughly equal in the two streams. Andrews Creek had larger annual VWM concentrations of SiO₂ and NO₃ than Icy Brook.

Seasonal Variation

The annual hydrograph was dominated by snowmelt, beginning in late April or early May and continuing through July (Figure 2a). During the early part of snowmelt, periods of fair weather that accelerate snowmelt alternated with spring snowstorms that resulted in significant snowpack accumulation. By July, most precipitation events were in the form of rain; however, peak flows were the product of snowmelt and occurred on warm sunny days, causing mean daily discharge to vary by a factor of 2–3 in the course of a few days time. During August and September, discharge decreased steadily, punctuated by small storm-event peaks. Some of these storms were in the form of snow at the higher elevations but were followed by warm sunny days that caused rapid melting. A trickle of streamflow was maintained year-round in Andrews Creek, but flow ceased in Icy Brook during the winter and returned in May once sufficient snowmelt runoff caused Glass Lake to overflow.

Concentrations of most of the major ions exhibited a strong seasonal pattern that was similar in the two streams (Figures 2b–2h). The earliest samples in Andrews Creek were collected before any snowmelt; thus they represent base flow from the shallow groundwater system. During early snowmelt, concentrations fluctuated from day to day, but there were no trends for most solutes; concentrations decreased from June 1 to sometime in late summer; and by August, concentrations leveled and began to increase. Discharge continued to decrease after concentrations began to increase in late summer/early autumn.

The relation between concentration and discharge demonstrates a large hysteresis effect; concentrations were higher while the stage was rising than at comparable discharge while the stage was falling (Figures 3a–3f). The seasonal pattern of changes in concentration can be modeled using a harmonic function of sample date to explain about 70% of the variance for most constituents or a simple regression against log (mean daily discharge) to explain about 60% of the variance. If the harmonic function of sample date is used, discharge does little to explain the remaining variance. The concentration-discharge relation changed over time for all constituents.

Seasonality of the concentration-discharge relations was ex-

amined in more detail by dividing samples into three periods for which least squares regression was used to relate selected chemical constituents to logarithm of discharge (Table 2). The time periods were defined qualitatively by examination of the concentration and discharge data. This separation removes some of the seasonality in the data, allowing the relation (or lack thereof) between concentration and discharge to become more obvious. The models are useful for comparative purposes only; the goal was not to develop a calibrated predictive model but to identify the relative strengths of the relations (expressed as *r* square) and the sign and magnitude of the regression coefficients.

During April and May in Andrews Creek, concentrations of the weathering products SiO₂ and Na exhibited a strong flow-dilution relation (large *r* square, negative regression coefficient); concentrations decreased when discharge increased, and concentration during days of low flow increased slightly. Ca and Mg concentrations did not follow this pattern; instead, they were relatively constant, showing only a slight flow-dilution relation during the snowmelt peak in late May. (Plots and statistics of Mg are not presented because patterns of Mg concentration mirror those of Ca.)

SO₄ concentrations show a flow-dilution pattern similar to SiO₂ and Na concentrations. NO₃ concentrations increased with increases in discharge through late May (flow-concentration relation). Concentrations of NO₃ in the streams during early snowmelt were large relative to NO₃ concentrations in the bulk snowpack. Cl showed no significant relation to discharge except during May in Icy Brook; low concentrations of Cl cause greater uncertainty in interpretations.

ANC shows a weak flow-dilution pattern in April–May. Weak organic acids were not measured directly but are reflected in the anion deficit. No trend in anion deficit over time or discharge was evident, but error in this computed value tends to be large because it incorporates error from all of the chemical analyses. Anion deficits in stream water were generally about 10 $\mu\text{eq L}^{-1}$.

Chemical concentrations in the streams were less complicated during the periods of June–July and August–September. Most of the snowmelt runoff occurred during June–July. By this time, most chemical constituents showed a steady decrease in concentration and were only weakly related to discharge. NO₃ concentrations in Andrews Creek switched from a strong flow-concentration relation in April and May to a weak flow-dilution relation in June and July, which was overshadowed by the steady decrease in NO₃ concentration during this period. During June and July, SiO₂ in Andrews Creek had a stronger relation to discharge than most of the other constituents, although the relation was not as strong as it was in April–May. The strong relation of ANC to discharge was caused by the complex interaction of base cations and acid anions: The steady decrease in base cations from weathering (which occurred somewhat independent of discharge) was accompanied by an equivalent decrease in the acid anions NO₃ and SO₄. None of the constituents in Icy Brook had a strong relation between concentration and discharge.

By August, most of the snow had melted, except around the permanent snowfields and glaciers. Discharge decreased steadily, although a few small peaks resulted from precipitation events. Concentrations of most chemical constituents began to increase during August or September, creating a flow-dilution relation in all of the chemical constituents.

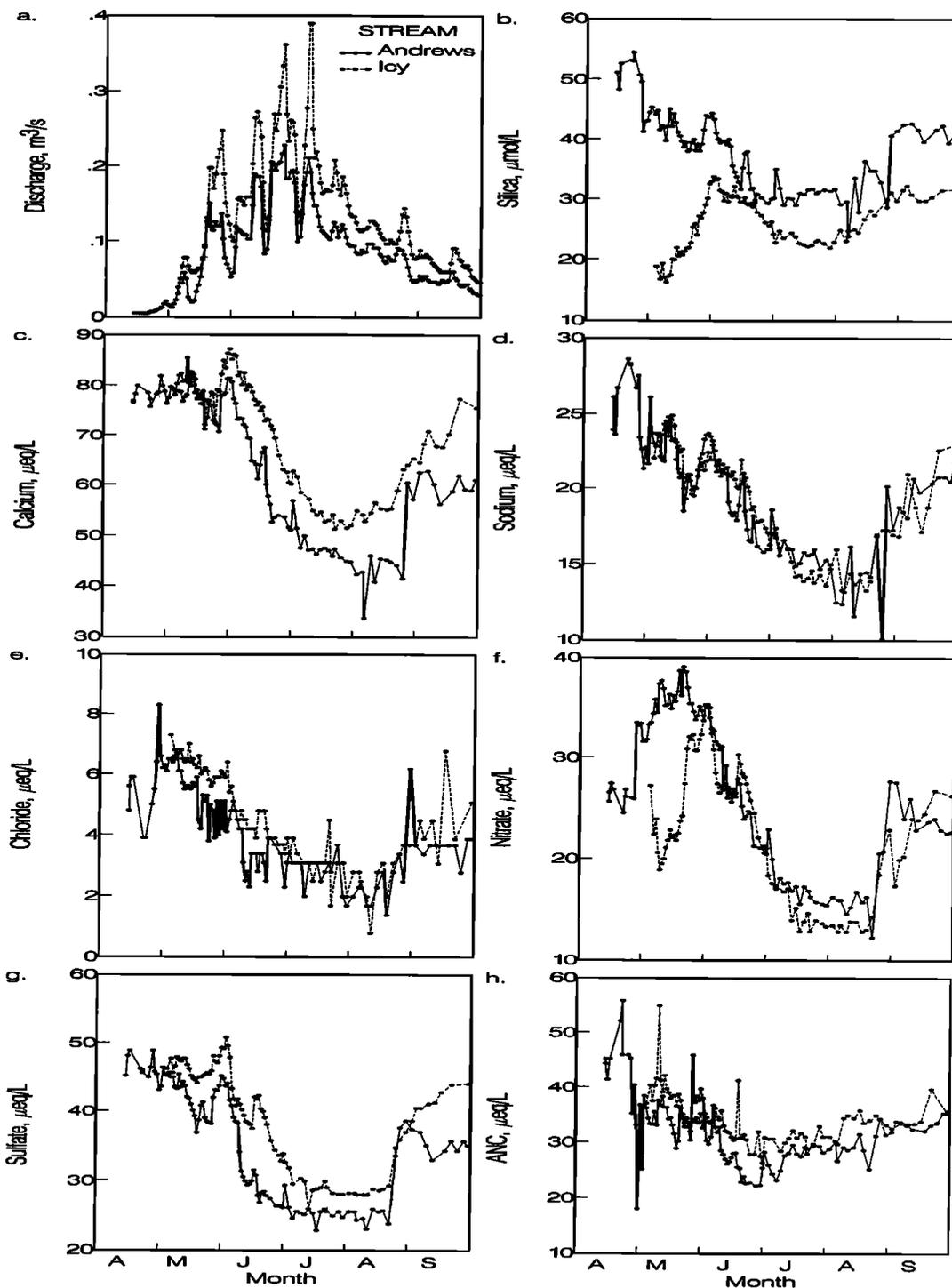


Figure 2. Stream discharge and chemical composition for Andrews Creek and Icy Brook water year 1992: (a) mean daily discharge; (b) SiO_2 ; (c) Ca; (d) Na; (e) Cl; (f) NO_3 ; (g) SO_4 ; (h) acid-neutralizing capacity (ANC).

Daily Variations

Daily fluctuations in discharge during snowmelt were driven by changes in the weather; the highest discharges were on warm, sunny days, particularly if nighttime temperatures remained above freezing. Examination of daily records over periods of a few days with large changes in discharge provides insight into the sources and flow paths of the stream water, without the complication of seasonality.

There were significant differences between patterns of

change among the various chemical constituents and in the pattern that each constituent followed during different parts of the year. The relations between chemical concentrations and discharge in Andrews Creek are shown in Figures 3a–3f. To see an example of how these relations changed over time, Figure 3b may be compared to Figure 2a; earliest samples are in the upper left on Figure 3b. Moving clockwise, the four major snowmelt peaks are seen in clusters on the right side with the earliest peak at the top; samples collected during the

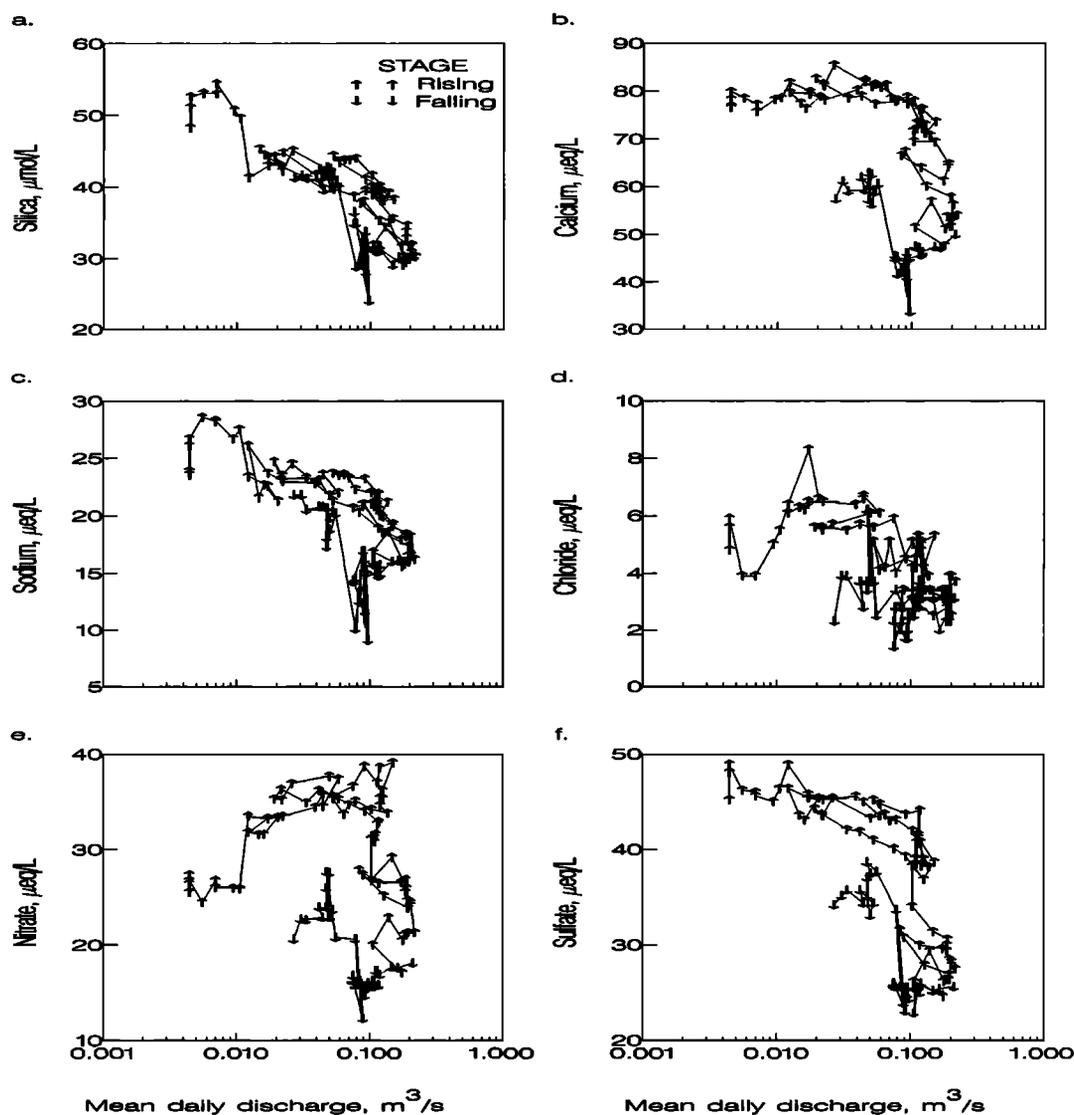


Figure 3. Concentration-discharge relations for Andrews Creek, water year 1992: (a) SiO₂; (b) Ca; (c) Na; (d) Cl; (e) NO₃; (f) SO₄. Symbol indicates direction in change of stage of annual hydrograph. Annual peak is defined as July 8, 1992 (refer to Figure 2a).

recession limb (falling stage) begin at the lower right and move toward the center of the plot.

An example of a constituent derived entirely from mineral weathering is SiO₂ in Andrews Creek. Earliest samples showed an increase to greater than 50 $\mu mol L^{-1}$. This was quickly followed by a decrease to 40–45 $\mu mol L^{-1}$, a range in which the concentration remained through early June (Figure 3a). After the first large snowmelt runoff peak in late May, SiO₂ concentration increased by less than 20% while discharge decreased by 65% (Figure 3a). During the second snowmelt peak, there was a slight decrease in SiO₂ concentration, followed by a slight increase during the low-flow interval, but most of the change in SiO₂ concentration reflected a steady decrease over time. There was a flow-dilution relation if individual peaks in the daily data (lasting about 1 week) are examined independently (middle right cluster of points). By the next week, however, during the last (and largest) snowmelt runoff peak (lower right cluster of points), SiO₂ concentration was not related to discharge. Late in the summer, SiO₂ con-

centrations increased steadily. Other constituents that are derived primarily from mineral weathering exhibited a similar pattern; that is, changes in concentration were small relative to changes in discharge.

The two chemical species that had a markedly different pattern from the others are Cl and NO₃ (Figures 3d and 3e). Early in the season, both showed a flow-concentration pattern characteristic of ion elution from the snowpack, increasing by approximately 50%. After this initial pulse, Cl and NO₃ concentration both decreased steadily, with no relation to discharge until snowmelt was nearly complete. At that time, discharge decreased steadily and concentrations increased.

Differences Between the Streams

Discharge in Icy Brook is controlled by the outlet of Glass Lake; in 1991–1993, streamflow ceased each winter due to evaporation and freezing. Flow resumed in May, once sufficient snowmelt caused Glass Lake to overflow. Snowmelt discharge peaks were not attenuated significantly by the lakes in

Table 2. Statistics for Least Squares Regression of Concentration on Log Mean Daily Discharge

Period	SiO ₂	Ca	Na	NO ₃	SO ₄	Cl	ANC
<i>R², Andrews Creek</i>							
April–May	0.77	0.10	0.64	0.70	0.69	NS	0.35
June–July	0.46	0.15	0.25	0.08	0.25	0.07	0.68
August–September	0.58	0.58	0.66	0.36	0.51	0.23	0.64
<i>R², Icy Brook</i>							
April–May	0.40	NS	0.45	0.35	NS	0.76	0.22
June–July	NS	NS	NS	NS	0.09	0.10	0.22
August–September	0.37	0.53	0.60	0.53	0.54	0.31	0.12
<i>Slope Coefficient, Andrews Creek</i>							
April–May	-8.6	-2.3	-4.1	+7.2	-5.1	NS	-8.3
June–July	-19.9	-31.5	-9.1	-13.5	-22.7	-1.7	-22.46
August–September	-22.5	-35.1	-16.8	-13.8	-20.0	-2.7	-11.3
<i>Slope Coefficient, Icy Brook</i>							
April–May	+10.4	NS	-4.1	+10.8	NS	-1.3	-8.2
June–July	NS	NS	NS	NS	-17.3	-2.6	-10.1
August–September	-8.8	-28.4	-12.9	-18.4	-23.0	-3.5	-4.3

Concentration as $\mu\text{eq L}^{-1}$ except SiO₂ as $\mu\text{mol L}^{-1}$. Mean daily discharge as $\text{m}^3 \text{s}^{-1}$. NS is no significant relationship (probability > *F* greater than 0.05).

Icy Brook (Figure 2a). The peaks did not occur much later in Icy Brook than in Andrews Creek, and they were approximately equal on a unit-area discharge basis. In general, temporal variations of dissolved species demonstrated patterns in Icy Brook that were similar to those for Andrews Creek. Two chemical constituents that exhibited a dissimilar seasonal pattern in the two streams were NO₃ and SiO₂, both of which were relatively low in Icy Brook early in the season and increased until around June 1, when concentrations in Icy Brook approximated those in Andrews Creek (Figures 2b and 2f). At that time, concentrations in Icy Brook reversed their trend and were similar to Andrews Creek for about 1 month, followed by a period in late summer and early autumn when concentrations were less than or equal to Andrews Creek.

Discussion

In this discussion we identify important hydrological, geochemical, and biological processes that control surface-water chemistry in Loch Vale. Previous studies at the plot scale have quantified certain processes at specific locations, while for other processes and locations (e.g., hydrology and geochemistry of talus), there is little or no information available due to inaccessibility and the difficulty of making representative measurements. Examination of the time-intensive chemical and discharge data for the streams enables us to determine the relative importance of different processes at the watershed scale.

Snowmelt input drives the annual hydrograph in alpine streams, and the chemical composition of snowmelt is determined by the ionic pulse from the bulk snowpack. In Loch Vale in 1992, concentrations of nitrogen in early snowmelt were 78% greater than in the bulk snowpack [Campbell *et al.*, 1995]; concentrations of all chemical constituents are typically greater during early melt than later melt [Johannessen and Henriksen, 1978]. Hydrologic flow paths determine the opportunity for various processes to chemically alter the snowmelt on its way to the stream: Direct snowmelt delivered to the streams by overland flow would be least altered, snowmelt that follows shallow

subsurface flow paths (interflow) would be in contact with the most reactive materials such as soil, and flow from saturated groundwater systems would likely contain weathering products in stoichiometric proportions. Piston-type flow may cause early snowmelt to flush shallow groundwater which has been stored since the previous year's runoff season. Because the subsurface flow systems in large parts of the Loch Vale watershed are poorly characterized (e.g., talus slopes), we will not attempt to separate various components of subsurface flow such as unsaturated- and saturated-zone groundwater.

Temporal variability in the chemical composition of snowmelt and shallow groundwater is partially blurred by spatial variability in the generation of runoff. During early snowmelt, only the lower elevations have warmed sufficiently to produce snowmelt runoff. As the season progresses, this source area grows larger, as snowmelt occurs at higher elevations, until at some point, most of the watershed contributes snowmelt. At this time the higher elevations are generating concentrated runoff from the ionic pulse in early snowmelt and flushing of concentrated shallow groundwater, while in the lower elevations, snowmelt is in the later stages, which produces dilute runoff from both snowmelt and shallow groundwater. Late in the summer, any snowmelt comes from high elevations only, and most runoff is generated from shallow groundwater with residence time of increasing duration.

Concentration-discharge plots for Andrews Creek (Figures 3a–3f) show that discharge varied by a factor of 50 (0.004–0.21 $\text{m}^3 \text{s}^{-1}$), whereas most of the major ions varied by factors of 1.5–3. An example is SiO₂, a constituent derived entirely from mineral weathering: If an increase in discharge was caused by direct snowmelt (no influence from watershed processes), a proportional decrease in stream-water SiO₂ concentration should result, because the snowpack contains no SiO₂. However, the daily changes in stream-water SiO₂ concentration during snowmelt were small compared to the changes in discharge. Thus fluctuations in surface-water chemical concentrations were moderated in these alpine watersheds, similar to

forested watersheds, which have much larger soil-water and groundwater reservoirs.

If the reservoir of shallow groundwater in these alpine basins were sufficiently large, short-term changes in concentration caused by the influx of snowmelt could be attenuated simply by mixing "old" and "new" water. Otherwise, a number of geochemical processes which act on timescales of hours or days would be required to regulate chemical concentrations in the streams (cation exchange, sulfate adsorption and desorption, and dissolution of amorphous aluminosilicates are discussed below). Therefore the size and nature of the shallow groundwater reservoir are important in determining hydrologic and geochemical processes which regulate stream chemistry.

Some rough calculations, which assume homogeneity throughout the watershed, can be made: For the entire Loch Vale watershed, *Baron and Denning* [1992] estimated that total shallow groundwater storage in forest and meadow soils is less than 5% of total annual outflow from the Loch. In Andrews Creek, total daily discharge at peak flow was equal to 1.5% of total annual discharge. Thus, if all of the streamflow was routed through this soil, residence time in the soil at peak flow would have been less than 4 days. In fact, hydrologic processes are anything but homogenous, and soil-water storage estimates have large uncertainty. However, the average contact time between the snowmelt-derived water and the forest and meadow soils is of short duration compared to most forested watersheds.

Hydrograph separation was performed on Andrews Creek 1994 data using SiO_2 and ^{18}O to determine percentages of total discharge contributed by snowmelt and old water [*Mast et al.*, 1995]. Results of the separation using SiO_2 indicated an old water contribution of 75% prior to June 1 (early snowmelt) and 45% from June 1 to July 15 (peak snowmelt). Results using ^{18}O indicated an old water contribution of only 33% during early snowmelt and <10% during peak snowmelt. It was inferred that the difference in the two methods was caused by new snowmelt water which passed rapidly through a shallow groundwater system, where it acquired SiO_2 in concentrations similar to the old water. The hydrograph separation using ^{18}O indicated a contribution of old water during the snowmelt hydrograph (May–July) of 5–10% of annual discharge; in this study an additional 7% of annual discharge was estimated during the winter months October–April, which would be also be old shallow groundwater. If total storage of shallow groundwater were equal to 15% of annual discharge, hydrologic residence time in the groundwater system during peak discharge would be roughly 10 days. The brief residence time in the shallow groundwater system means that fast geochemical processes must play an important role in regulating stream chemistry.

The lack of forest and meadow soils in these alpine basins indicates that other shallow groundwater matrices must be functioning similarly to the true soils in regulating chemistry and discharge in the streams. These would most likely be in the poorly sorted material on talus slopes and in the valley bottom. Because of the difficulty of collecting samples from a matrix of particles ranging in size from silt to tens of meters in diameter, little is known about the physical or chemical properties of this material or the pore water within it.

SiO_2 reactions that involve the formation or dissolution of crystalline minerals are kinetically limited and could not regulate concentrations during large changes in discharge over a few days time. Faster reactions (with a timescale of hours to days) involving amorphous aluminosilicates have been sug-

gested as the primary control on SiO_2 concentrations in natural waters [*Paces*, 1978]. Soil solutions at an intensively studied plot in the alpine zone of Loch Vale were slightly oversaturated with respect to amorphous aluminosilicates during low-flow conditions and slightly undersaturated during high-flow conditions, indicating that amorphous aluminosilicates may play an important role in regulating SiO_2 concentrations in shallow alpine soils [*Clow*, 1992]. A previous study in the mountains of northern California attributed the relative invariance of SiO_2 concentrations to dissolution of amorphous aluminosilicates in shallow soil horizons [*Kennedy*, 1971].

The other weathering products in surface waters of Loch Vale were present in ratios expected from stoichiometric weathering of the silicate minerals, plus an excess of Ca, probably from rapid weathering of trace amounts of calcite [*Mast*, 1992]. Cations produced by weathering were regulated in streamflow similarly to SiO_2 ; that is, changes in concentration were small relative to changes in discharge. Cation exchange reactions may partially control concentrations of these constituents. At the Emerald Lake watershed in California, cation exchange occurred in soils and in talus and was the principal control on base cation concentrations in streamflow throughout the snowmelt runoff season [*Williams et al.*, 1993].

SO_4 followed a flow-dilution pattern similar to SiO_2 and Na. The ionic pulse of the snowpack SO_4 could cause high concentrations during early snowmelt and low concentrations during late snowmelt. Summer rains, with relatively large SO_4 concentrations (Table 1), could cause stream-water concentrations of SO_4 to increase during late summer. This would create a seasonal pattern very similar to the flow-dilution relation seen in some of the weathering products. However, the large difference between the Andrews VWM SO_4 in precipitation and stream water (Table 1) and the distinct ^{34}S isotope signature of the stream water support the existence of a source of SO_4 from weathering in the watershed. In a previous study of the entire Loch Vale watershed, adsorption and desorption of sulfate were not believed to play a major role in regulating sulfate, because sulfate retention is low in both mineral and organic components of soil [*Baron et al.*, 1992]. The small range in concentration of sulfate may be the product of a complex interaction between precipitation from different seasons, snowmelt processes, weathering, and other terrestrial and limnological processes, most of which are poorly understood at this time.

NO_3 in the streams is controlled not only by hydrologic flowpaths and the ionic pulse from the snowpack but also biological processes. Andrews Creek NO_3 concentrations increased with increases in discharge through late May (flow-concentration relation). Concentrations of NO_3 in the streams during early snowmelt were large relative to peak NO_3 concentrations in early meltwater, and minimum concentrations in streamflow were equal to minimum concentrations in late meltwater [*Campbell et al.*, 1995]. Nitrogen pathways in the terrestrial ecosystem are poorly understood, but shallow groundwater may contain large amounts of nitrogen which was present in deposition as NH_4 and converted to NO_3 by mineralization and nitrification [*Rascher et al.*, 1987]. Thus high NO_3 eluted from the snowpack is augmented by high NO_3 in shallow groundwater, causing very high concentrations in stream water during snowmelt. Additional biologic controls on nitrogen are present in the aquatic ecosystem of Icy Brook.

Uptake of nutrients and SiO_2 by phytoplankton in Sky Pond and Glass Lake, two main stem lakes on Icy Brook, caused

NO_3 and SiO_2 concentrations to be much lower in Icy Brook than in Andrews Creek during May. Phytoplankton blooms beneath ice cover are documented for the Loch [Spaulding *et al.*, 1992], and diatoms were present in large numbers in Sky Pond at the onset of snowmelt runoff [McKnight *et al.*, 1986]. Uptake of NO_3 and SiO_2 by phytoplankton during the winter and early spring could cause concentration minima to occur, because the lakes are closed systems during the winter. When snowmelt begins, NO_3 - and SiO_2 -rich water from snowmelt and shallow groundwater mixes with the lake water, gradually increasing the concentration in the lakes; which supply most of the water for Icy Brook. On the basis of lake volume measurements [McKnight *et al.*, 1986] and measured discharge in Icy Brook, total discharge equal to about two lake volumes had passed the gage at Icy Brook by June 1, when the concentrations of SiO_2 and NO_3 equalled those in Andrews Creek. During peak flows in late June and July, large populations of phytoplankton are present, but the rapid turnover of lake waters minimizes their effect on chemical concentrations [McKnight *et al.*, 1986].

Other significant differences in processes occurring in the Andrews and Icy Brook subbasins may be inferred by comparing annual VWM concentrations (Table 1) and time plots of concentrations (Figures 2a–2h). Slight differences in mineralogy may exist between the subbasins, but available geologic maps are not of sufficient spatial resolution to make this distinction. Physical weathering of fresh rock surfaces by Andrews Glacier (in Andrews Creek) and Taylor Glacier (in Icy Brook) may differ significantly but cannot be quantified with available information. Effects of late-summer meltwater discharge from Andrews glacier are unknown.

On the basis of the current knowledge of these systems, the hydrologic flow paths and geochemical processes controlling stream chemistry through the runoff season can be postulated: At the onset of snowmelt runoff in late April, there was a pulse of old water from a source with a slightly different chemical composition than the shallow groundwater which contributes to streamflow during most of the year (more concentrated with Na and SiO_2 but not Ca and Mg). During early runoff in May, concentrations of most constituents except Cl and NO_3 showed a slight flow-dilution effect for individual events but did not decrease much compared to the large increase in discharge. During this time, much of the flow may have come from piston-type displacement of old shallow groundwater by snowmelt runoff.

By June 1 the reservoir of old shallow groundwater had been significantly depleted, and a gradual dilution of the shallow groundwater by snowmelt began. At that time, about 10 cm of runoff had occurred in the streams since snowmelt runoff began; this may be indicative of the volume of the entire shallow groundwater reservoir or just the more reactive portion in the shallow layers.

Late in summer, concentrations begin to increase again, reflecting either (1) increasing contact time for weathering reactions in shallow groundwater or (2) a change in dominant flow paths to deeper groundwater which would reflect more weathering reactions and fewer exchange reactions. A study of forest soil solutions in Loch Vale demonstrated that soil lysimeters that yielded low sample volumes (indicating low hydraulic conductivity and a longer contact time between water and soil) had relatively high concentrations of weathering products [Arthur and Fahey, 1993], indicating kinetic limitations on concentrations of base cations in shallow groundwater.

Conclusions

Despite a low percentage of area covered by true soils, chemical concentrations in Loch Vale streams appear to be regulated by the same processes that are attributed to soils in forested watersheds. Much of the snowmelt is delivered rapidly to the stream by piston-type displacement of shallow groundwater. The groundwater system has little effect on short-term changes in discharge but does regulate changes in chemical concentrations. Much of the shallow groundwater must be stored in areas such as boulder fields, which are quite different from materials that store soil water and groundwater in forested watersheds. The shallow groundwater reservoir is not large enough to attenuate chemical changes over many weeks time, nor is the hydrologic residence time of sufficient duration for weathering of primary minerals reactions to control stream chemistry. Fast reactions in the shallow groundwater matrix that controls chemical concentrations in the streams include cation exchange and exchange of SiO_2 between dissolved and amorphous phases.

The chemical composition of the source waters in these alpine watersheds changes through time. Because of the ionic pulse effect the meltwater coming out of the snowpack is most concentrated early in the runoff season and becomes more dilute later. This snowmelt is the input to shallow groundwater reservoirs. Before melt begins, groundwater is concentrated, having accumulated the products of weathering and decomposition throughout autumn and winter without any flushing. The initial snowmelt begins mixing with and flushing this old water, which is reflected in the decreasing chemical concentrations during June and July. Thus both snowmelt and shallow groundwater are most concentrated during the early season and become more dilute as snowmelt progresses. By August, most of the snow has melted and shallow groundwater has a significantly longer contact time with primary and secondary minerals, causing concentrations of weathering products to increase. There is spatial heterogeneity in the timing of snowmelt-related processes as well, as snowmelt occurs earliest at lowest elevations and moves upward in elevation later in the spring and summer.

In addition to the regulation of surface-water chemistry by hydrologic flow paths and geochemical reactions, there is biological control on SiO_2 and NO_3 in the aquatic ecosystem of Icy Brook. Diatom blooms in alpine lakes during winter and spring lower the concentrations of these constituents during early runoff and may affect annual VWM concentrations in Icy Brook.

Acknowledgments. A sincere thanks goes to all of the people who have helped collect and interpret the information presented here. Special thanks to Jill Baron and the many other Loch Vale researchers who laid the foundation for this work; to Terry Brinton, Paul Schuster, and others for their analytical expertise; and to the dedicated staff of Rocky Mountain National Park. The manuscript was substantially improved by comments from David Naftz, Jill Baron, and two anonymous reviewers. This work was funded by the U.S. Geological Survey, Water Resources Division, as part of the Water, Energy, and Biogeochemical Budgets program.

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(Received October 7, 1994; revised June 26, 1995; accepted June 30, 1995.)