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Atmospheric deposition, mass balances, and processes regulating streamwater solute concentrations in mixed-conifer catchments of the Sierra Nevada, California

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Abstract. Solute concentrations in atmospheric deposition and stream water were measured from 1984 through 1993 to determine the fate and mobility of solutes in two gauged mixed-conifer catchments (Tharp's and Log creeks) located in the Sierra Nevada, California. The two catchments contain mature forest stands dominated by *Abies concolor* (white fir), *Sequoiadendron giganteum* (giant sequoia), *Abies magnifica* (red fir) and *Pinus lambertiana* (sugar pine). Ammonium, Cl^-, Ca^{2+} and NO_3^- were highest in concentration of the solutes measured in wet deposition; bulk deposition was highest in SO_4^{2-}, NH_4^+, Cl^- and H^+. Net retention of H^+, NO_3^-, NH_4^+, SO_4^{2-} and Cl^- occurred in both catchments. Discharge was dominated by spring snowmelt with the largest export yields for acid neutralizing capacity (ANC), SiO_2, and Ca^{2+}. Export yields of H^+, NO_3^-, NH_4^+ and PO_4^{3-} were relatively small (0.5 kg ha^{-1} y^{-1}). Discharge-concentration relationships for ANC, SiO_2, Na^+, K^+, Ca^{2+} and Mg^{2+} were inverse and their concentrations in stream water were primarily influenced by discharge and annual differences in the relative contributions of snowmelt and groundwater. The mobility of these solutes is controlled by the rates of mineral weathering and ion exchange. The positive relationship of SO_4^{2-} concentration with increasing discharge suggests that atmospherically deposited SO_4^{2-} is temporarily stored and that its release is controlled by the extent of soil water flushing.

Introduction

Determining the biogeochemical processes that occur in forested catchments can be done by comparing atmospheric inputs to fluvial outputs (Likens & Bormann 1995; Lewis & Grant 1979a, b; Stednick 1989; Likens et al. 1994). However, mass balances are difficult to interpret without knowing the successional stage of a forest, and without having multiple years of data covering a range of conditions (Vitousek & Reiners 1975; Vitousek 1983). Input-output budgets are often limited by incomplete data on the intrasystem fate and mobility of ions, and by the accuracy of both atmospheric inputs and stream export (Lynch & Corbett 1989). Multiple years of data reduce the chance that input-output budgets are biased by climatic and hydrologic variability. Pertinent studies in the Sierra Nevada are relatively short-term and, therefore, cannot address biogeochemical invariance or trends (Leonard et al. 1979; Stohlgren et al. 1991). Other studies in catchments of the central Rockies (Bond 1979; Gosz 1980; Lewis 1982; Baron & Bricker 1987; Stottlemyer & Troendle 1987) and western Oregon (Sollins et al. 1980) show site-specific differences in hydrochemical dynamics.

Discharge-concentration relationships are helpful in evaluating the biogeochemical and physical processes that influence streamwater solute concentrations. Separating annual discharge-concentration relationships into trajectories of time, discharge, and ion concentration has been used to determine processes that regulate streamwater composition (Bond 1979; Lewis & Grant 1979a, b; Stednick 1989). Although long-term changes in streamwater composition arising from ecosystem succession (Vitousek & Reiners 1975; Vitousek 1983) and anthropogenic inputs complicate trajectories (Driscoll et al. 1988), catchments with simple annual discharge patterns driven by spring snowmelt and low anthropogenic inputs are suitable for trajectory analysis (Bond 1979; Driscoll et al. 1988). About 95% of the stream discharge in the mixed-conifer catchments of Sequoia National Park, California, is attributed to spring snowmelt, and most pollution is deposited in the summer and autumn when rainfall generally is not high enough to generate streamflow (Stohlgren et al. 1991). Hence, trajectories can be used to identify the important hydrological, geochemical and biological processes that control streamwater chemistry in these catchments.

Streamwater composition of forested catchments is regulated strongly by the availability of anions in soil solution. Nitrate and PO_4^{3-} are usually transformed by biological reactions, Cl^- is regulated by inorganic chemical reactions, and SO_4^{2-} can be either adsorbed or transformed (Johnson & Cole 1980). With the addition of NO_3^- and SO_4^{2-} to an ecosystem from atmospheric sources, the subsequent loss of acid-neutralizing capacity in forest soils can lead to the acidification of surface waters. The poor resiliency of alpine ecosystems in the Sierra Nevada to acid precipitation is documented (Melack et al. 1996), yet a paucity of information exists on the biogeochemical responses of forested catchments in the Sierra Nevada to acid inputs under a variety of conditions.

We report here a continuous 10-year data record of precipitation and stream runoff yields from the Tharp’s and Log creek catchments located in the mixed-conifer zone of Sequoia National Park, California. This study has a 6-year drought period bracketed by wet years. We use precipitation and stream runoff data to examine the dependence of solute yield on discharge for years with widely different maximum discharges, and evaluate the fate and mobility of solutes. The objectives of this study were to determine: 1) the mineral acidity and relative proportions of wet and dry constituents in atmospheric deposition, 2) atmospheric inputs and fluvial outputs, 3) streamwater discharge-concentration relationships, and 4) the important hydrochemical and biological processes that control streamwater chemistry.

Study area

Tharp's and Log creek catchments (36°34′N, 118°44′W) are located in the Giant Forest area of Sequoia National Park, California (Figure 1). Tharp's Creek is an intermittent stream that flows from November to July and drains a 13-ha mixed-conifer catchment that was burned in October 1990. Log Creek is a perennial stream draining an adjacent 50-ha catchment. Both catchments have >95% soil and forest coverage and have stream outflows at an elevation of 2067 m. Soils are dominated by Pachic (80–85%) and Lithic Xerumbrepts (10–15%), with smaller areas occupied by rock outcrops (about 3%), Typic Haploxerults (about 2%) and Aquepts (<1%) (Huntington & Akeson 1987). Typical depths of the umbric epipedon are about 1 m (Chorover et al. 1994). Bedrock is granodiorite of the Lodgepole pluton. Dominant tree species are *Abies concolor* (white fir), *Sequoiadendron giganteum* (giant sequoia), *Abies magnifica* (red fir), *Pinus lambertiana* (sugar pine), and *Pinus jeffreyi* (jeffrey pine). *Abies concolor* has the highest density of any tree species in both catchments, although the Log Creek catchment has proportionally more basal area attributable to *Sequoiadendron giganteum* (Stohlgren et al. 1991). Effective fire prevention efforts over the last century created an aggrading stage of ecosystem development in the mixed-conifer forests of Sequoia National Park. However, with the introduction of fire in the Giant Forest area about 20 years ago, the developmental stage now approximates a steady state (pers. comm., Annie Esperanza, Sequoia and Kings Canyon Field Station, National Biological Service). No fires had occurred in the Tharp's and Log creek drainages for about 80 years prior to the prescribed fire that burned the entire Tharp's Creek catchment in the fall of 1990.

Methods

Wet deposition – The chemical composition of wet deposition chemistry was monitored at Giant Forest, about 4 km west of the study site at an elevation of 1856 m. Samples were collected weekly from two Aerochem Metrics Model

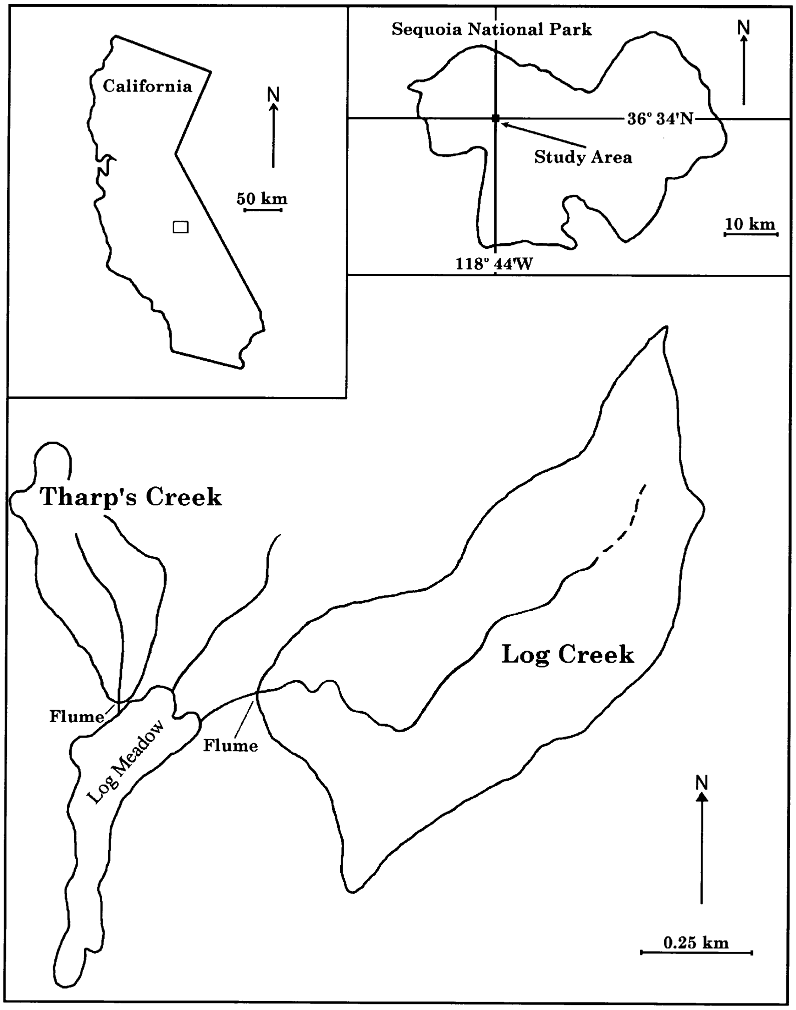

Figure 1. Map showing the locations of Sequoia National Park and the Tharp’s and Log creeks catchments.

201 samplers. Weekly precipitation was measured using a Belfort recording rain gauge. Bulk deposition was collected weekly at the location of the Aerochem samplers. A Plexiglas funnel pre-rinsed with distilled-deionized water (DDW) was used for the collection of bulk rain (Stohlgren et al. 1991). Bulk snow samples were collected weekly in a 55 gallon container fitted with a new plastic liner that was pre-rinsed with DDW.

A Belfort weighing rain gauge located 1 km southwest of the study area (1992 m) was used from 1984 through 1986. Precipitation recorded at this site averaged 9% (±4%) more per water year than the Giant Forest site (Stohlgren et al. 1991). All precipitation depth data from the Giant Forest area were corrected by 9% to compute water balances for the Tharp's and Log creek catchments and maintain consistency with the previous study.

Stream discharge and sampling – Stream discharge was measured using 12" and 3" Parshall flumes for Log and Tharp's creeks, respectively, equipped with Stevens Type-F strip chart recorders. Strip charts were summarized manually to obtain daily discharge. In 1990 and 1991, Stevens Type A/F electronic data loggers were installed at Log and Tharp's creeks, respectively. Annual discharge volumes derived from daily mean stage height recorded on strip charts were comparable to those derived from data loggers (±5%).

Stream samples were collected every two weeks in both catchments immediately upstream of the flumes. Daily sampling was conducted to monitor post-burn streamflow from March 3 to April 10, 1991 and weekly during the remaining snowmelt periods of 1991 to 1993. Samples were collected in acid-washed Nalgene polyethylene bottles that were rinsed several times with DDW and pre-rinsed with sample water.

Chemical analyses – Unfiltered precipitation and streamwater samples were analyzed for *p*H, conductivity, and ANC within 6 hours of collection. An Altex model 3500 *p*H meter with Beckman glass body probe for dilute water was used from 1984 to August 1990 and was subsequently replaced by a Beckman model phI 40. Conductivity was measured through September 1990 with a Beckman model RC-16C meter and YSI 3402 conductivity cells (k = 0.1); this meter was replaced by a YSI model 34. ANC was determined by titration (Gran 1950; 1952), which was performed with 0.1 N HCl in an open beaker on quiescent samples between *p*H 4.5–3.5. Filtered subsamples were analyzed colorimetrically for SiO_2 using the silicomolybdate method (Strickland & Parsons 1972), NH_4^+ by an indophenol blue method and PO_4^{3-} by a molybdate method (APHA 1981).

Filtered samples were stored at 4 °C prior to SiO_2, NH_4^+ and PO_4^{3-} analyses at Sequoia National Park (NPS). Analyses of NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} were done at Michigan Technological University (MTU) within 40 days of collection; NH_4^+ and PO_4^{3-} were also measured at MTU. From 1990 to the end of the study, filtered subsamples were sent to the Rocky Mountain Forest and Range Experimental Station in Ft. Collins, Colorado. Samples sent to MTU or Ft. Collins were refrigerated at 2 °C until analyzed on an automated Dionex 2020 ion chromatograph according to methods and QA/QC procedures detailed in Stottlemyer & Troendle (1987) and Stottlemyer (1987). Both independent laboratories are henceforth referred to as MTU.

Quality assurance and control procedures included: 1) following guidelines of the National Acid Precipitation Assessment Program, 2) bi-annual lab audits by the United States Geological Survey and the California Air Resources Board, and 3) inter-laboratory comparisons.

Data-analysis – Volume-weighted mean (VWM) concentrations were calculated for solutes in precipitation and stream water. The equation for calculating VWM concentrations for *n* measured precipitation events can be represented as

$$VWM = \frac{\sum_{i=1}^{n} C_i V_i}{\sum_{i=1}^{n} V_i} \qquad (1)$$

where C_i = observed concentration of combined events for a weekly sample *i*, V_i = size of combined events *i* (mm), and the denominator is the annual or 10-year Σ *V*. The same equation is used for calculating VWM concentrations in stream water, but in that case C_i = observed concentration of instantaneous streamflow *i*, V_i = discharge volume (liters) for the two-week period with sample data as the midpoint of the period *i*, and the denominator is the annual or 10-year Σ discharge volume. Sampling periods were summed by water year, defined as beginning October 1 and ending September 30 to coincide with stream discharge and Sierran precipitation patterns. Water years are referred to by the year including their January-September months.

Quality assurance – Results from NPS and MTU PO_4^{3-} and NH_4^+ analyses were similar. Only NPS values were used. When no data were available, MTU values were substituted. Replicated chemical data were averaged, and contaminated precipitation samples were removed from the data set. Conductivity and *p*H data were corrected when temperature data were available. Samples with charge balance ratios <0.5 or >2 were individually examined and, when obvious, the ion(s) responsible for the imbalance were removed.

Results and discussion

Atmospheric deposition and the fate of strong acid anions – Approximately 50% of annual precipitation in Giant Forest falls as rain and 50% falls as snow or a mixture of rain and snow (Stephenson 1988). Precipitation amount was typical for mountainous regions of California (California Department of

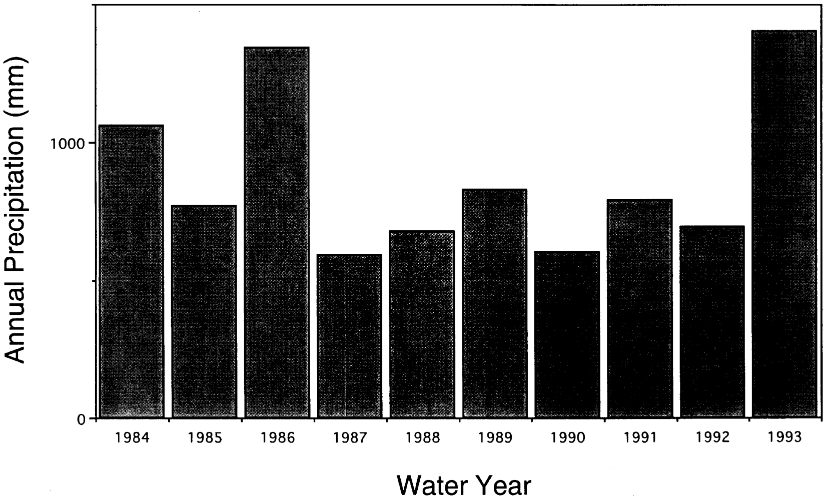

Figure 2. Annual precipitation depth for the Tharp's Creek area from 1984 to 1993.

Water Resources 1930–1996) and varied by up to 58%, with 8 years below the annual average of 1100 mm (Figure 2). The two years with the largest annual precipitation (1986 and 1993) bracketed a 6-year drought period, which had quantities of precipitation as low as 53% of the long-term average (6-year mean = 697 mm).

Most solutes were well correlated with each other in precipitation ($r > 0.5$). Ammonium usually contributed most to ionic sum, and represented 23% of the cation balance over the 10-year period followed by Ca^{2+} (21%), Mg^{2+} (19%), H^+ (17%), Na^+ (12%) and K^+ (7%); for the anions, Cl^- (37%) was followed by NO_3^- (33%), SO_4^{2-} (30%) and PO_4^{3-} (<1%; Table 1). Values of *p*H ranged from 4.8 to 5.5 with a VWM of 5.1 ($n = 219$). Annual mean conductivity was 6.0 μS cm^{-1} ($SE = 0.7$; $n = 220$) and was slightly higher in dry years.

Significant dilution occurred with increasing storm size for most solutes ($p < 0.05$; Table 1), although there was high annual variability. The effect was small but significant for most solutes ($r^2 \leq 0.25$), and solute dilution with increasing storm size was not pronounced enough to counteract a concomitant increase in deposition. The dependence of solute concentration on sample size required volume weighting in calculations of annual means. VWM anion deficit (deficit = Σ cations – Σ anions) for annual precipitation was 17 μeq L^{-1}, part of which may be attributed to the presence of organic acids (Galloway et al. 1982; Likens et al. 1987).

Wet and bulk atmospheric deposition of the Giant Forest area were influenced by anthropogenic sources of acidity. N and S oxides are converted

Table 1. Comparison of volume-weighted means (VWM), depositional loading and regression statistics for selected solutes in wet and bulk deposition. VWM values derived from the subset of storms sampled over the 1984–1993 study period (n = 166) were used in conjunction with the measured rainfall amount of 8034 mm for wet deposition. Average annual depositional loading in meq m^{-2} was calculated as 10% of the product of VWM solute concentration and total rainfall amount for 10 years of wet and bulk deposition. Regression statistics of concentration versus storm size were calculated using data from all storms chemically analyzed. “WET” and “BULK” are used to describe wet and bulk deposition of the Giant Forest area, respectively.

SOLUTE	ANNUAL WET	ANNUAL BULK	WET	BULK	CONCENTRATION VS STORM SIZE	
	- - - μeq L^{-1} - - -		- - - meq m^{-2} - - -		r^2	p
H^+	7.3	10.2	5.9	8.2	0.01	NS
NH_4^+	9.9	11.0	8.0	8.8	0.11	0.001
Na^+	5.1	6.3	4.1	5.1	0.04	0.0123
K^+	3.0	1.8	2.4	1.4	0.04	0.0318
Ca^{2+}	9.0	10.0	7.2	8.0	0.07	0.0005
Mg^{2+}	8.0	3.8	6.4	3.1	0.05	0.0202
Cl^-	9.1	10.2	7.3	8.2	0.02	NS
SO_4^{2-}	7.5	11.8	6.0	9.5	0.10	0.0001
NO_3^-	8.3	9.8	6.7	7.9	0.25	0.0001
PO_4^{3-}	0.0	0.3	0.0	0.2	0.00	NS
Cations	42.3	43.1	34.0	34.6		
Anions	24.9	32.1	20.0	25.8		
Ionic sum	67.2	75.2	54.0	60.4		
Anion deficit	17.4	11.0				

NS = not significant.

to strong mineral acids in the atmosphere, and these acids are of particular interest because of their potentially harmful effects on terrestrial and aquatic ecosystems (Galloway et al. 1984; Chan et al. 1987). The relationship between NH_4^+ and NO_3^- in this study was highly significant ($r^2 = 0.95$; $p < 0.01$), which indicates that ammonium nitrate (NH_4NO_3) is likely to be the principal NO_3^- containing aerosol in wet deposition. Production of NH_4^+ in certain areas of southern California is high, and nitrous oxide emissions can exceed those of SO_2 (Wolff 1984); these areas favor the production of NH_4NO_3. Prevailing winds indicate that the San Joaquin Valley is a strong source of NH_4NO_3 to Giant Forest. Ammonium nitrate is not a source of H^+, which explains the relatively mild acidity of wet deposition despite the moderate concentrations of NO_3^- and SO_4^{2-} present. There were also weak relationships between H^+ and the sum of NO_3^- and SO_4^{2-} concentrations, which indicate less H^+ than would be expected assuming complete dissociation of the strong mineral acids.

Bulk rain had higher concentrations of most solutes than wet deposition (Table 1). Higher bulk-rain concentrations are generally attributed to significant dry deposition inputs (Sisterson et al. 1990), which increase with increasing turbulence, area, and surface roughness. Stable temperature gradients and low surface roughness of snow generally result in low deposition velocities and, consequently, little dry deposition to snow surfaces in the winter (Whelpdale & Shaw 1974). Contrastingly, the high surface area of forest vegetation strongly suggests that the majority of dry deposition occurs on vegetation surfaces. The extent to which these inputs are transformed by or leached from the forest canopy is not well known, although Chorover et al. (1994) have shown that throughfall in the Log and Tharp's creeks catchments has significantly higher concentrations of most solutes than wet deposition. Dry N input (NO_3^- + NH_4^+) calculated from bulk minus wet deposition was 0.9 kg ha^{-1} yr^{-1}; SO_4^{2-} deposition calculated similarly was 1.7 kg ha^{-1} yr^{-1} (Table 1). Dry deposition using these estimates contributed 14% and 37% of the N and S atmospheric inputs to these catchments, and these proportions did not significantly differ over the range of annual precipitation measured in this study.

Mass balances indicate that terrestrial processes limit acidification and the quantity of atmospherically derived N and S entering Tharp's and Log creeks (Table 2). However, an analysis of the susceptibility of these streams to acidification requires looking at possible seasonal or short-term acidification events. Fluctuating streamwater concentrations of ANC and *p*H are the best indicators of acid pulses. For instance, ANC was generally depressed at the onset of snowmelt, but returned to pre-snowmelt concentrations by late summer or autumn (Figures 3a and 4a). This pattern occurs because the ratio of surface runoff to groundwater inputs in stream water becomes increasingly smaller throughout the year, thereby increasing the effect of soil contact and acid neutralization. High ANC concentrations suggest that the process of streamwater acidification is quickly suppressed, although ANC dilution by snowmelt runoff increased the influence of H^+ in stream water temporarily (Figures 3a and 4a). *p*H also was depressed temporarily by rain events in some years.

Likens et al. (1996) observed depletion of Ca^{2+} in forest soils at Hubbard Brook after extended and high levels of acid precipitation. In contrast, the catchments of Tharp's and Log creeks are not subjected to comparatively high levels of strong acid anions in precipitation. The *p*H of precipitation and stream water in our study are roughly 1 and 2 orders of magnitude higher than those of Hubbard Brook, respectively. Hence, acid inputs to

Table 2. Comparison of annual precipitation inputs (wet deposition) and streamwater outputs for selected solutes. Precipitation depth and stream runoff are in mm; ionic input and output values are in kg ha^{-1} y^{-1}. Water years are from October 1 to September 30.

	YEAR									
SOLUTE	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
Precipitation										
Depth:	1063	767	1345	588	679	831	601	788	692	1404
H^+	0.02	0.07	0.10	0.06	0.07	0.07	0.05	0.04	0.04	0.08
NH_4^+	0.6	2.2	2.5	1.2	2.0	1.4	1.5	1.5	0.8	1.3
Na^+	1.2	1.1	1.9	0.7	1.3	1.0	0.7	0.9	0.5	1.0
K^+	1.7	3.5	2.6	0.5	0.9	0.4	0.2	0.1	0.2	0.1
Ca^{2+}	1.3	1.6	2.7	0.9	1.7	1.6	1.5	1.1	0.4	2.9
Mg^{2+}	1.2	0.6	2.3	0.5	0.7	0.8	0.6	0.4	0.8	0.5
Cl^-	7.8	1.6	4.3	2.5	2.9	1.9	1.9	2.4	1.7	1.2
SO_4^{2-}	3.3	3.6	5.4	2.8	3.3	2.7	2.7	3.1	2.4	2.2
NO_3^-	5.3	3.0	6.2	4.8	4.6	4.7	5.5	4.5	3.2	4.4
PO_4^{3-}	0.20	0.17	0.04	0.02	0.02	0.03	0.04	0.05	0.02	0.00
Tharp's Creek										
Runoff:	372	163	880	52	25	45	3	121	49	481
H^+	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NH_4^+	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.11	0.00	0.06
Na^+	4.3	3.8	16.0	1.4	0.6	1.2	0.1	3.7	1.6	12.6
K^+	2.3	1.4	6.4	0.4	0.2	0.4	0.0	1.5	0.7	4.4
Ca^{2+}	3.9	3.6	19.7	0.8	0.8	1.7	0.1	8.7	2.0	16.6
Mg^{2+}	0.4	0.6	3.5	0.1	0.1	0.2	0.0	0.9	0.4	3.1
Cl^-	2.1	1.3	4.2	0.4	0.1	0.2	0.0	3.1	1.0	5.0
SO_4^{2-}	0.5	0.3	1.5	0.1	0.1	0.1	0.1	8.4	0.7	10.8
NO_3^-	0.05	0.06	0.09	0.01	0.00	0.00	0.00	1.83	1.24	1.71
PO_4^{3-}	0.01	0.01	0.06	0.00	0.00	0.00	0.00	0.06	0.01	0.13
SiO_2	23.1	15.1	56.1	4.1	1.8	2.9	0.3	8.2	3.1	25.5
ANC	33.5	21.9	88.8	7.6	3.1	5.3	0.3	29.8	7.0	74.7
Log Creek										
Runoff:	457	372	1240	228	175	198	157	227	156	515
H^+	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NH_4^+	0.02	0.02	0.02	0.00	0.01	0.05	0.01	0.00	0.01	0.05
Na^+	8.9	10.3	28.2	7.8	6.0	6.6	6.0	5.6	5.9	14.5
K^+	4.7	3.5	10.9	2.1	1.6	1.9	1.5	1.4	1.5	3.6
Ca^{2+}	15.3	11.9	40.8	8.0	8.2	9.4	8.2	7.4	6.7	14.1
Mg^{2+}	2.9	1.7	6.5	0.6	0.9	1.0	0.9	0.6	0.9	2.3
Cl^-	3.5	2.6	6.3	0.9	0.9	1.0	0.8	0.9	0.7	1.9
SO_4^{2-}	0.4	0.8	3.0	0.4	0.4	0.6	0.4	0.8	0.5	1.7
NO_3^-	0.01	0.01	0.06	0.01	0.01	0.01	0.00	0.05	0.00	0.00
PO_4^{3-}	0.08	0.07	0.15	0.04	0.02	0.00	0.03	0.04	0.05	0.12
SiO_2	42.0	35.3	89.1	22.6	15.4	15.1	12.6	17.9	11.7	30.6
ANC	89.3	71.2	184.8	50.0	36.7	36.5	34.5	35.2	22.6	78.8

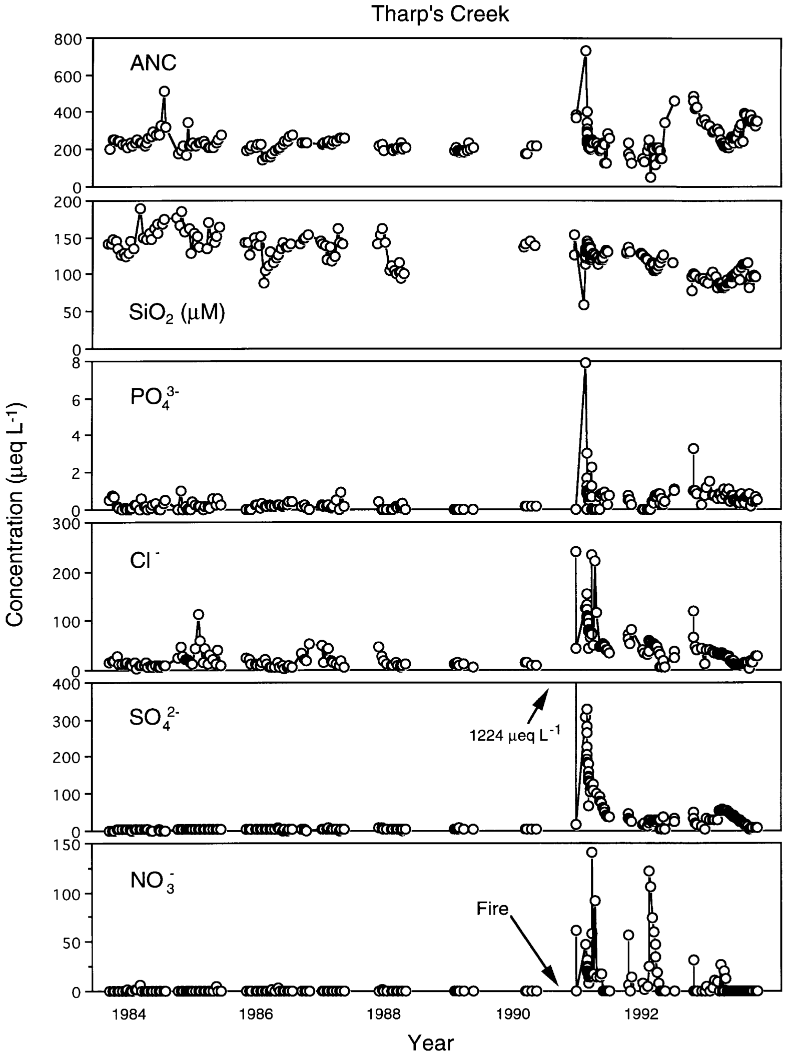

Figure 3. a, b. Time series of selected solutes for Tharp's Creek.

these catchments are continuous, but the ecological implications at present levels are not serious. Time series do not indicate that depletion of base cations is occurring (Figures 3b and 4b). Hydrogen ion was not a large fraction of the total cations in rain and does not account for most of the cation excess. Accordingly, there were no strong relationships with anion deficit and H^+ (mean $r^2 = 0.07$). Large ANC and the capacity of vegetation and soils to retain mobile anions like NO_3^-, SO_4^{2-} and Cl^- (Chorover et al. 1994) appear capable of protecting Tharp's and Log creeks from acid pulses

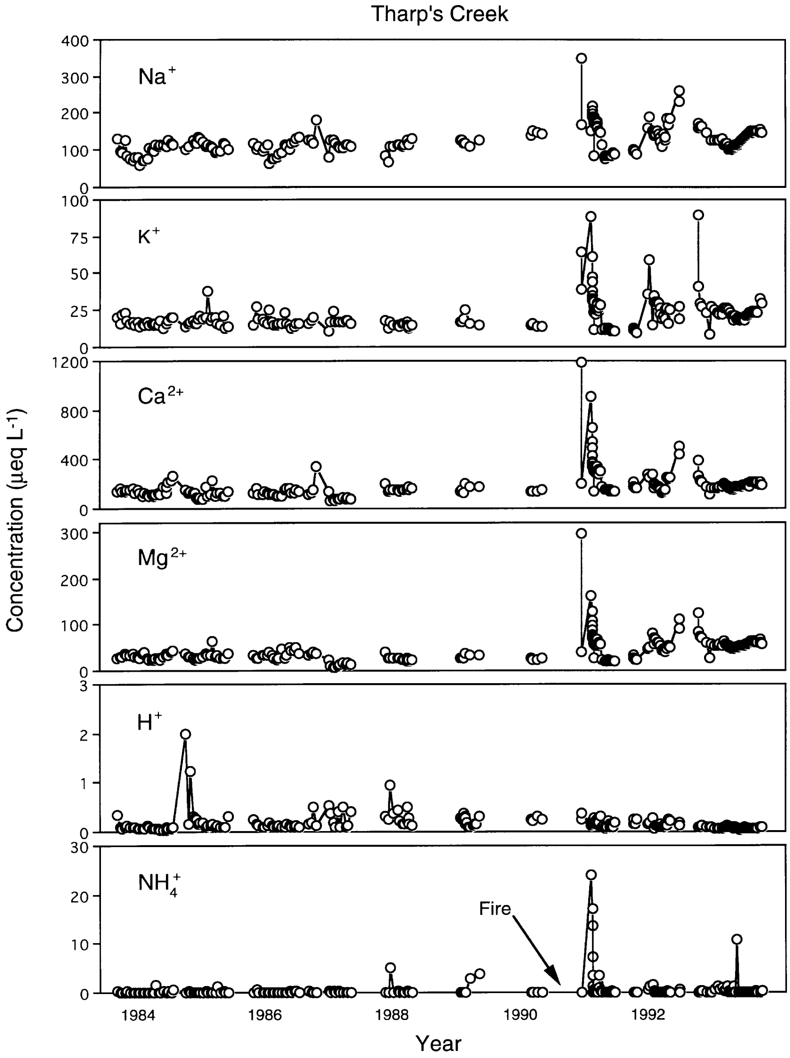

Figure 3. Continued.

during snowmelt and rain events. ANC yields exceeded H^+ inputs for both catchments, and acidity present in wet deposition was terrestrially neutralized. This indicates that the watersheds of the area are adequately buffered to resist acidification at the levels of anthropogenically derived inputs presently occurring in the wet deposition of Giant Forest (i.e. Σ NO_3^-, SO_4^{2-} and Cl^- = 9.6 kg ha^{-1} yr^{-1}). However, data on precipitation and streamwater chemistry from Hubbard Brook are extensive compared to those of the Tharp's and Log

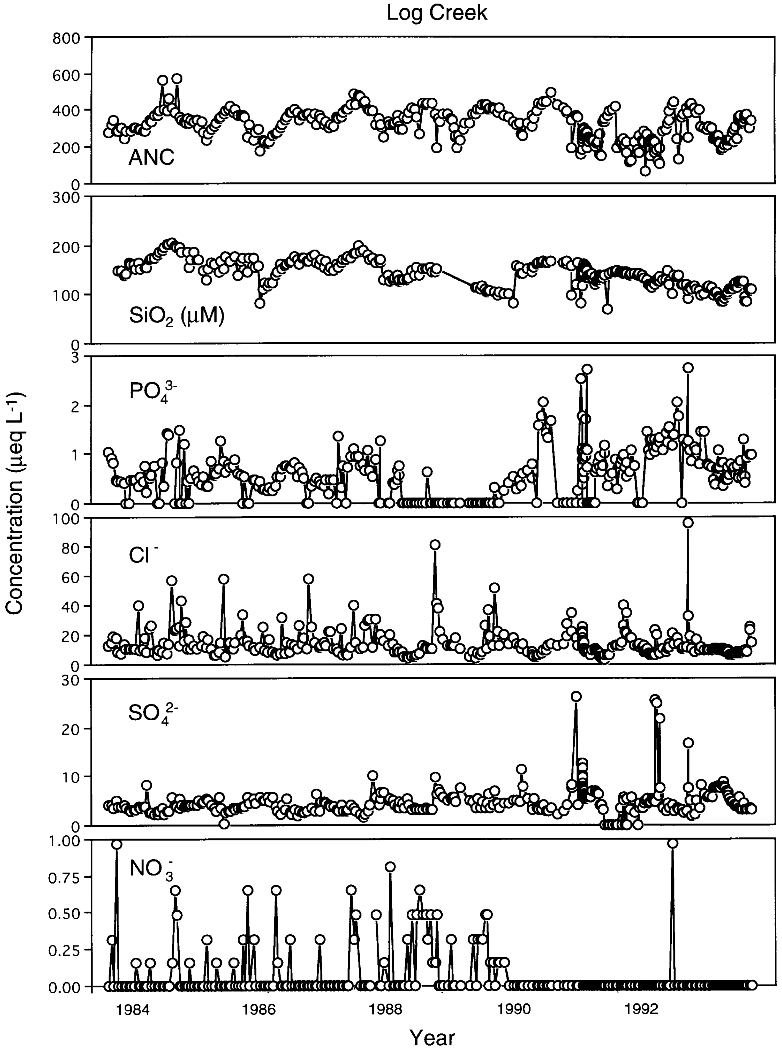

Figure 4. a, b. Time series of selected solutes for Log Creek.

creek catchments, which suggests that detecting cation depletion of the latter may require additional long-term monitoring.

Streamwater composition and mass balances – Annual hydrographs for Log and Tharp's creeks had similar patterns, with peak discharge driven by spring snowmelt (Figure 5). Tharp's Creek annual discharge ranged from 2% to 93% of that for Log Creek (Table 2). Runoff varied considerably between catchments and among years. Precipitation minus stream discharge was nearly

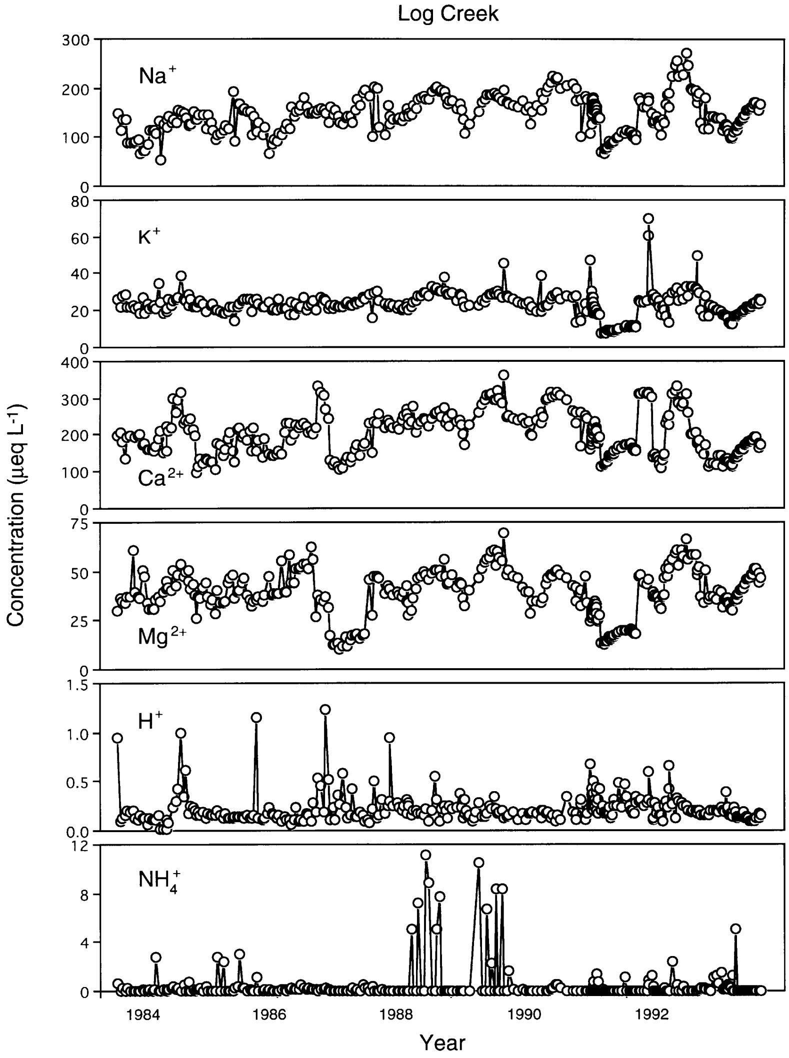

Figure 4. Continued.

constant for the first 9 years in Tharp's Creek (mean = 627 mm yr^{-1}; SE = 33), whereas it was considerably higher in the 1993 water year (923 mm yr^{-1}). Log Creek was more variable with a mean of 503 mm yr^{-1} (SE = 68). Runoff coefficients (the ratio of runoff to rainfall amount) for both creeks were highest in the largest water years (1986 and 1993), and lowest in the drought years of 1987 through 1992 (Figure 6). The lower runoff coefficients for the 1993 water year compared to the similar wet year of 1986 are likely

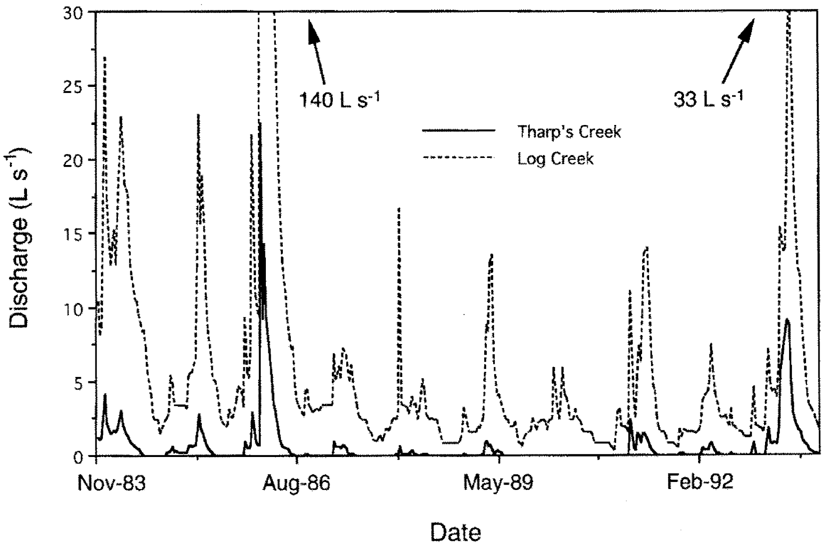

Figure 5. Hydrographs for Tharp's and Log creeks as 10-day running means for the 1984 through the 1993 water years.

attributable to low antecedent precipitation causing water stressed conditions in vegetation and depleted groundwater reservoirs.

The seasonal variation in streamwater solute concentrations was similar in pattern between the two catchments, and most of the major ions had their annual concentration maximum in the beginning snowmelt period of March–April (Figures 3a, b and 4a, b). In contrast, SO_4^{2-} commonly had an annual concentration maximum coinciding with maximum discharge. Concentrations of ANC, SiO_2, Ca^{2+} and Na^+ were highest among the solutes analyzed in stream water. Nitrate, NH_4^+ and PO_4^{3-} concentrations were usually at the limits of detection except for the post-burn phase in Tharp's Creek. Annual VWM streamwater concentrations of most ions were relatively consistent among water years and showed no strong patterns. VWM *p*H was 6.9 for both creeks, and was approximately neutral during most snowmelt periods despite considerable interannual variation in discharge. Pre-burn VWM conductivity was 16.8 and 24.1 μS cm^{-1} in Tharp's and Log creeks, respectively. Annual [VWM] of H^+, NO_3^-, NH_4^+ and PO_4^{3-} showed no significant correlation with annual discharge, and pre-burn annual [VWM] of Ca^{2+}, Mg^{2+}, Na^+, K^+, ANC and SiO_2 were higher in Log Creek than Tharp's Creek.

Although the magnitude of net retention and export varied among years, mass balances comparing atmospheric inputs to fluvial outputs commonly showed net retention of acid anions, NH_4^+, PO_4^{3-} and H^+, and net export of ANC, SiO_2 and the base cations (Table 2). Other watershed studies report

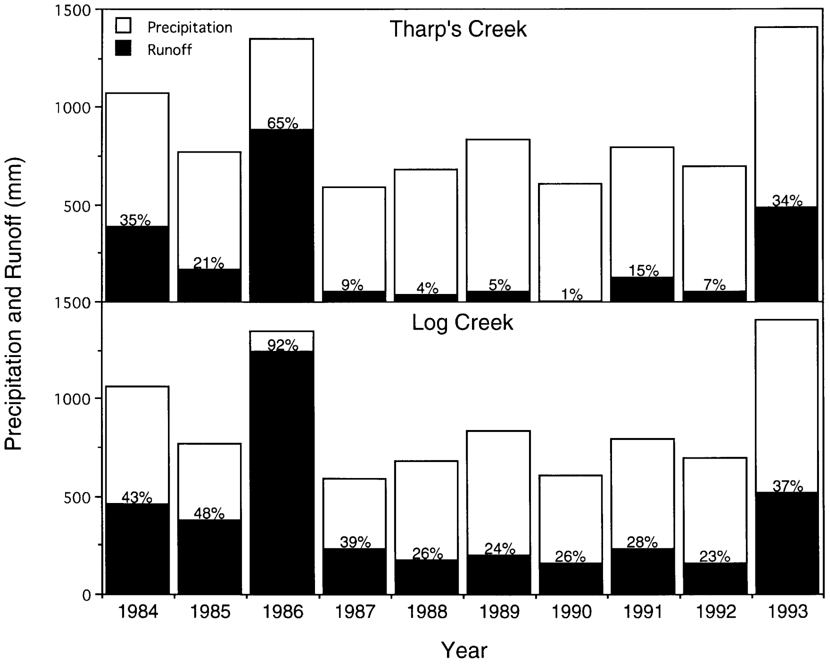

Figure 6. Runoff coefficients for the Tharp's and Log creeks catchments for each year of the study.

cation losses similar to those for Log and Tharp's creeks ($Ca^{2+} >> Na^{+} > Mg^{2+}$ and K^{+}) (Likens & Bormann 1995; Knight et al. 1985). Net exports per unit area of ANC, SiO_2, Ca^{2+}, Na^{+} and K^{+} in Log Creek were roughly double those in Tharp's Creek before the fire in the Tharp's Creek catchment. Higher outputs of these solutes from the Log Creek catchment are partially due to perennial stream flow and longer flow paths where groundwater remains in contact with weathering rock and soil minerals for longer periods of time (Dunne & Leopold 1978). Additional Ca^{2+} in Log Creek may come from leaching of the abundant, calcium-rich leaf litter of *Sequoiadendron giganteum* (Stohlgren 1988b), which dominates the basal area of the Log Creek catchment (Stohlgren et al. 1991) and causes greater fluxes of Ca^{2+} from throughfall than in the Tharp's Creek catchment (Chorover et al. 1994).

Low concentrations of strong mineral acid anions in stream water compared to precipitation indicate that the anthropogenic NO_3^- and SO_4^{2-} inputs were biologically incorporated, transformed or consumed by watershed processes. The correlation between the sum of H^{+}, NO_3^-, SO_4^{2-} and Cl^- net consumption (acid proxy ions) and ANC and SiO_2 net exports is not significant, with <10% of net export accounted for by net consumption. Thus, the system is chemically imbalanced and may not be in a steady state stage of ecosystem development. Nevertheless, these catchments have a large capacity for neutralizing atmospheric acid inputs, and biological transformations likely account for part of the N losses. Denitrification may occur in the poorly drained riparian areas of the Tharp's Creek drainage (Riegel et al. 1988; Stohlgren 1988a), although these account for <0.5% of the catchment area. Gaseous N outputs are known to exceed leaching losses in some catchments, especially after disturbances such as fire (Grier 1975; Schoch & Binkley 1986; Lobert et al. 1991), but gaseous losses were not measured in this study. Part of N immobilization is likely due to its incorporation into organic matter by processes of organic N formation. Schimel & Firestone (1989) observed rapid $^{15}NH_4^+$ uptake in the O2 horizon of a mixed-conifer forest in central California; microbes in bulk soil had faster assimilation rates than those of other soil compartments, although large amounts of N were incorporated into coarse woody materials after 31 days. Davidson et al. (1992) determined that microbial assimilation of NO_3^- was significant in mature coniferous forests of California, and could be an important mechanism of NO_3^- retention. Increased organic matter mineralization and a subsequent state of rapid nitrification are probably responsible for the large pulses of NO_3^- in stream water that were observed after burning the Tharp's Creek catchment (Figure 3a).

Although SO_4^{2-} retention commonly occurs from adsorption onto sesquioxides in soils (Chao et al. 1962; Parfitt 1978), hydrous oxides were not observed in the study site catchments (Huntington & Akeson 1987). Sulfate is incorporated into organic matter by microbial processes (Fitzgerald et al. 1982), and the organic fraction can comprise up 95% of total S in forested catchments (Stanko & Fitzgerald 1990; Mitchell et al. 1991). Vegetative and microbial processes are known to immobilize SO_4^{2-} in areas with low S deposition rates and background SO_4^{2-} (Mitchell et al. 1991; Johnson & Lindberg 1992), and such characteristics exist in the Log and Tharp's creeks catchments (Chorover et al. 1994).

Annual retentions averaged 4.6 and 4.1 kg ha^{-1} for NO_3^-, and 2.2 and 0.9 kg ha^{-1} for SO_4^{2-} in the Log and Tharp's creeks catchments, respectively. Additional inputs derived from estimates of dry deposition (bulk minus wet deposition) indicate that annual retentions in undisturbed watersheds are higher (about 5.3 and 5.0 kg ha^{-1} yr^{-1} for NO_3^- and SO_4^{2-}, respectively). This estimate of S retention is similar to values found by Vitousek et al. (1988) who suggest that biological S requirements for forests range from 1 to 5 kg ha^{-1} yr^{-1}. Ion exchange or adsorption in soils are possible mechanisms responsible for the reduced H^+ concentrations found in

Tharp's and Log creeks, and mineral weathering may also consume protons. Stottlemyer & Toczydlowski (1990; 1991) suggest that immobilization processes are generally more influential several weeks after peak snowmelt when the period of water contact with soil is greater. Knight et al. (1985) have shown that nutrient retention in lodgepole pine ecosystems is dependent on leaf area, the duration of vernal transpiration and the carbon/nutrient ratios of the forest floor, whereas losses occur primarily after disturbances such as fire.

Most solutes showed considerable variability at the beginning of the spring snowmelt period. Part of this variability can be attributed to solute pulses from the melting snowpack. Migration of solutes occurs with the beginning of snowmelt (Johannessen & Henriksen 1978; Jeffries & Snyder 1981; Cadle et al. 1984; Davies et al. 1987), and significant solute losses from the snowpack can affect streamwater concentrations (Williams & Melack 1991). Some solute pulses from melting snowpacks probably went unobserved because of our two-week sampling interval. Nevertheless, missing these solute pulses would amount to insignificant differences in annual solute export estimates, even in larger water years, because H^+, NH_4^+, NO_3^- and SO_4^{2-} were immobilized or transformed as they percolated through leaf litter and soils. Furthermore, ANC, SiO_2 and base cation concentrations in snowmelt were very low in comparison to those found in stream water, thereby making only small contributions to export.

Mass balance uncertainties – Stream discharge from spring snowmelt is responsible for up to 95% of the water exported from the Tharp's and Log creek catchments (Stohlgren et al. 1991). Although stormflow runoff normally accounts for only a small portion of their water budgets, high-volume rain events sometimes account for larger solute exports than those estimated using an equal volume of baseflow discharge. Because our routine sampling program did not sample storm events, our export values may be underestimates. However, such underestimates are small for most solutes because of the high proportion of low-intensity, low-volume rain events characteristic of the Giant Forest area. Alternatively, due to the general dilution effects seen in discharge-concentration relationships (below), solute concentrations could be even more diluted during storm events. Several events (total of 29 cm) in March 1991 were responsible for large solute pulses in the post-burn Tharp's Creek drainage (Figures 3a, b). However, losses attributable to other large events were not observed.

Further examination of the uncertainties associated with export estimates was conducted by evaluating the errors associated with precipitation and streamwater collection and analysis. It is not unusual for errors of about ±5%

to occur with point estimates of annual precipitation (Winter 1981), while the expected error associated with measurements of annual discharge using a calibrated flume and water level recorder is typically less than ±5%. Since the catchment area was determined from a combination of ground surveys and aerial photos with measurement errors of about ±4%, annual discharge divided by the catchment area should have a maximum total error (E_T) of about ±6% calculated as

$$E_T = (E_D^2 + E_A^2)^{1/2} \tag{2}$$

where E_D and E_A are the uncertainties of any two associated parameters; in this case discharge and area, respectively.

Although representative streamwater samples of baseflow conditions were obtained with our sampling schedule, chemical measurements involved some degree of analytical error. While the error associated with measuring the concentration of a particular solute is generally low (Stottlemyer & Troendle 1987; Stottlemyer et al. 1989), the representativeness of mean solute concentrations derived from these measurements has inherently more uncertainty. Tukey's jackknife method (Sokal & Rohlf 1981) was used to evaluate the representativeness of solute means and the propagated error associated with solute export values. This technique estimates the variability of a mean solute concentration by iteratively computing the mean after removing single observations from the sample set. Variability of these values is used to calculate a standard error. For example, SiO_2 has an uncertainty of about 2% calculated with the standard error of the mean. Since baseflow discharge has an error of about 5%, propagating these errors gives an uncertainty of about 5% in the estimate of SiO_2 export from Log Creek in the 1993 water year (Table 3).

Increased solute export resulting from storm flow that was not sampled probably adds to this uncertainty. However, even without measurements of stormflow solute concentrations, we can assume that solute export uncertainties calculated using base flow are not much different because larger errors associated with short periods of storm flow have little effect on the uncertainty of total annual solute export. The relatively large discharge volumes and accurate solute concentration measurements of baseflow keep the uncertainty low. For instance, if it is assumed that the representativeness of stormflow $[SiO_2]$ has an uncertainty of 50% and that annual stormflow discharge has an uncertainty of 20% (5% of the total annual volume), using the equation above would give an error of 54%. Propagating this error with that of baseflow discharge (5%) would change the overall export error to just under 6%.

Many water years showed strong relationships of solute concentrations with increasing discharge. Such relationships constitute a large portion of the inherent variability seen in most solute concentrations and their associated

Table 3. Comparison of solute concentrations and export of discharge for Log Creek in the 1993 water year. The standard errors of mean baseflow concentrations (SE) are derived from Tukey's jackknife procedure. The approximate standard errors of solute export were calculated by propagating measurement errors. Mean SiO_2 concentration is in μM and export is in moles. Nitrate was undetected and, therefore, not included in this analysis.

Solute	Mean Baseflow Concentration ± SE	Solute Export ± SE
Baseflow Volume: 257,500 m^3		
	Microequivalents per Liter	*Equivalents*
H^+	0.03 ± 0.008	8 ± 26%
NH_4^+	0.32 ± 0.13	82 ± 41%
Na^+	140.72 ± 4.19	36,235 ± 6%
K^+	23.19 ± 1.02	5,971 ± 7%
Ca^{2+}	156.26 ± 4.30	40,237 ± 6%
Mg^{2+}	43.27 ± 1.21	11,142 ± 6%
Cl^-	11.77 ± 2.06	3,031 ± 18%
SO_4^{2-}	5.74 ± 0.40	1,478 ± 9%
PO_4^{3-}	1.01 ± 0.07	260 ± 9%
SiO_2	108.50 ± 1.91	27,939 ± 5%
ANC	302.00 ± 11.00	77,765 ± 6%

errors. Conversely, H^+, NO_3^-, NH_4^+ had very low concentrations, undefinable discharge-concentration relationships and higher relative variability. Higher variability resulted in larger associated errors, but they contributed little to the overall export of solutes, which are terrestrially immobilized or transformed. Although non-conservative solutes are important indicators of water quality, it is unlikely that maximum yields calculated (± SE) would have deleterious localized effects. Water years with above-average precipitation consistently had more variation in solute concentrations compared with those measured during the drought period. Nevertheless, their associated errors are not significantly larger than values calculated for below-average water years, which indicates that these uncertainties are representative of the entire study.

Discharge-concentration (DC) relationships – Discharge-concentration analysis can help identify the important hydrochemical and biological processes regulating the ionic concentration of stream water (Bond 1979; Lewis & Grant 1979b; Stednick 1989; Campbell et al. 1995). The general patterns observed in DC relationships of composite (annual) data for the 10-year study period are summarized below. The DC relationships for Tharp's and Log creeks were usually significant ($p < 0.05$) for ANC, SiO_2, SO_4^{2-}, and the base cations. Hydrogen ion had moderate variability, low concentrations and few significant DC relationships. Chloride had high variability and no significant relationships to discharge, although there was noticeable dilution from low to moderate flows. Sulfate had positive, logarithmic DC relationships at low to high flows. Concentrations of NO_3^- and PO_4^{3-} were variable, low and occasionally significant. DC relationships in Log Creek commonly were strong (i.e. $r^2 > 0.5$) with all solutes except PO_4^{3-}, H^+, NH_4^+ and Cl^-, although ANC, SiO_2 and Na^+ were most consistent among years. In Tharp's Creek, relationships were similar to those of Log Creek for individual ions and significant ($p < 0.05$) in at least one water year for all ions except H^+, NH_4^+ and NO_3^-, with ANC, SiO_2 and Na^+ showing most consistency among years. Discharge commonly explained a moderate amount of the variability in solute concentrations ($0.05 < r^2 < 0.35$) of composite (annual) data.

Further analysis of individual years was conducted to identify the prominent hydrological pathways and biogeochemical processes controlling streamwater chemistry in Tharp's and Log creeks. DC relationships from 1993 were used since this was the wettest year of the study and fluctuations in discharge were high. In 1993, streamwater discharge in Tharp's Creek increased gradually until March, then increased rapidly throughout the snowmelt period until its peak in early May; after several weeks of discharge > 6 L s^{-1}, streamwater runoff decreased to < 3 L s^{-1} until the end of the water year in September (Figure 5). Discharge was higher (35 L s^{-1} daily maximum) and fluctuations were more gradual in Log Creek than in Tharp's Creek. During snowmelt in Log Creek, streamwater concentrations of the solutes that had inverse relationships with discharge (i.e. base cations, ANC and SiO_2) fluctuated and decreased until peak discharge in late spring; subsequently, these solutes tended to increase in concentration until late autumn. In contrast, concentrations of ANC, SiO_2 and the base cations in Tharp's Creek decreased and leveled several weeks before peak discharge occurred (rising limb of the hydrograph), decreasing gradually after peak discharge, albeit with concentrations lower than at comparable discharge while the stage was rising (Figures 7a, b, c).

The DC relationships for Tharp's Creek had clockwise hysteresis of most solutes, not including SO_4^{2-} (Figure 7c). In contrast, solutes in Log Creek had a combination of clockwise and counter-clockwise hysteresis, and differences in concentrations between the increasing and decreasing limbs of the hydrograph for the same instantaneous discharge were generally small. Since hysteresis confounds DC relationships, we attempted to remove the effects of hysteresis on composite (annual) DC relationships by examining samples along the increasing and decreasing discharge limbs of the hydrograph. The best-fit regression among normal, logarithmic, exponential and second-

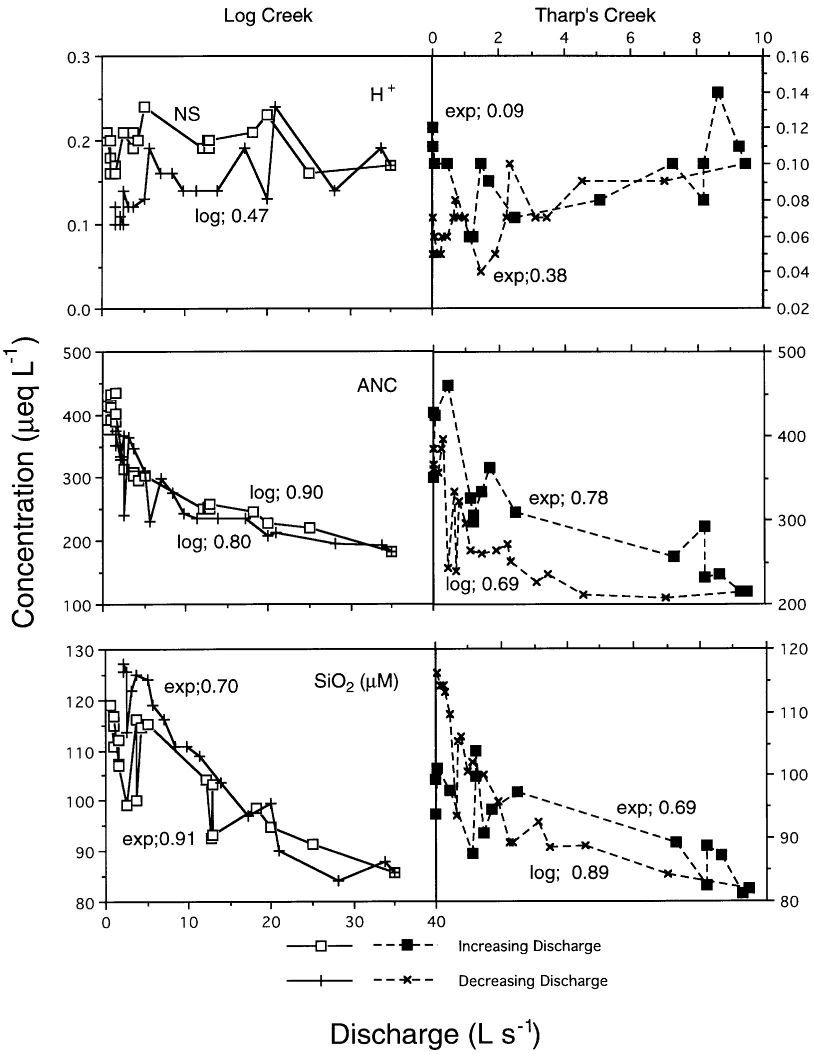

Figure 7. a, b, c: Trajectories of solute concentration versus discharge for selected solutes in Tharp's and Log creeks during the 1993 water year. The terms "log" and "exp" refer to logarithmic or exponential relationships, respectively.

order polynomial functions was chosen. The separation removed some of the seasonality in the data and increased the coefficients of determination and significance in most instances. Dividing the hydrograph into increasing and decreasing discharge limbs (trajectories) was used to identify the relative strengths and signs of the DC relationships.

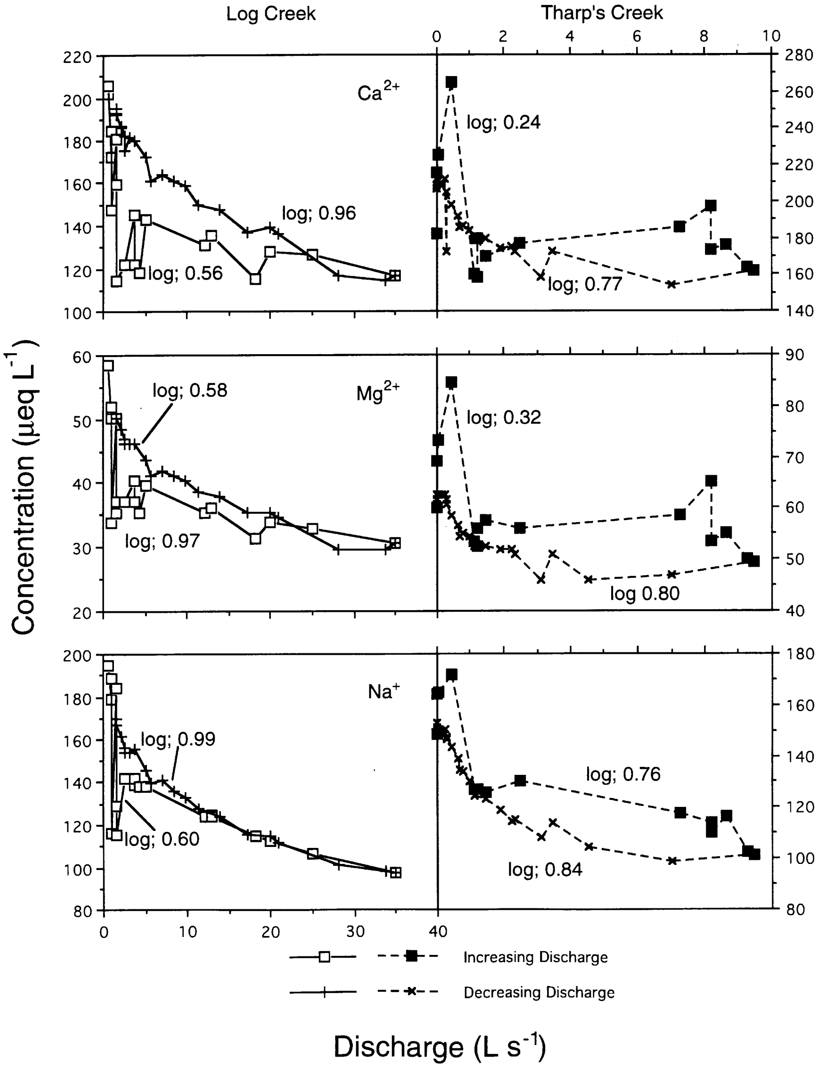

Figure 7. Continued.

Trajectories of solute concentration versus discharge were constructed by connecting successive dates of instantaneous discharge and solute concentration (Figures 7a, b, c). Trajectory limbs usually assumed highly significant ($p < 0.01$) inverse logarithmic or exponential relationships, except for SO_4^{2-}, which was positive. Solutes regulated by biological processes (NO_3^-, NH_4^+, PO_4^{3-} and H^+) were more difficult to interpret, and trajectories were better used on conservative solutes in wetter years with a wide range of discharges.

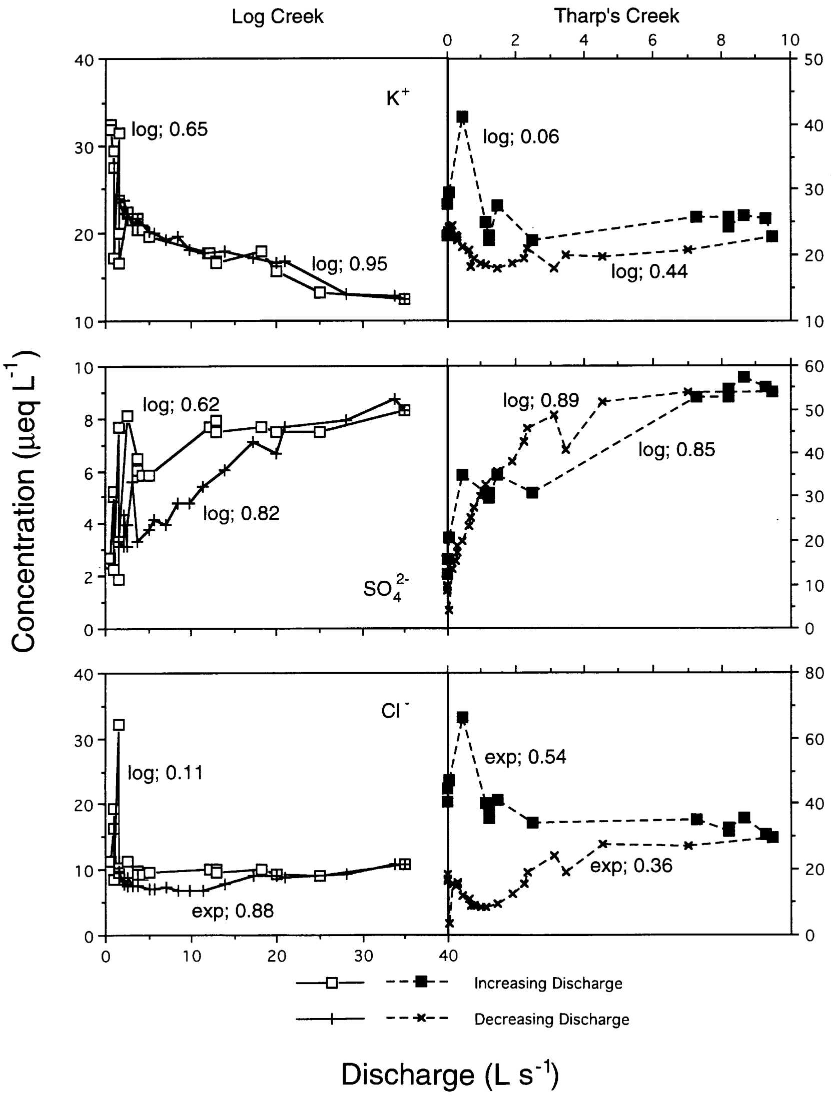

Figure 7. Continued.

Although an interpretation of trajectories from the 1993 water year data is used, conclusions drawn from most other water years were similar. Prescribed burning of the Tharp's Creek catchment in the autumn of 1990 probably had some influence on post-burn years because the successional allocation of elements by aggrading vegetation can confound DC relationships (Vitousek & Reiners 1975). However, we found that the 1993 water year showed only minor differences in streamwater solute concentrations compared to pre-burn means.

Trajectories were effectively used to determine DC relationships hidden in scatterplots of composite (annual) data sets. For instance, Tharp's Creek in the 1993 water year had 5 solutes with significant DC relationships, and Log Creek had 7. Conversely, an analysis using trajectory limbs showed more significant DC relationships and a higher level of significance (Figures 7a, b, c). Significant DC relationships of composite (annual) data occurred with 34% and 52% frequency in Tharp's and Log creeks, respectively, many relationships with low to moderate levels of significance ($0.10 > p > 0.05$). Frequency increased to 73% and 79% using trajectory analysis, most relationships having high levels of significance ($p < 0.01$) and up to 99% of the variation in solute concentration attributable to changing discharge.

Streamwater discharge varied by factors of 9 and 35 in Tharp's and Log creeks in 1993, whereas solute concentrations varied by 1.5 to 4.7 and 1.4 to 12, respectively. ANC and SiO_2 concentrations had significant ($p < 0.05$) inverse relationships with increasing discharge (Figure 7a, mean r^2 for both catchments = 0.79 and 0.80, respectively). Because the contributions of ANC (HCO_3^-) and SiO_2 to stream water are derived mostly from the mineral weathering of soils and bedrock outcrops in these catchments, an increase in snowmelt driven runoff would result in a proportional decrease in the concentration of ANC or SiO_2 if there were negligible groundwater influences. The lack of proportional fluctuations in discharge and solute concentrations indicates that soil/groundwater contributions (henceforth referred to as groundwater) largely influenced the chemical concentration of Tharp's and Log creeks during the snowmelt period.

Soils can accumulate weathering products during the winter which are subsequently flushed into streams during spring snowmelt. Stottlemyer & Troendle (1992) observed that SiO_2 dilution during the rising discharge limb of the hydrograph was a result of meltwater inputs exceeding soil hydraulic capacity in catchments of the Fraser Experimental Forest, which resulted in a larger fraction of meltwater quickly passing as overland runoff or through near-surface macropores to the streams. Similarly, a rapid increase in dilute runoff from snowmelt to the stream mixed with soil water contributions is likely responsible for the dilution of streamwater ANC and SiO_2 concentrations in Tharp's and Log creeks. The similarity in the trajectories of ANC and SiO_2 indicates that these solutes have similar weathering reactions, and that concentration differences between catchments were partly determined by residence time and flow routing.

The base cations had trajectories similar to ANC and SiO_2. High base cation concentrations occurred prior to peak discharge in Tharp's and Log creeks (Figures 7b, c), followed by a decline due to the rapid increase in dilute snowmelt to the stream mixed with limited soilwater inputs. Of the base cations, [K^+] decreased the least with increasing discharge (Figure 7c). The leaching of this highly mobile ion from organic material in the snowpack or forest floor and the relatively high exchangeable K^+ levels in the upper soil horizons of the forest floor (Chorover et al. 1994) are probably important factors regulating [K^+] in stream water. Soils of the area are thawed throughout the winter, and decomposing forest litter releases K^+ during the period of spring snowmelt (Stohlgren 1988b). Hence, K^+ release into the streams during the late spring and summer is probably due to mineralization of the forest litter layer, with a contribution from mineral weathering and ion exchange reactions.

The similarity in the rising and falling trajectory limbs for ANC, SiO_2 and the base cations in Log Creek stream water suggests that the contribution of soil water to total stream discharge during the rising and falling hydrograph limbs was fairly uniform. Similar trajectory limbs also suggest that there were negligible or consistent effects of evapotranspiration or decomposition, which can both result in concentrating solutes in stream water. In contrast, stronger hysteresis of solutes in Tharp’s Creek than in Log Creek stream water suggests that the contribution of groundwater to the stream was seasonally different in Tharp’s Creek. Clockwise hysteresis in Tharp’s Creek indicates that there was a smaller contribution of concentrated soil water to the stream after peak discharge, which may have been caused by the complete flushing of “old” more concentrated soil water by “new”, less concentrated meltwater soon after peak discharge occurred.

The variation in the relative contributions of snowmelt and soil water is most complex later in the snowmelt period when meltwaters are most dilute. This complexity is caused by the greater diurnal variation in solute release because of steadily increasing daytime temperatures and the increasingly larger area of the catchments that contributes to streamwater runoff, some of the area having been previously flushed and concentrated soil waters replaced by dilute meltwater. As temperatures rise, the daily input of meltwater flows on top of increasingly saturated soils, and soil saturation accelerates meltwater passage, probably as near-surface lateral flow through large macropores to the stream (Stottlemyer & Troendle 1992). Although overland flow was low due to the porous soils, channeling in the riparian zone of the Tharp’s Creek catchment was apparent, and steep slopes in these catchments may have further reduced meltwater residence times and contact with near-surface soil exchange sites. Channeling and reduced residence time of meltwater in the Tharp’s and Log creek catchments would contribute to the dilution of base cation concentrations in stream water during peak discharge.

Streamwater [H^+] was very low and stream discharge accounted for little variation, although there was slightly elevated [H^+] with increasing discharge during the initiation of snowmelt runoff in Log Creek. Hydrogen ion was higher in precipitation than in stream water, and its release from melting snow along with SO_4^{2-} and NO_3^- is generally faster than for most other ions during the initial thaw (Johannessen & Henriksen 1978). This ionic pulse coupled with increasing runoff, which reduces ecosystem retention times and the opportunity for exchange within the soil, may have contributed to temporary increases in streamwater [H^+]. Alternatively, the ionic pulse could reflect organic acid inputs from winter decomposition in forest soils or the H^+ generated from nitrification, which can occur during winter months in forested catchments (Stottlemyer & Troendle 1992). However, the small export of H^+ suggests that rapid exchange in surface mineral soils and adsorption generally limit the extent of H^+ mobilization in Tharp's and Log creeks.

Of the solutes analyzed, [NO_3^-] had the greatest differences between wet deposition and stream water, and discharge did not account for a significant portion of the variation seen in streamwater [NO_3^-] in either catchment. Although soil solution [NO_3^-] was initially high, perhaps due to low biological uptake, overwintering N mineralization, or nitrification (Chorover et al. 1994), the concomitant processes of immobilization, transformation or biological uptake consistently depressed streamwater NO_3^- to detection limits. Fahey et al. (1985) have shown that rapid assimilation of mineral N, precipitation of organic solutes in the mineral soil, and limited opportunity for deep percolation of water help to account for the effective immobilization of NO_3^- in lodgepole pine forests; these mechanisms likely affect N mobility in the Tharp's and Log creek catchments.

Large changes in [Cl^-] in the beginning phase of snowmelt are attributable to ion elution mechanisms in the early stages of snowmelt runoff (Figure 7c). Available information on Cl^- generally suggests that biological requirements are low in temperate zone forests (Johnson 1984; Vitousek et al. 1988) and indicates that the winter snow pack temporarily stores Cl^-. The lack of a significant increase or decrease in concentration with changing discharge after the initial stages of snowmelt suggest that the concentrations of Cl^- in snowmelt and soil water were similar.

The positive relationship of [SO_4^{2-}] in Tharp's and Log creeks versus discharge was in contrast to those of other ions. Stream discharge accounted for significant variation in [SO_4^{2-}] in both catchments (Figure 7c). Highly positive trajectories with little influence from precipitation inputs indicate that multiple SO_4^{2-} storage reservoirs exist in the Tharp's and Log creek catchments. Sulfate is largely controlled by soil processes (Fitzgerald et al. 1982; 1988), and SO_4^{2-} concentrations in soil waters are greater than in stream water in the Tharp's and Log creek catchments (Chorover et al. 1994). However, because SO_4^{2-} retention by hydrous oxides appears to be limited in these Sierran mixed-conifer catchments (Chorover et al. 1994), the periodic mobilization of SO_4^{2-} from organic matter mineralization should contribute more to fluctuations observed in streamwater SO_4^{2-} concentrations than contributions from the release of adsorbed soil SO_4^{2-} (Fitzgerald et al. 1988). The positive trajectories of SO_4^{2-} in the Tharp's and Log creek catchments suggest that seasonal rates of organic S oxidation vary considerably and SO_4^{2-} mobility is regulated by the hydrologic responsiveness of these catchments.

Lynch & Corbett (1989) recognized that soil SO_4^{2-} storage derived from atmospheric sources can occur during the summer and autumn when soil moisture deficits are sufficient to prevent saturated flow from occurring. A combination of SO_4^{2-} from atmospheric inputs, natural weathering and the oxidation of organic matter would then be stored within the catchment during the drier summer and autumn seasons. Mobilization from SO_4^{2-} reservoirs would account for higher streamwater concentrations during the spring runoff period when saturated soil conditions are more prevalent. Sulfate contributions to stream flow occur during other periods of the year, but only when saturated areas are in hydrologic contact with the stream. Thus, SO_4^{2-} storage reservoirs are spatially distributed. For instance, SO_4^{2-} reservoirs next to the stream influence baseflow SO_4^{2-} concentrations due to organic matter mineralization, natural weathering, and atmospheric sources that fall in or near the channel area. The lower slopes are the first to release stored SO_4^{2-} because they are located nearest the channel, and as saturated or near-saturated conditions continue, SO_4^{2-} stored in the upper portions of the watershed eventually reach the channel. Highly significant and positive trajectories suggest that these catchments exhibit both a direct and a delayed response in that most of the SO_4^{2-} is temporarily stored until the soils of a particular reservoir become saturated. Sulfate is preferentially released during snowmelt because a larger proportion of the catchments are water saturated at this time. Thus contributions from meltwater (initially) and soil macropores (mineralized organic matter and absorbed S) increase streamwater $[SO_4^{2-}]$ until snowmelt begins to subside. During the spring high-flow phase, there are intermittent periods when gravitational flow will cease from some portions of the watershed and SO_4^{2-} transport slows in response to drier soil moisture conditions. Sulfate decreases during the descending limb of the discharge hydrograph since biological or mineral exchange processes immobilize SO_4^{2-}, and there is progressively less water-saturated area in the catchments.

No significant DC relationships were determined for NH_4^+ and PO_4^{3-}, which were at the limits of detection throughout the study period. Snow deposition followed by warming trends, which melts snow in several phases, accentuates the biological processes (uptake or conversion) that regulate [NH_4^+] in stream water. Phosphate is regulated by biological uptake and adsorption with soils, which would effectively remove PO_4^{3-} due to longer soil contact and residence times when meltwater episodes are smaller. Hence, intermittent rain and snowmelt in drier years would tend to exacerbate the already weak or erratic DC relationships of NH_4^+ and PO_4^{3-}.

On the basis of our trajectory analysis, we postulate that streamwater chemistry of the Tharp's and Log creek catchments is seasonally regulated by several important hydrological pathways and biogeochemical processes. In wetter years where there is a seasonal accumulation of the snowpack, such as in alpine catchments, and in the winter season until the onset of snowmelt runoff, stream water is primarily determined by groundwater baseflow. Warmer temperatures induce snowmelt which releases ions in the snowack via preferential elution. Water percolating to the soil/snow interface then flushes soil macropores, which increases streamwater solute concentrations, namely for weathering products (ANC and SiO_2) and solutes more influenced by ion exchange reactions (i.e. base cations), or preferential elution (Cl^- and H^+). Non-conservative solutes (inorganic N and P) that are immobilized or biologically utilized are reduced to detection limit concentrations in stream water throughout the year. Thus, trajectories could not be used to infer whether there are seasonal differences in the biogeochemical processes that affect inorganic N and P. Sulfate concentration is low in stream water at the beginning of snowmelt due to the small saturated area of the catchments before snowmelt begins.

After the beginning of snowmelt through peak discharge, most solutes are diluted in stream water (inverse relationships to discharge), but not in proportion to increasing discharge. Low flow-dilution of solutes indicates that there is a strong influence of soil and groundwater inputs to the streams during snowmelt, probably as piston type displacement of soil and groundwater with meltwater. Hydrogen ion and Cl^- concentrations show little change with increasing streamwater discharge. Higher [H^+] and similar [Cl^-] in the snowpack compared to streamwater concentrations indicate that H^+ is neutralized by contact with groundwater, whereas [Cl^-] in the snowpack and groundwater are similar. The saturated area of the catchments increases with increasing streamwater discharge, thereby flushing increasingly more sulfate-rich groundwater into the stream and resulting in a positive relationship of [SO_4^{2-}] with discharge.

Streamwater concentrations of ANC, SiO_2 and the base cations gradually increase after peak discharge. Clockwise hysteresis of ANC, SiO_2 and the base cations in Tharp's Creek suggests that the soilwater reservoir was significantly depleted in these solutes, whereas the similar trajectory limbs in Log

Creek indicate that a larger soilwater reservoir exists that was not depleted during snowmelt. Toward the end of snowmelt, the increasing residence time of water and a decrease in the amount of dilute meltwater inputs to the streams would account for most of the concentration increase. Longer residence times of snowmelt and biogeochemical processes of adsorption by soils (PO_4^{3-}), neutralization (H^+), uptake and conversion (NO_3^- and NH_4^+) tend to minimize non-conservative solute concentrations in stream water after peak discharge. The reduction of snow-covered area and progressive drying reduces the saturated area contributing SO_4^{2-} to the stream, decreasing [SO_4^{2-}] gradually with decreasing streamwater discharge.

Conclusions

Wet deposition inputs in the Giant Forest area were typically highest in NH_4^+, Cl^-, Ca^{2+} and NO_3^-. Concentrations were commonly higher in bulk than wet deposition, and dry deposition contributed a significant portion of the N and S inputs. Acidic inputs from wet deposition were buffered by strong soil ANC but periodically caused brief decreases in stream *p*H during larger storm events. Solute export was dominated by ANC, SiO_2, Ca^{2+} and Na^+, while H^+, NO_3^-, NH_4^+ and PO_4^{3-} were relatively small. Although the magnitude of net retention and export changed among years, mass balances commonly showed net retention of NO_3^-, SO_4^{2-}, NH_4^+, PO_4^{3-} and H^+ due to immobilization, uptake, or losses to the atmosphere, and net export of ANC, SiO_2, Ca^{2+}, Na^+, K^+, and Mg^{2+} from weathering or ion exchange reactions.

The general patterns observed in annual DC relationships for both creeks were inverse and logarithmic for ANC, SiO_2, Na^+, K^+, Ca^{2+}, and Mg^{2+}. Sulfate exhibited positive, logarithmic DC relationships at low to high flows. Concentrations of NO_3^- and PO_4^{3-} were variable, low and occasionally significant. Trajectory limbs usually assumed strong and highly significant inverse logarithmic or exponential relationships, except for SO_4^{2-}, which was positive. Patterns of solute concentrations in Tharp's and Log creeks were influenced primarily by the relative contributions of snowmelt and groundwater, and SO_4^{2-} is temporarily stored then released from organic matter reservoirs in soils due to the increased flushing of soils that occurs during the snowmelt runoff period.

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