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Atmospheric deposition and solute export in giant sequoia — mixed conifer watersheds in the Sierra Nevada, California

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Abstract. Atmospheric depostion and stream discharge and solutes were measured for three years (September 1984 — August 1987) in two mixed conifer watersheds in Sequoia National Park, in the southern Sierra Nevada of California. The Log Creek watershed (50 ha, 2067—2397 m elev.) is drained by a perennial stream, while Tharp's Creek watershed (13 ha, 2067—2255 m elev.) contains an intermittent stream. Dominant trees in the area include *Abies concolor* (white fir), *Sequoiadendron giganteum* (giant sequoia), *A. magnifica* (red fir), and *Pinus lambertiana* (sugar pine). Bedrock is predominantly granite and granodiorite, and the soils are mostly Pachic Xerumbrepts. Over the three year period, sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-) were the major anions in bulk precipitation with volume-weighted average concentrations of 12.6, 12.3 and 10.0 μeq/1, respectively. Annual inputs of NO_3-N, NH_4-N and SO_4-S from wet deposition were about 60 to 75% of those reported from bulk deposition collectors. Discharge from the two watersheds occurs primarily during spring snowmelt. Solute exports from Log and Tharp's Creeks were dominated by HCO_3^-, Ca^{2+} and Na^+, while H^+, NO_3^-, NH_4^+ and PO_4^{3-} outputs were relatively small. Solute concentrations were weakly correlated with instantaneous stream flow for all solutes ($r^2 < 0.2$) except HCO_3^- (Log Cr. $r^2 = 0.72$; Tharp's Cr. $r^2 = 0.38$), Na^+ (Log Cr. $r^2 = 0.56$; Tharp's Cr. $r^2 = 0.47$), and silicate (Log Cr. $r^2 = 0.71$; Tharp's Cr. $r^2 = 0.49$). Mean annual atmospheric contributions of NO_3—N (1.6 kg ha^{-1}), NH_4-N (1.7 kg ha^{-1}), and SO_4—S (1.8 kg ha^{-1}), which are associated with acidic deposition, greatly exceed hydrologic losses. Annual watershed yields (expressed as eq ha^{-1}) of HCO_3^- exceeded by factors of 2.5 to 37 the annual atmospheric deposition of H^+.

Introduction

Measurements of chemical inputs and outputs from watersheds have been used to detect long-term trends in biogeochemical processes affected by forest management practices and acidic deposition (Likens et al. 1977).

Such studies provide a first approximation of which chemical constituents are accumulating within and which are lost from an ecosystem (Vitousek 1983). They also provide information on the direction and magnitude of nutrient movements into and out of an ecosystem as a basis for comparison among ecosystems (Likens et al. 1977; Bond 1979; Stottlemyer & Troendle 1987; Meyer et al. 1988).

Input/output budgets developed for western coniferous forest watersheds are largely limited to the Rocky Mountains (Lewis & Grant 1979a; Bond 1979; Gosz 1980; Baron & Bricker 1987; Stottlemyer & Troendle 1987), western Oregon (Sollins et al. 1980) and southwestern British Columbia (Feller 1977). Only one study has been conducted in the Sierra Nevada of California, a three year study of Ward Creek in the Lake Tahoe basin (Leonard et al. 1979). Despite differences in location, watershed size, input chemistry and vegetation type, most western coniferous forest watersheds have been shown to retain nitrogen and sulfate and lose base cations (Likens et al. 1977).

There is a growing concern that the southern Sierra Nevada of California receives atmospheric contaminants from anthropogenic emissions (Parsons & Graber 1985; Stohlgren & Parsons 1987; California Air Resources Board 1988). A logical first step in evaluating the potential sensitivity of the region to atmospheric contaminants is to quantify the chemical inputs and exports of these watersheds. Hence, we present three years of data on atmospheric deposition and solute export via stream discharge for two watersheds in the giant sequoia mixed-conifer forests of Sequoia National Park in the southern Sierra Nevada of California.

Our objectives were to:

- determine the chemical inputs and outputs for two mixed conifer watersheds;
- analyze the relationships of solute concentrations to streamwater discharge and season;
- determine the fate of ions commonly associated with acidic deposition (i.e., H^+, NO_3^- and SO_4^{2-}); and
- compare our results with data from other coniferous forest watersheds.

Study sites

The study sites are in the Giant Forest area of Sequoia National Park, California (Fig. 1). Log Creek is a perennial stream draining a 50 ha watershed dominated by white fir (*Abies concolor*), giant sequoia (*Sequoiadendron giganteum*), red fir (*A. magnifica*), sugar pine (*Pinus lambertiana*)

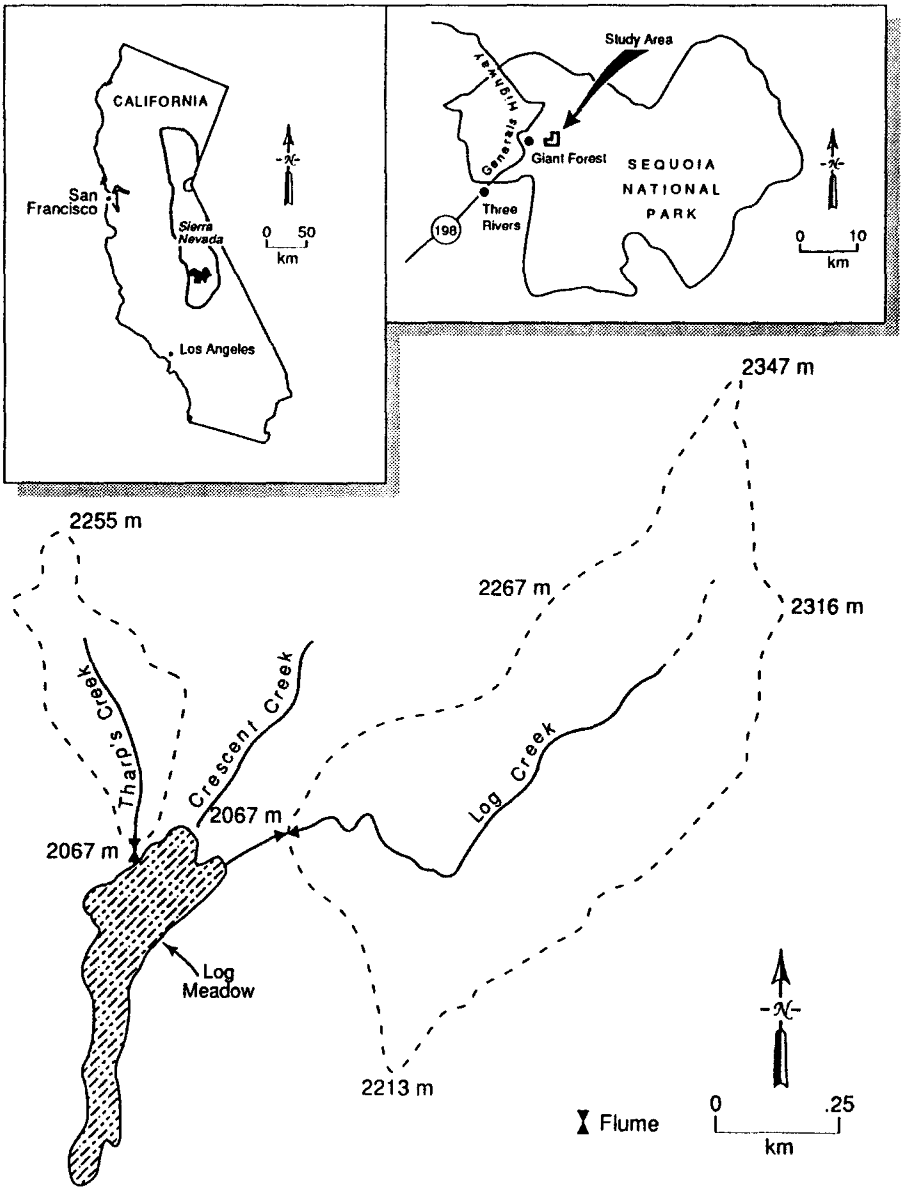

Fig. 1. Locations of Log and Tharp's Creek watersheds in Sequoia National Park, California.

and Jeffrey pine (*P. jeffreyi*) (Table 1). Tharp's Creek is an intermittent stream that generally flows from November to June or July. The Tharp's Creek watershed (13 ha in area) has fewer giant sequoia and more sugar pine than the Log Creek watershed (Table 1).

The soils in both watersheds are predominantly Pachic Xerumbrepts

Table 1. Physical, soil, and vegetation characteristics in the Log and Tharp's Creek watersheds in Sequoia National Park, California.

Characteristic	Log Creek		Tharp's Creek	
Size[a]	50ha		13ha	
Elevation range	2067—2397 m		2067—2255 m	
Slope	12—15%		10—12%	
Aspect	S—SW		S—SE	
Soil-type (% area)[b]				
Pachic Xerumbrepts	80%		85%	
Lithic Xerumbrepts	15%		10%	
Typic Haploxerults	2%		2%	
Aquepts	< 1%		< 1%	
Rock outcrops	3%		3%	
Forest trees species[c]	Trees/ha	Basal area (m^2/ha)	Trees/ha	Basal area (m^2/ha)
Abies concolor	387	36.0	283	41.6
Sequoiadendron giganteum	7	52.3	2	0.7
Abies magnifica	27	4.6	3	0.7
Pinus lambertiana	18	2.6	56	8.4
Pinus jeffreyi	5	1.4	25	4.5
Other	6	0.1	8	0.2
	450	97.0	377	56.1

[a] Based on planimetric projections of large scale orthophotographs.

[b] Huntington & Akeson 1987.

[c] National Park Service, Sequoia and Kings Canyon National Parks, unpublished data.

that are 0.5—1.5 m deep, well drained acid soils formed in granitic rock residuum (Huntington & Akeson 1987). Typically, the soils are coarse sandy loams with at least 10 cm of organic matter in the 0 horizon. Lithic Xerumbrepts, the next most common soil subgroup, are shallower (< 0.5 m) and strongly acid. The underlying geologic pluton is chiefly granodiorite (Ross 1958; Wharhaftig et al. 1984). Rock outcrops are common in the watersheds. The study area has a Mediterranean climate with warm, dry summers, and cool, wet winters. Mean annual precipitation at Giant Forest (1950 m elevation, 4 km W of the study area) is 110 cm, much of which falls as snow. The area receives acidic deposition, particularly during low-volume summer storms in which concentrations of H^+,SO_4^{2-} and NO_3^- average 18.0, 19.4 and 24.1 μeq/1, respectively (Stohlgren & Parsons 1987).

Methods

Precipitation sampling

Bulk precipitation chemistry was monitored from September 1, 1984 to August 31, 1987 at an elevation of 1856 m, 6 km W of the study area. Rain samples (generally June to October) were collected weekly using a plexiglas funnel (28 × 28 cm; Lewis & Grant 1978). Snow samples were collected in a large, 55 gallon container with a clean acid-washed plastic liner. Precipitation collectors were sampled weekly then washed with distilled-deionized water (bulk precipitation collector) or a new clean plastic liner was installed. No attempt was made to collect dry deposition. The collectors were rinsed with distilled water following weeks without precipitation. Weekly precipitation depth was measured with a standard Belfort weighing rain gauge in conjunction with a co-located National Atmospheric Deposition Program (NADP) station (site 057550, see Stohlgren & Parsons 1987).

Precipitation depth from the NADP site was compared to that measured with a tipping bucket gauge located 1 km from the study area at an elevation of 1950 m. Intermittent failure of the latter system prohibited reliance on its precipitation data throughout the study. Comparison between the two monitoring stations (n = 91 weeks) showed similar total precipitation depths and seasonal deposition patterns (140 cm for the tipping bucket station, and 128 cm for the NADP station).

Stream measurements and sampling

Stream discharge was measured using Parshall flumes with Steven's Type-F strip chart stage recorders. Strip charts were summarized manually to obtain daily discharge.

Samples for chemical analysis were collected every two weeks at both streams immediately upstream from the flumes. Samples were taken at mid-stream and mid-depth by syringe, and filtered (0.45 micron membrane) directly into acid-washed, well-rinsed polyethylene containers. A separate, unfiltered sample was collected for measurements of pH and alkalinity. Samples were immediately returned to a laboratory at Sequoia National Park for analysis of pH, alkalinity, PO_4^{3-} and NH_4^+; and subsamples were mailed in insulated boxes maintained at cool temperatures to the National Park Service laboratory at Michigan Technical University (MTU), Houghton, Michigan for further chemical analysis (see below).

Chemical analysis

Precipitation and stream samples were refrigerated (4 °C) until analysis. Within 6 hr of collection, unfiltered subsamples were analyzed for pH with an Altex Model 3500 meter (Beckman probe # 39835) and alkalinity (HCO_3^-) (within 24 hr by Gran titration; Talling 1973). Ammonium and phosphate were analyzed colorimetrically (indophenol blue and molybdate methods, respectively; APHA 1981) within 24 hr, on filtered subsamples. Filtered subsamples were analyzed colorimetrically (silicomolybdate method; Strickland & Parsons 1972) for silicate. The quality assurance and quality control (QA/QC) program included, in part, adherence to a standardized sampling protocol, analysis of precision (10% split samples for precipitation, 10% replicates of stream samples, inter-laboratory comparisons) and analysis of accuracy (participation in Environmental Protection Agency audit program).

Once received at MTU, samples were refrigerated (2 °C) until analysis for Ca^{2+}, Mg^{2+}, Na^+, K^+, NO_3^-, SO_4^{2-}, and Cl^- on an automated Dionex 2020 ion chromatograph according to methods and QA/QC procedures detailed in Stottlemyer & Troendle (1987) and Stottlemyer (1987).

Data analysis

Where replicate or split samples were taken, the sample with the cation/anion ratio closest to 1.0 was used in the input-output calculations. Nine of the 81 weekly bulk precipitation samples were contaminated with bird feces, insects or other debris. For those weeks (beginning February 5, 1985, March 5, 1985, March 26, 1985, October 22, 1985, February 25, 1986, June 3, 1986, February 17, 1987, March 10, 1987, and April 7, 1987), we substituted wet deposition data from the co-located NADP station for input calculations.

Biweekly volume-weighted stream outputs were calculated by multiplying the solute concentration of each sample by the total discharge for the two week period with sample data as the midpoint of the period. Both inputs and outputs were summed by hydrologic year defined here as September 1 to August 31 to coincide with stream base flow.

To test the relationship of instantaneous flow to solute concentration, linear, exponential, logarithmic and power curve models were applied to the data. The model resulting in the highest coefficient of determination was used.

Several studies suggest standard Belfort rain gauges underestimate snow catch by 15—65% depending on wind speeds and gauge placement (Larson & Peck 1974; Goodison & Metcalfe 1982; Marks et al. 1988). Our

Belfort rain gauge was located at 211 m below the lower elevation range of the study watersheds. Because this area receives much of its precipitation as snow with moderate winds, precipitation depths were multiplied by a correction factor of 1.35 to account for measurement deficiency as suggested by Marks et al. (1988).

Results

Annual bulk precipitation and streamflow amount and chemistry

The amount and chemistry of precipitation varied considerably over the three year sampling period (Table 2). Total precipitation in the hydrologic years 1984—85 and 1986—87 was only 63% and 55%, respectively, of the long-term average for Giant Forest (110 cm). In contrast, precipitation in 1985—86 was 144 cm; more than 30% above the long-term average. Total water yield ranged from 30 to 122 cm yr^{-1} in the Log Creek watershed and from 8 to 91 cm yr^{-1} in the Tharp's Creek watershed.

Volume-weighted mean concentrations of H^+, PO_4^{3-}, Ca^{2+}, K^+, and Cl^- in precipitation were lowest in 1985—86, the year with the greatest total precipitation; concentrations of most ions were highest during 1986—87,

Table 2. Volume-weighted precipitation and stream chemistry for Log and Tharp's Creeks watersheds in Sequoia National Park, California. All units are microequivalents per liter except silicate (micromolar) and water (cm). Hydrologic year is September 1 to August 31.

	Bulk precipitation			Log Creek			Tharp's Creek		
Constituent	84—85	85—86	86—87	84—85	85—86	86—87	84—85	85—86	86—87
H^+	10.0	5.5	13.0	0.2	0.2	0.3	0.2	0.1	0.3
NH_4^+	10.1	11.1	21.8	0.2	<0.1	0.1	0.3	<0.1	0.1
Ca^{2+}	9.8	6.2	10.5	244.0	271.3	176.1	173.1	188.7	78.8
Mg^{2+}	2.8	2.5	3.2	38.5	42.4	25.5	34.2	34.4	13.4
Na^+	7.2	7.3	6.8	125.1	98.0	150.8	105.9	80.6	117.1
K^+	2.9	1.5	3.5	22.2	21.9	23.5	17.7	18.9	18.2
NO_3^-	9.9	11.7	16.5	<0.1	<0.1	<0.1	0.2	<0.1	0.1
SO_4^{2-}	8.0	9.6	24.9	4.2	5.0	3.4	4.1	3.6	4.7
PO_4^{3-}	0.5	0.2	0.4	0.5	0.3	0.5	0.2	0.2	0.2
HCO_3^-	—	—	—	318.7	243.0	361.4	222.2	167.6	240.2
Cl^-	12.9	6.5	15.1	15.6	13.5	15.3	20.3	13.4	30.2
Silicate	—	—	—	163.2	119.3	165.7	145.1	107.1	139.0
H_2O (cm)	69.6	144.0	61.1	38.3	122.1	30.3	18.4	90.9	8.2

the year of lowest total precipitation. Annual volume-weighted concentrations of NO_3^-, NH_4^+ and SO_4^{2-} increased over the three-year study period. Charge balances (annual averages) had a slight (2% to 15%) excess of cations, but organic acid anions were not measured and contribute 10—20% of the anionic charge in Sierra snow and rain (Sickman & Melack 1989).

Annual inputs of NO_3-N, NH_4-N and SO_4-S from wet deposition (at the co-located NADP site) were about 60 to 75% of those reported from our bulk precipitation collectors for the first two years of the study period (Table 3). Thus, the bulk precipitation collectors were collecting significant amounts of dry deposition and we used these data as inputs in the solute balance analyses. Over the three year period, sulfate (SO_4^{2-}), nitrate (NO_3^-), and chloride (Cl^-) were the major anions in bulk precipitation with volume-weighted average concentrations of 12.6, 12.3 and 10.0 μeq/1, respectively. These concentrations of NO_3^- are more than twice that found in precipitation in remote areas of the world (Galloway et al. 1984).

Stream chemistry in both watersheds was dominated by the cations, Ca^{2+} and Na^+ and the anion, HCO_3^- (Table 2). Nitrate, ammonium and phosphate concentrations were consistently at or below detection limits. Although volume-weighted mean solute concentrations varied between watersheds and years, some patterns were evident. Stream concentrations of H^+, NO_3^-, NH_4^+, PO_4^{3-}, Na^+, HCO_3^- and Cl^- were lowest and Ca^{2+} and K^+ were highest in both streams during the wettest water year, 1985—86. Mean annual volume-weighted concentrations of PO_4^{3-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^- and silicate were consistently higher in Log Creek than in Tharp's Creek.

Seasonal variation in streamflow chemistry

The hydrographs for Log and Tharp's Creeks were similar in pattern, with peak discharge during spring snow melt, low or intermittent midsummer flow, and increased flow during rain events in the autumn or spring (Fig. 2). Tharp's Creek flow (when present) was approximately one quarter that of Log Creek, which is proportional to their relative watershed areas (Table 1). The heavy snow year in 1985—86 produced the highest discharge in both streams in spring 1986.

Stream pH, despite considerable variation, was near neutral during most winters in both watersheds. It tended to increase half a pH unit from winter to summer, but pH was erratic at low stream flow particularly during the drought year of 1986—1987.

Alkalinity (HCO_3^-), the major anion in both streams, had a strong seasonal pattern inversely related to flow (Fig. 3). Concentrations of HCO_3^- were low with the onset of spring snow melt, and increased as

Table 3. Wet deposition (NADP), bulk deposition and input-output balances for Log and Tharp's Creeks. Hydrological year is September 1 to August 31. All units are kg ha^{-1} except H_2O (cm). n.d. = no data.

Year/ Constituent	Wet Dep. (NADP)	Bulk Inputs (I)	Tharp's Creek Outputs (O)	Tharp's Creek I–O	Log Creek Outputs (O)	Log Creek I–O
1984–85						
H^+	0.0	0.0	0.0	0.1	0.0	0.1
NO_3-N	0.7	1.0	0.0	0.9	0.0	1.0
NH_4-N	0.6	1.0	0.0	1.0	0.0	1.0
PO_4-P	0.0	0.0	0.0	0.0	0.0	0.0
Ca^{2+}	0.6	1.4	4.1	−2.8	18.7	−17.3
Mg^{2+}	0.3	0.2	0.8	−0.5	1.8	−1.6
Na^+	0.7	1.2	4.5	−3.3	11.0	−9.9
K^+	0.6	0.8	1.3	−0.5	3.3	−2.5
SO_4-S	0.9	0.9	0.1	0.8	0.3	0.6
Cl^-	1.3	3.2	1.3	1.9	2.1	1.1
HCO_3^-	n.d.	n.d.	24.0	−24.9	74.5	−74.5
Silicate	n.d.	n.d.	16.0	−16.0	37.5	−37.5
H_2O (cm)	69.6	69.6	18.4	51.2	38.3	31.3
1985–86						
H^+	0.0	0.1	0.0	0.1	0.0	0.1
NO_3-N	1.4	2.4	0.0	2.4	0.0	2.3
NH_4-N	1.7	2.3	0.0	2.3	0.0	2.3
PO_4-P	0.0	0.0	0.0	0.0	0.0	0.0
Ca^{2+}	0.6	1.8	20.6	−18.8	39.8	−38.0
Mg^{2+}	0.3	0.4	3.8	−3.4	6.8	−5.9
Na^+	1.0	2.4	16.8	−14.4	27.5	−25.1
K^+	0.3	0.8	6.7	−5.9	10.5	−9.6
SO_4-S	1.4	2.2	0.5	1.7	1.0	1.2
Cl^-	1.8	3.3	4.3	1.0	5.8	−2.5
HCO_3^-	n.d.	n.d.	93.0	−93.0	181.0	−181.0
Silicate	n.d.	n.d.	58.5	−58.5	87.5	−87.5
H_2O (cm)	144.0	144.0	90.9	53.2	122.0	23.0
1986–87						
H^+	n.d.	0.1	0.0	0.1	0.0	0.1
NO_3-N	n.d.	1.4	0.0	1.4	0.0	1.4
NH_4-N	n.d.	1.9	0.0	1.9	0.0	1.9
PO_4-P	n.d.	0.0	0.0	0.0	0.0	0.0
Ca^{2+}	n.d.	1.3	1.3	0.0	10.7	−9.4
Mg^{2+}	n.d.	0.2	0.1	0.1	0.9	−0.7
Na^+	n.d.	1.0	2.2	−1.2	10.5	−9.6
K^+	n.d.	0.8	0.6	0.2	2.8	−2.0
SO_4-S	n.d.	2.4	0.1	2.4	0.2	2.3
Cl^-	n.d.	3.3	0.9	2.4	1.6	1.6
HCO_3^-	n.d.	n.d.	12.1	−12.1	66.9	−66.9
Silicate	n.d.	n.d.	6.9	−6.9	30.2	−30.2
H_2O (cm)	61.1	61.1	8.2	52.9	30.3	30.8

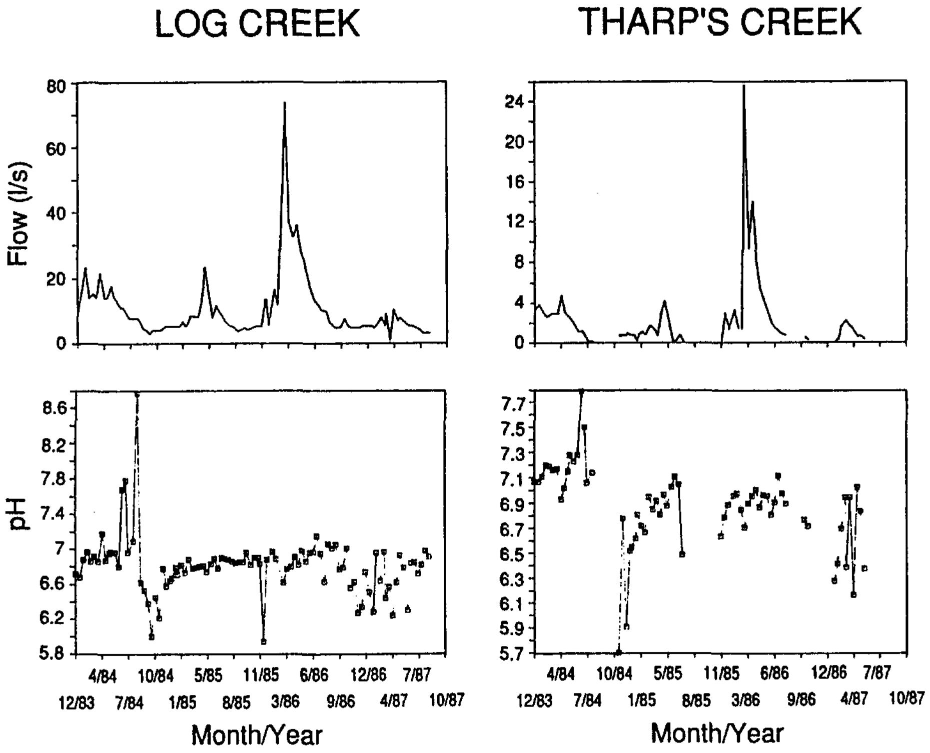

Fig. 2. Time series plots of streamflow and pH for Log and Tharp's Creeks from December 15, 1983 to August 31, 1987.

snow melt continued and flow decreased. Chloride peaks occurred in the early summer and autumn (at low flows) and to a lesser extent, during the peak flow period in each hydrologic year (Fig. 3). Sulfate concentrations were less variable than those of alkalinity and chloride, and were slightly higher in the autumn compared to late-spring or summer with a peak at high flow (Fig. 3). Silicate concentration in both creeks had patterns that matched those of alkalinity (Fig. 3).

The seasonal variation in cation concentrations was similar in pattern between the two creeks (Fig. 4). Calcium concentrations tended to decrease at the onset of spring melt, and then increase with decreasing flow. A second decrease and subsequent rise in Ca^{2+} concentration in the autumn each year was most conspicuous in Log Creek in September—December 1986. Concentrations of Na^+, Mg^{2+} and K^+ followed similar patterns as Ca^{2+} and HCO_3^- in the two streams. In 1986—87, however, Ca^{2+} and Mg^{2+} concentrations generally decreased while Na^+ and K^+ concentrations slightly increased.

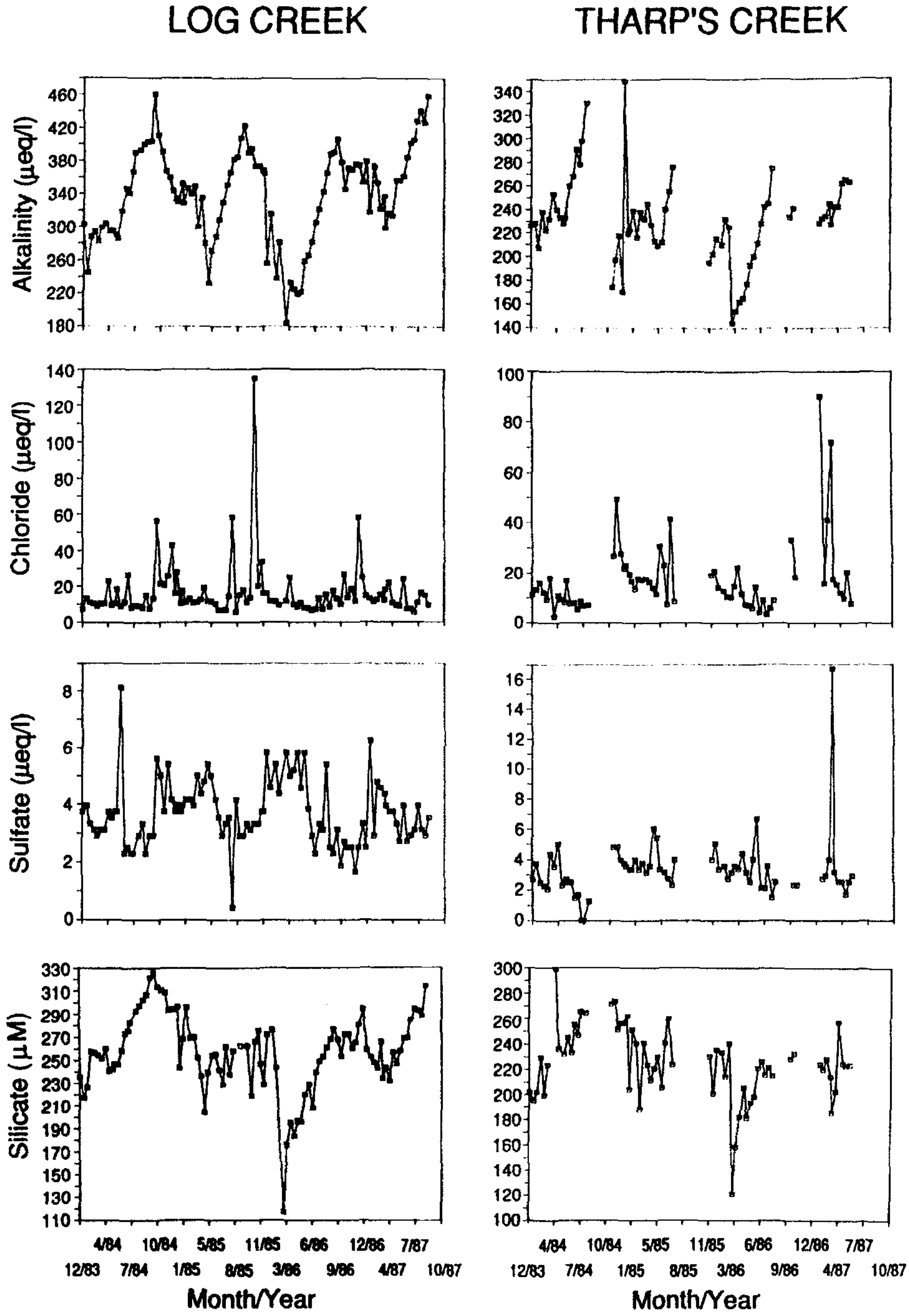

Fig. 3. Time series plots of major anions and silicate for Log and Tharp's Creeks from December 15, 1983 to August 31, 1987.

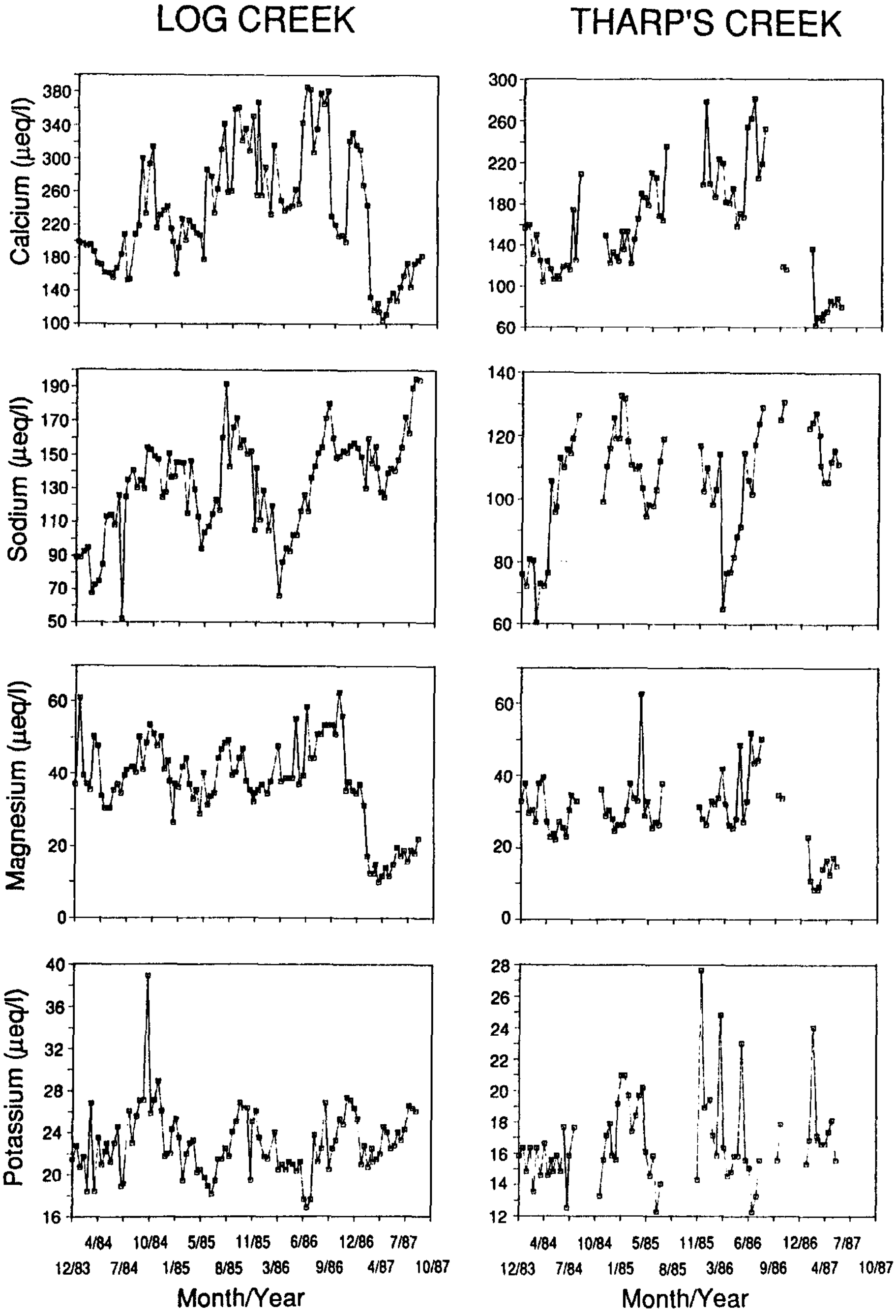

Fig. 4. Time series plots of major cations for Log and Tharp's Creeks from December 15, 1983 to August 31, 1987.

Three general patterns were observed between ionic concentrations and stream flow (Fig. 5 and 6):

- a gradual dilution with increasing flow occurs for alkalinity, silicate, and sodium and to a lesser extent, potassium;
- the concentrations of H^+ and Cl^- in Log Creek, and to a lesser extent in Tharp's Creek, have high variability at low flows and low concentrations at moderate and high flows; and
- calcium, Mg^{2+} and SO_4^{2-} concentrations in both streams had variable ionic concentrations at low and moderate flows and moderately high ionic concentration at higher flows.

Flow measurements were not strongly correlated with ionic concentrations (Fig. 5 and 6). Strong relationships (i.e., with coefficients of determination >0.50) to flow were only found for Na^+, HCO_3^-, and silicate concentrations in Log Creek. Moderate relationships (i.e., with coefficients of determination >0.35 but <0.50) to flow were found for Na^+, HCO_3^-, and silicate concentrations in Tharp's Creek. Low r^2 values show that the amount of variation in concentrations of H^+, Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-} and Cl^- explained by flow was low.

Input-output balance

Precipitation inputs were generally dominated by Cl^-, SO_4-S, NH_4-N, NO_3-N, Ca^{2+} and Na^+, in decreasing order (Table 3). Outputs from both Log and Tharp's Creeks were dominated by HCO_3^-, Ca^{2+} and Na^+, while H^+, NO_3^-, NH_4^+ and PO_4^{3-} are retained or transferred to gases in the ecosystem. The mass balances were generally similar among years and between watersheds, showing retention of NO_3^-, SO_4^{2-}, NH_4^+, PO_4^{3-} and H^+, and loss of HCO_3^-, Ca^{2+}, Na^+, K^+ and Mg^{2+}. The major difference between the Log and Tharp's Creek watersheds was in the magnitude of chemical fluxes. The outputs of HCO_3^-, Ca^{2+} and Na^+ were generally twice as great per unit area in the Log Creek watershed compared to the Tharp's Creek watershed.

Hydrologic output varied considerably between watersheds and among years but precipitation minus stream discharge was nearly constant for Tharp's Creek (51, 53, and 53 cm yr^{-1}) and only slightly less so for Log Creek (31, 23 and 31 cm yr^{-1}). The proportion of precipitation that was not accounted for by stream discharge varied from 0.45, 0.16, and 0.50 for the Log Creek watershed and 0.74, 0.37, and 0.86 for the Tharp's Creek watershed for 1984—85, 1985—86, and 1986—87, respectively (Table 3).

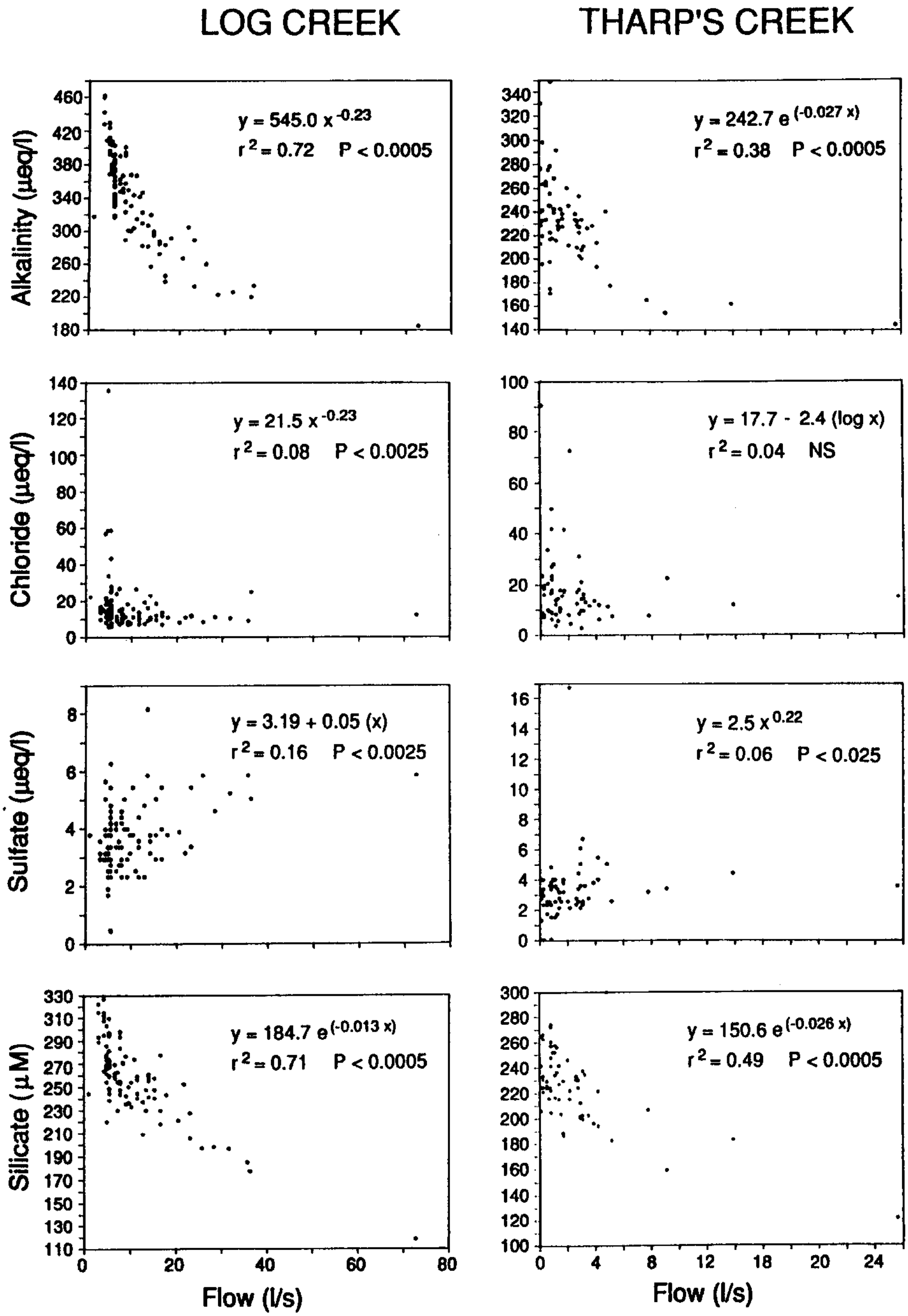

Fig. 5. Relationship of concentrations of major anions and silicate to instantaneous stream flow for Log (n = 71) and Tharp's Creeks (n = 66).

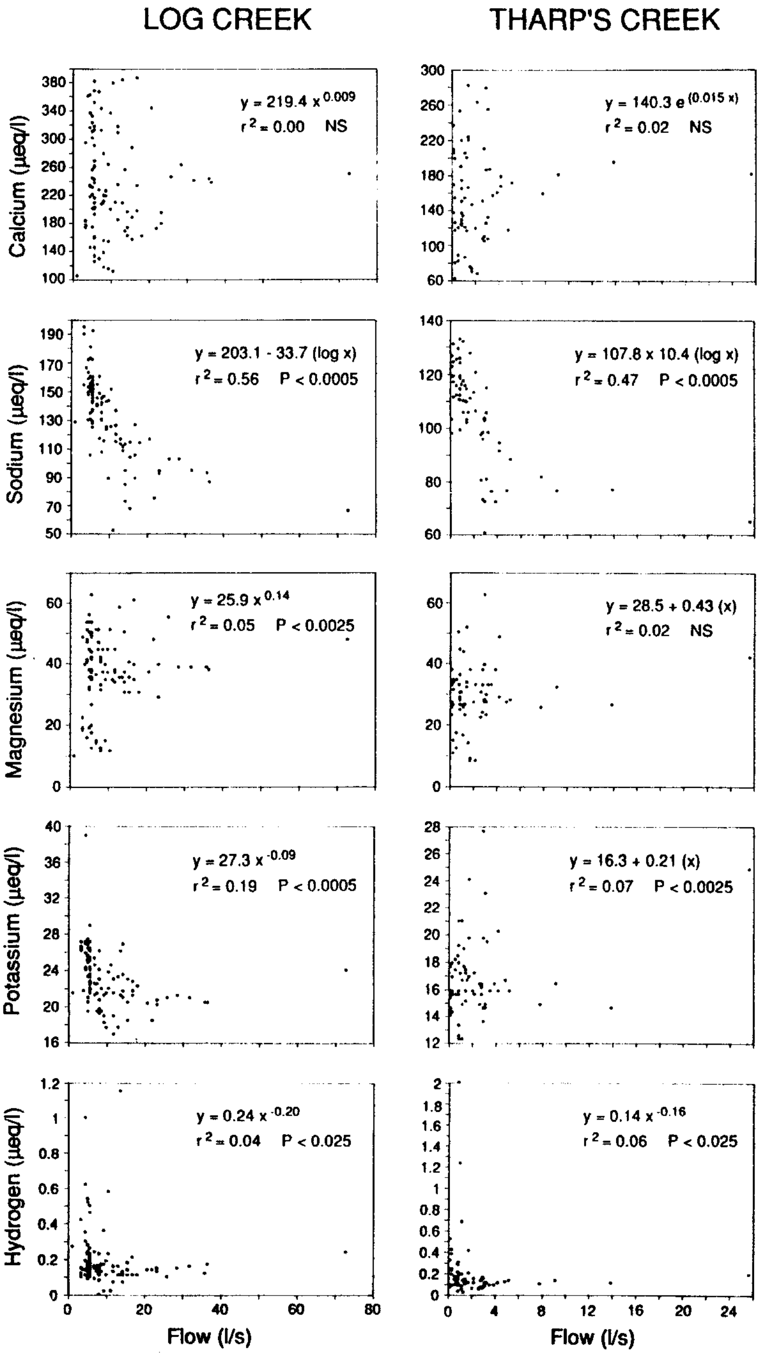

Fig. 6. Relationship of concentrations of major cations to instantaneous streamflow for Log (n = 71) and Tharp's Creeks (n = 66).

Discussion

Input-output balance

In both the Log and Tharp's Creek watersheds, nearly all inputs of H^+, NO_3^-, NH_4^+ and PO_4^{3-} were retained (Table 3) or in the case of NO_3^- potentially denitrified. This is expected given the moderate depth of soil and large standing biomass and productivity of trees (Riegel et al. 1988, Stohlgren 1988a). These data corroborate other studies of temperate conifer watersheds that show nearly all the sites retain nitrogen and phosphorous (Likens et al. 1977; Table 4). As in other studies in montane coniferous watersheds, annual average atmospheric contributions of NO_3-N (1.6 kg ha^{-1}) and NH_4-N (1.7 kg ha^{-1}) greatly exceeded hydrologic losses (Table 4).

Normal protocols for sampling atmospheric deposition probably underestimate N inputs (Gosz 1980; Swank 1984; Lindberg et al. 1986; Lewis et al. 1987; Boring et al. 1988). The collector used in this study was constructed of smooth plexiglass (see Lewis & Grant 1978) and thus, aerosol impaction was underestimated (Bowden 1986); also, we excluded weeks with no precipitation. And, to estimate cloudwater and dry deposition, information is needed on pollutant concentrations and deposition velocity; the latter is difficult to quantify accurately (Smith 1990). One study of cloudwater chemistry (based on 12 samples) suggests concentrations of H^+, NO_3^-, NH_4^+ and SO_4^{2-} can be high in this area (Collett et al. 1989) but deposition can not be accurately quantified due to a lack of information on vapor flux through the forest. Other studies adjacent to our study sites measuring some components of dry deposition (i.e., aerosol concentrations, wind speed, deposition to pine needles and surrogate surfaces) indicate that cloudwater and dry deposition combined account for approximately half the wet + dry deposition of ammonium, nitrate and sulfate (Blanchard et al. 1989). Our data also show bulk deposition values about 1.8 times as great as wet deposition values for the same year, suggesting that dry deposition is an important constituent of total deposition in this region.

Annual SO_4-S accumulations for Log and Tharp's Creek watersheds averaged 1.4 and 1.6 kg ha^{-1}, respectively (Table 4). These values are probably underestimates. As with N, actual accumulation of S in the ecosystem requires information on biological S requirements, organic S leaching, reduction of SO_4^{2-}, and volatilization of H_2S, dimethyl sulfide or other gaseous S compounds (Johnson 1984, Waring & Schlesinger 1985). The biological S requirements for forests are thought to be 1—5 kg ha^{-1} yr^{-1} (Vitousek et al. 1988; Johnson 1984). The S accumulation rates

Table 4. Comparisons of mean annual inputs (kg/ha) and inputs-outputs (kg/ha) for selected montane coniferous watersheds throughout the world.

	Sequoia National Park, California USA[1].			Fraser Experimental Forest, California USA[2].				Como Creek Watershed, Colorado USA[3]		Langtjern Watersheds, Norway[4]				Karpenissi Watersheds, (5 and 7) Greece[5]	
Constituent		Log Cr.	Tharp's	Dead Horse Cr.		Lexen Cr.					LAEO1	LAEO2	LAEO3		
	Inputs	I—O	I—O	Inputs	I—O	Inputs	I—O	Inputs	I—O	Inputs	I—O	I—O	I—O	Inputs	I—O
H^+	0.1	0.1	0.1	—	—	—	—	—	—	0.6	0.5	0.5	0.5	—	—
NO_3-N	1.6	1.6	1.6	1.1	0.5	1.4	0.8	1.8	1.8	3.5	3.4	3.4	3.4	3.0	2.2
NH_4-N	1.7	1.7	1.7	0.6	0.6	0.8	0.8	1.2	1.2					7.6	3.8
PO_4-P	<0.1	0.0	<0.1	—	—	—	—	0.2	0.2		—		—		
Ca^{2+}	1.5	−19.6	−7.2	2.8	−38.2	3.4	−30.7	4.0	1.7	1.4	−5.6	−6.2	−5.0	33.1	−56.4
Mg^{2+}	0.3	−2.7	−1.2	0.2	−9.5	0.3	9.0	0.4	−0.2	0.4	−0.9	−0.9	−1.1	4.3	−13.3
Na^+	1.5	−14.8	−6.3	1.8	−6.7	2.3	−6.6	2.0	0.4	2.3	−1.1	−1.1	−1.5	5.9	−33.7
K^+	0.8	−4.7	−2.0	2.4	−1.4	2.9	0.0	1.6	1.3	1.4	0.3	0.3	0.4	4.0	−2.8
SO_4-S	1.8	1.4	1.6	2.3	−0.2	2.8	−0.2	3.1	3.0	10.1	2.5	2.2	2.1	20.6	−8.5
Cl^-	3.3	0.1	1.1	—	—	—	—	—	—	3.7	0.0	0.0	−0.2	29.6	−32.7
H_2O cm	92	58	31	65	35	65	50			88	58	58	58	161	93
range	61—144	30—122	8—91	58—84	26—54	58—84	31—81			82—105		43—71		130—189	64—121
Vegetation	*Abies concolor, Sequoiadendron giganteum, Pinus lambertiana*			*Picea engelmannii, Pinus contorta*, and *Abies lasiocarpa*				*Abies lasiocarpa, Picea engelmanni, Pinus contorta, Pinus flexilis*		Sparse coniferous forest				*Abies cephalonica*	
Geology	Granite, granodiorite			Sedimentary sandstone				Granite		Granite, gneiss				Argillites, siltstones shales, marl	

1. This study (mean of 1984, 1985, 1986).
2. Stottlemyer and Troendle 1987 (mean from 1965, 1970, 1971, 1982, 1984)
3. Lewis and Grant 1979a.
4. Wright 1983 (mean from 1974 through 1980).
5. Nakos and Vouzaras 1988 (mean of two watersheds for 4 years: 1980—81 through 1983—84).

reported here (Table 4) are within this range, but SO_4^{2-} adsorption measurements in this forest suggest rates of organic S formation may be as high as 8—9 kg ha^{-1} yr^{-1} (J. Fitzgerald, pers. comm.).

Most of the watershed studies in coniferous forests (Likens et al. 1977; Table 4) report losses of the base cations. Many of these studies showed ionic proportions in cation losses similar to those for Log and Tharp's Creeks ($Ca^{2+} \gg Na^{+} \geqslant Mg^{2+}$ K^{+}) (Tables 3 and 4).

The higher outputs of HCO_3^-, Ca^{2+}, and Na^+ from the Log Creek watershed compared to those from Tharp's Creek are, in part, due to perennial stream flow in Log Creek where groundwater may remain in contact with weathering rock and soil minerals for longer periods of time compared to intermittent Tharp's Creek (Dunne and Leopold 1978). Another source of high calcium in the Log Creek drainage is in the abundant, calcium-rich leaf litter of *Sequoiadendron giganteum* (Stohlgren 1988b). Giant sequoia, as the dominant tree species (in terms of basal area; Table 1), may precipitate greater fluxes of calcium in the Log Creek watershed than in the Tharp's Creek watershed. The lower basal area pine-fir forest in the Tharp's Creek watershed probably has lower litterfall rates and proportionally more pine trees that release Ca^{2+} more slowly in decomposing leaf litter (Stohlgren 1988b; Klemmedson et al. 1985). Thus, the internal cycling of Ca^{2+} is likely different in the two watersheds despite their similarities in soils and geology.

Seasonal changes in precipitation and streamflow chemistry

Stohlgren & Parsons (1987) reported high seasonal variation of ionic concentrations in wet deposition at Giant Forest. Ionic concentrations were low for most high-volume winter storms and highest for the rarer, low-volume summer or fall storms. Similar patterns were observed at our sites. Volume-weighted precipitation chemistry (Table 2) and annual ionic inputs (Table 3) appear strongly related to total precipitation but there are too few years of data to assess trends. The observed annual increases in volume-weighted concentrations of NO_3^-, NH_4^+ and SO_4^{2-} in precipitation warrant continued monitoring.

The seasonal patterns of HCO_3^- and silicate concentrations (Fig. 3) and the strong relationships of flow to their ionic concentrations (Fig. 5) suggest uniform weathering rates. The magnitude of the weathering rates also may be partly determined by the residence time of water and flow path of water in the watershed. This would account for the higher HCO_3^- and silicate concentrations in Log Creek compared to the Tharp's Creek watershed (Fig. 3) and explain the poorer relationship of flow to those ion concentrations in the intermittent Tharp's Creek watershed.

Whereas the seasonal patterns of HCO_3^- and silicate are largely controlled by snow melt processes, Ca^{2+} and Mg^{2+} patterns may be influenced by biological factors as well as hydrology. The soils in the area are thawed throughout winter (Sequoia National Park, unpublished data) and nutrient release from decomposing forest litter is greatest during the winter and spring (Stohlgren 1988b). Moderate to high concentrations of Ca^{2+} and Mg^{2+} in the streamwater in the late spring and summer may be due, in part, to solute release from the well-developed litter layer.

Unlike some other montane forested watersheds (e.g., Lewis & Grant 1979b; Stottlemyer & Troendle 1987; Baron & Bricker 1987), the chemistry of these mid-elevation Sierran streams appears not wholly controlled by the spring snow melt. While snow melt processes dominate stream alkalinity and silicate, high concentrations of H^+, Cl^- and SO_4^{2-} in streamwater also may result from recent rain events, particularly during the summer and autumn when pollutant concentrations are at their highest (Stohlgren & Parsons 1987). Both Cl^- and SO_4^{2-} show bimodal patterns of ionic concentrations over time with peaks in early fall (i.e., the onset of the precipitation year) and during early snowmelt when solutes are released from the snow pack. The pattern is more obvious for the intermittent Tharp's Creek. Thus, although biological requirements of S and Cl are thought to be low for temperate forest ecosystems (Vitousek et al. 1988; Johnson 1984), the winter snow pack and well-drained soils in the summer may act as temporary sinks for both S and Cl.

The hydrology of these California mixed conifer watersheds is confounded by mild winter weather. Precipitation may fall as rain or snow or mixed rain and snow. Winter storms may arrive several weeks apart with intermittent warming trends. Solute concentrations in streams may be influenced by recent precipitation events. This was particularly true during the 1986—87 drought year that showed highly fluctuating solute concentrations and stream flow even in mid-winter.

Susceptibility of the watersheds to acidic deposition

The susceptibility of watersheds to acidic deposition is largely a function of the amount of inputs and the acid neutralizing capacity (ANC) of the soils and water, and the capacity of the ecosystem to retain potentially mobile anions (e.g., NO_3^-, SO_4^{2-}). Therefore, an integrated indication of the susceptibility of watersheds is the relative magnitude of hydrogen ion deposition and net yield of ANC from the watershed. When expressed as equivalents ha^{-1} yr^{-1}, the ANC (expressed as HCO_3^-) yields exceed by large margins the hydrogen inputs for Log and Tharp's Creek watersheds

(Table 5). Furthermore, both watersheds retain all the N and nearly all the S deposited from the atmosphere (Table 4).

Wyels (1986) investigated the sensitivity of soils in Sequoia National Park to sulfuric acid additions. She rated soils using three primary variables: soil pH, percent base saturation, and cation exchange capacity; and three variables of secondary importance: percent organic carbon, soil depth, and parent material. The dominant soil types in our study area ranked as sensitive to very sensitive to acid deposition. The A horizons of the Pachic-Xerumbrept and Lithic Xerumbrept soils had low sum of bases (7.0 and 5.5 meq/100 g), moderate % base saturation (58.3 and 54.5%) and low cation exchange capacity (12.1 , 10.1 meq/100 g) compared to other soils in the Park. However, Stanko & Fitzgerald (1990) found high rates of S mobilization and low organic S formation potentials that coincide with low amounts of SO_4^{2-} (~5.0% of total S) for these forest soils. This suggests that although the soils might be "sensitive" to acid deposition and have a fairly low buffering capacity, the buffering capacity is "adequate" to resist acidification at the current low levels of SO_4^{2}-S inputs (i.e., 0.9 to 2.4kg ha^{-1} yr−1).

Annual inputs and outputs of ionic constituents may not be as important in evaluating a watershed's susceptibility to acidification as are the deviation and resiliency of the system to short-term acidic precipitation events. Time series plots (Fig. 3) showed that alkalinity was temporarily depressed at onset of snowmelt but that it rebounded during the summer and fall. pH was generally lowest following spring snow melt but was also temporarily depressed by rain events in the drought year of 1987 (Fig. 2). We suspect precipitation events, rain in particular, caused peaks in Cl^-

Table 5. Hydrogen ion atmospheric inputs and HCO_3^- yields for Log and Tharp's Creeks by hydrologic year. Units are equivalents ha^{-1} yr^{-1}.

Year/ Constituent	Log Creek	Tharp's Creek
1984—85		
H^+	70	70
HCO_3^-	1221	408
1985—86		
H^+	80	80
HCO_3^-	2967	1525
1984—85		
H^+	80	80
HCO_3^-	1097	198

concentrations in stream water. While some chloride adsorption (Feth et al. 1964) and SO_4^{2-} adsorption (Wyels 1986; Stanko & Fitzgerald 1990) are known to occur, acidic events may have a temporary impact on stream chemistry.

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