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Solution chemistry profiles of mixed-conifer forests before and after fire

JON CHOROVER[1], PETER M. VITOUSEK[2], DANIEL A. EVERSON[3], ANNE M. ESPERANZA[3] and DOUGLAS TURNER[2]

[1] *Department of Environmental Science, Policy and Management, University of California at Berkeley, Berkeley CA 94720; Corresponding author. Present address: Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, Sciences II, CH-1211, Genève 4, Switzerland;* [2] *Department of Biological Sciences, Stanford University, Stanford CA 94305;* [3] *Research Office, Sequoia and Kings Canyon National Parks, Three Rivers, CA 93271*

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Abstract. Solution chemistry profiles of mixed-conifer forests in granitic catchments of the Sierra Nevada were measured for three years before (1987–1990) and three years after (1990–1993) prescribed fire. Wet deposition, throughfall and soil solution samplers were installed in both white-fir and giant-sequoia dominated forest stands underlain by poorly developed inceptisols. Stream water chemistry was monitored as part of an ongoing study of catchment outputs. Calcium, NO_3^- and Cl^- were the major ions in precipitation. Canopy leaching increased mean concentrations of all major ions, especially K^+ and Ca^{2+}. Water flux through the soil occurred largely during spring snowmelt. Forest floor leachate represented the most concentrated solutions of major ions. Interaction with the mineral soil decreased mean concentrations of most species and the average composition of soil solutions closely resembled stream water at baseflow. Bicarbonate alkalinity, Ca^{2+}, Mg^{2+}, and Na^+ were enriched in stream water relative to precipitation whereas inputs of H^+, NH_4^+, NO_3^- and SO_4^{2-} were retained within the catchments.

Burning of the forest understory and litter layer increased solute concentrations in soil solution and stream water. Mean soil solution Ca^{2+}, Mg^{2+} and K^+ concentrations increased more than 10 fold, but the relative predominance of these cations was not affected by burning. Sulfate concentration, which was very low in soil solutions of undisturbed stands (< 25 $mmol_c$ m^{-3}), increased more than 100 times following fire. Ammonium concentration exhibited a rapid, short-term increase and then a decrease below pre-burn levels. Changes in soil solution chemistry were reflected in catchment outputs.

Introduction

Changes in solution chemistry, as water passes vertically through forest ecosystems from canopy to stream, are characterized by *solution chemistry profiles* (e.g. Feller 1977; Binkley et al. 1982; Mollitor & Raynal 1982; Stottlemeyer & Hanson 1989; Probst et al. 1990). Information regarding solution chemistry at the forest stand scale complements catchment input-output budgets because runoff is often a mixture of individual sources (Beck et al. 1990) and element fluxes at the forest stand scale can not be inferred from measurements of precipitation and stream water alone (Binkley et al. 1982; Vitousek 1983). Studies of stand scale solution chemistry are especially important in ecosystems prone to natural or anthropogenic disturbance; intrasystem element transfers mediated by solution may not be detectable by stream water chemistry (Vitousek 1983).

Solution chemistry profiles

The chemistry of solutions reaching the forest floor is influenced by the chemistry of incident precipitation, washoff of dry-deposits and surficial canopy materials, and material exchange between canopy biomass and incoming precipitation (Lovett et al. 1989). Processes affecting throughfall chemistry have been studied for many canopy types and have been reviewed by Parker (1983) and Johnson & Lindberg (1992). The canopy often contributes major solutes to throughfall, but independent measurements of dry and wet deposition fluxes are required to quantify separately the solute masses derived from atmospheric deposition and leaching of canopy biomass (Johnson & Lindberg 1992).

Many factors interact to control solution chemistry within forest soils including solute adsorption and ion exchange, dissolution/precipitation reactions, and biotic uptake or release (Johnson et al. 1977; Cronan et al. 1978; Mollitor & Raynal 1982; Ugolini & Dahlgen 1987; Sposito 1989). In the temperate zone, forest soils contain significant quantities of 2:1 clay minerals and organic matter which confer a net negative charge upon the bulk solid phase (Dixon & Weed 1989). Negative surface charge is balanced by the adsorption of cations (Sposito 1989). Therefore, external and internal sources of hydrogen ions (H^+) and mobile anions mediate the mobilization and transport of cations in soil solution (Nye & Greenland 1960; Johnson & Cole 1980; Cronan 1980; Sollins et al. 1980; Reuss & Johnson 1986; Binkley & Richter 1987). The pool sizes of the major anions found in soil solutions (HCO_3^-, NO_3^-, Cl^-, SO_4^{2-} and organic anions) are regulated by internal ecosystem cycling and atmospheric inputs.

Nitrate and SO_4^{2-} are strong acid anions which can contribute significantly to cation leaching over the entire pH range encountered in soils. In addition to atmospheric sources, these anions are produced within forest ecosystems as a result of microbial mineralization and oxidation of organic matter. In areas subject to intensive acidic precipitation, cation transport may be controlled by external sources of strong mineral acids, but biotic assimilation of nitrate (Cronan 1980; Davidson et al. 1992) and surface adsorption or biotic uptake of sulfate (Harrison et al. 1989; Mitchell et al. 1991) regulate the mobility of these strong acid anions. Many undisturbed temperate forest ecosystems are N limited and thus NO_3^- uptake by vegetation and the soil biota limits NO_3^- leaching even for forests subject to high N deposition (Van Miegroet et al.

1992). In less polluted areas, internal sources of carbonic and organic acids may control the ionic composition of soil solutions (McColl & Cole 1968; Sollins et al. 1980). Organic acids, primarily derived from the decomposition products of litterfall and root mortality, are the dominant leaching agents in acid forest soils unimpacted by acidic deposition (Johnson et al. 1977). For forest soils at high latitudes or high elevation, organic acids become increasingly important as the dissociation of carbonic acid is suppressed at low pH (Johnson et al. 1977; Ugolini et al. 1977).

Vertical differences in the physical, chemical and biological properties of forest ecosystems cause differences in anion concentrations along solution chemistry profiles. Organic acids may play a dominant role in surface horizon leaching, but they are often retained in subsurface horizons, resulting in an increase in pH and HCO_3^- concentrations in systems not dominated by NO_3^- or SO_4^{2-} leaching (Ugolini et al. 1977). Nitrate production is often greatest in the litter and A horizons, whereas uptake of NO_3^- may occur at depth (Gosz 1981; Hart & Firestone 1991). Increased concentrations of iron and aluminum oxides in many forest subsoils contribute to the retention of SO_4^{2-} at depth (Parfitt 1978). Thus chemical fluxes between soil horizons will often exceed fluxes into or out of the boundaries of a forest stand.

Effects of fire

In addition to the gaseous efflux of elements during fire (Boerner 1982; Raison et al. 1985; Schoch & Binkley 1986; Tiedemann 1987), further ecosystem losses can occur by the erosion and leaching resulting from subsequent precipitation (Grier 1975; Bayley & Schindler 1991). The ash produced by combustion of natural organic matter consists largely of soluble oxides of alkaline earth (Group 2A) cations which require high temperatures (> 500 °C) for volatilization (Viro 1974). These oxides are rapidly altered to carbonates, which increase acid neutralizing capacity (ANC) and soil pH (Tiedeman et al. 1978). Dissolution of nutrients from the ash can increase soil base cation concentrations and generate significant leaching losses (Smith 1970; Grier & Cole 1971; Grier 1975; Woodmansee & Wallach 1981; Boerner & Forman 1982).

Burning may increase or decrease post-fire N availability (Woodmansee & Wallach 1981; Raison et al. 1990). For example, Schoch & Binkley (1986) found that accelerated decomposition of the forest floor, following prescribed fire, resulted in a large release of inorganic-N the following growing season. Efflux of nutrients (especially N and P) from burned watersheds can alter ground and surface water quality (Tiedemann et al. 1978; Schindler et al. 1980; Feller & Kimmins 1984; Bayley & Schindler 1991) either by contributing to stream and lake eutrophication or by increasing solute concentrations (e.g. NO_3^-) above prescribed levels.

Although several studies have documented biogeochemical effects of fire by analysis of soil samples (e.g. St. John & Rundel 1976; Binkley et al. 1982; Gillon & Rapp 1989; Kutiel & Shaviv 1989; Tomkins et al. 1991), and changes in stream and lake water chemistry (e.g. McColl & Grigal 1975, 1977; Wright 1976; Richter et al. 1982; Bayley & Schindler 1991) relatively few have actually measured the change in solution chemistry profiles *in situ* resulting from burning (Smith 1970; Boerner & Forman 1982). In the present study, the chemical compositions of precipitation, throughfall, forest floor leachate, soil solution and stream water were measured for three years before and three years after burning in mixed-conifer forest of the Sierra Nevada, California. The objectives were (1) to determine the influence of forest canopy, litter layer and mineral soil horizons on solute movement in undisturbed mixed-conifer forests and (2) to evaluate the effects of prescribed fire on solution mediated element fluxes.

Methods

Study site

The study site is located in the Giant Forest area of Sequoia National Park, California (Fig. 1). The experimental catchments are drained by Log, Crescent and Tharp's Creeks which vary in annual water fluxes in proportion to catchment area. 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*) and Jeffrey pine (*P. jeffreyi*). Tharp's Creek, an intermittent stream draining a 13 ha catchment, generally flows from November to June or July. The Tharp's Creek catchment is dominated by white fir, and contains fewer giant sequoia than the Log Creek watershed (Stohlgren et al. 1991). Crescent Creek, a perennial stream which drains the central catchment, was not monitored in the present study. Stands of giant sequoia are common in hollows or on deeper soils along the perennial streams where they likely receive drainage waters from surrounding slopes. Granitic outcrops are common at higher catchment elevations.

The soils of the study area are classified as Pachic and Lithic Xerumbrepts. They are typically 0.5–1.5 m deep, dark colored, well to excessively drained acid soils formed in granitic rock residuum. Mean annual soil temperatures at 50 cm depth range from about 8–10 °C. Mean winter and summer soil temperatures differ by more than 5 °C. In most years, soil profiles are moist from late fall through early summer, as a result of fall rains and snowmelt.

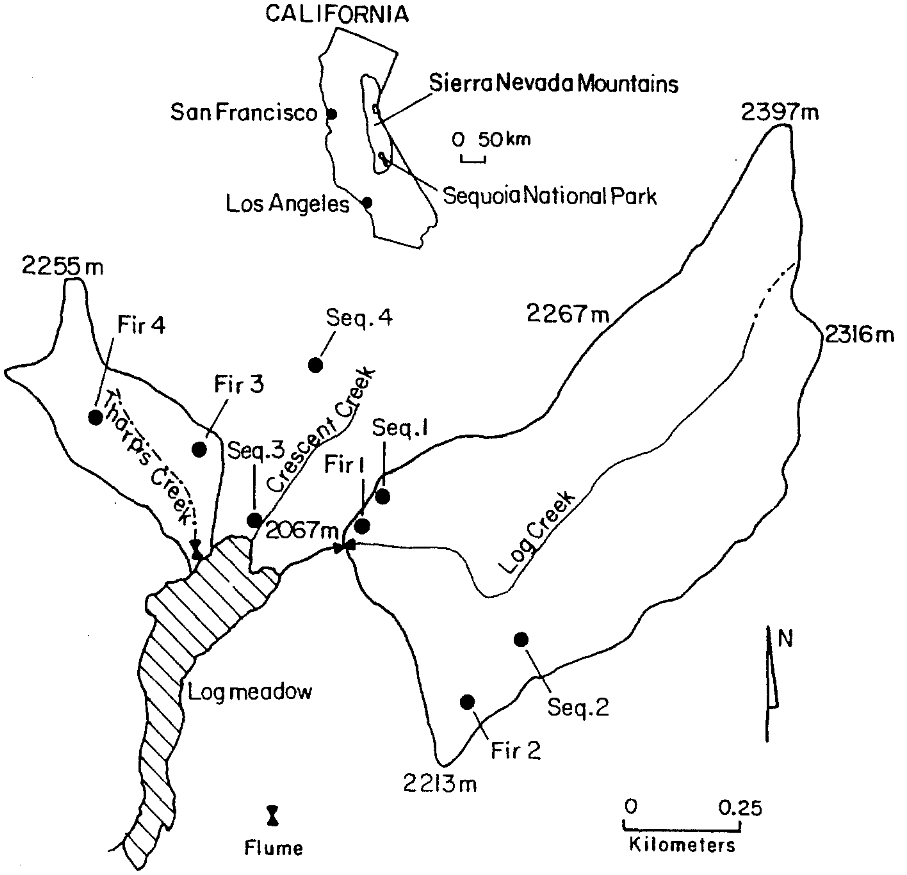

Fig. 1. Location of the study site and plots. The Log Creek (50 ha) and Tharp's Creek (13 ha) catchments are located in the Giant Forest area of Sequoia National Park. Plot locations and forest types (fir or sequoia) are shown. Numbers 1–2 indicate control plots and numbers 3–4 indicate burn plots.

From early summer to fall, the profiles are dry, except that the surface horizons may be moistened by thundershowers. Textures range from loamy coarse sand to coarse sandy loam. Fine gravel constitutes 15–35% of the volume in most horizons. Transitional horizons below the surface soil horizons are lighter in color (less than 10 g kg^{-1} organic carbon) but are similar in texture. The clay fraction contains quartz, mica, vermiculite, smectites and small quantities of kaolinite. Selected physical and chemical characteristics of representative soil profiles from white fir dominated (*mixed fir*) and giant sequoia dominated (*sequoia*) forest stands are presented in Table 1.

Table 1. Selected physical and chemical characteristics of representative soil profiles from mixed-fir and giant sequoia stands (<2 mm size fraction)[1].

Horizon	Depth (cm)	Texture Sand	Silt	Clay	Organic Matter C	N	pH^2_{sp}	Extractable Cations[3] Ca^{2+}	Mg^{2+}	K^+	Na^+	CEC^4
		....	($g\ kg^{-1}$)		....			....	($mmol_c\ kg^{-1}$)		....	
					Mixed-Fir							
A1	0–8	761	174	65	19.0	0.8	6.4	45.7	2.6	4.2	2.0	107
A2	8–38	804	135	61	12.3	0.6	6.2	18.9	2.1	4.5	2.2	107
A3	38–57	801	125	74	9.4	0.3	6.1	7.5	1.2	4.7	3.8	79
AC	57–100	770	151	79	4.7	0.3	5.4	3.9	1.0	4.1	3.6	30
					Giant Sequoia							
A1	0–5	545	335	120	124.0	2.5	6.2	253.3	22.3	8.4	1.5	526
A2	5–30	755	179	66	14.4	0.5	6.1	50.5	4.7	5.1	0.8	138
A3	30–71	751	174	75	7.1	0.1	6.0	27.8	4.3	6.1	0.8	128
AC	71–112	813	133	54	2.6	0.1	6.0	16.9	3.3	5.2	0.7	76
C	112–142	816	134	50	1.9	0.1	5.7	20.3	3.2	4.6	0.9	28

[1] Data from Huntington and Akeson (1987)

[2] pH of saturated paste in H_2O

[3] Ammonium acetate extraction, pH 7

[4] Barium saturation method (Rhoades 1982)

Field instrumentation and sample collection

Two sites were selected in burn and control areas in each of the two major vegetation types to provide a measure of within-watershed variation in ion flux. In the summer of 1987, throughfall and soil solution samplers were installed in 0.1 ha plots within or adjacent to larger sites which had been established previously as part of a long-term study of vegetation dynamics. These plots are considered representative of the two watershed vegetation types based upon a quantitative characterization of stand structure (Sequoia Watershed Research Project, unpublished data). The two fir burn plots and the two sequoia burn plots were located in the Tharps Creek and Crescent Creek catchments, respectively. All control plots were contained in the Log Creek catchment (Fig. 1).

Six throughfall collectors constructed from 0.038 m^3 polyethylene containers were dispersed systematically to sample the full expanse of each plot. These collectors were fastened to the top of telescoping 8 and 10 cm diameter

PVC pipes that, when extended to their full height, stand in excess of 3 m. The use of tall throughfall containers was necessary to maintain a height above the depth of accumulated snowpack (> 2 m depth on some sampling dates) and to avoid the reach of black bears who frequent the study area. Throughfall collectors were lined with polyethylene bags and covered with nylon mesh prior to sampling in spring and autumn. For collection of throughfall snow, mesh covering was not used. The cross-sectional area of each throughfall collector was 0.17 m^2. Three open precipitation collectors, constructed like the throughfall collectors, were installed adjacent to the forested sites on an exposed granite slope.

One soil pit was located in each quadrant of each plot (four soil pits per plot) and excavated to a depth of 1.2 m. Soil-solution samplers were installed in the uphill side of each pit below the forest floor (O horizon), within the A horizon, and in the AC horizon. All samplers were constructed from porous ceramic material. Funnel-type collectors (64 cm^2 cross-sectional sampling area) were installed below the forest floor and within the A horizon. Porous cup collectors (Soil Moisture Corp.) were installed in the AC horizon. A siphon apparatus constructed from a hanging water column produced suction in glass collection bottles necessary to sample soil-water to a matric potential of −0.01 MPa. Zero tension snowmelt samplers, constructed from polyethylene trays (cross-sectional sampling area of 324 cm^2) were installed above the forest floor at each soil pit prior to the first snowfall in winter 1992–1993. All instrumentation for soil solution collection was contained within the excavated pit which was covered by a sheet of plywood between sample collections.

Precipitation and throughfall were sampled on an event basis between November 1987 and March 1992. It was sometimes impractical to collect samples between storms which occurred within the same week. Therefore, some samples integrated storms over a maximum time period of one week. Upon sample collection, the amount of precipitation or throughfall present in the polyethylene lining was assessed gravimetrically with a spring-loaded scale. Snowmelt samples were collected when available during the 1993 snowmelt period. Soil-solution and stream water were collected approximately biweekly, when available, between November, 1987 and March, 1993. Stream water samples were taken at mid-stream and mid-depth in an area of turbulence. Stream water discharge was measured using Parshall flumes and Stevens type F stream height recorders at the time of sampling (Stohlgren et al. 1991). Soil solution and Tharp's Creek sampling was primarily limited to spring snowmelt and periodic summer or fall rainstorms. Subsamples of all collected solutions were transferred to acid-washed 250 ml high-density polyethylene containers and transported immediately to the lab for analysis.

In fall 1990, a controlled burn was applied to assess the effects of prescribed fire on element fluxes. The entire 13 ha Tharps Creek catchment was burned to study fire effects on both soil solutions and stream water. Crescent Creek solution chemistry was not monitored, but the experimental giant sequoia plots situated along Crescent Creek were burned at the plot (0.1 ha) scale. The Log Creek catchment was left unburned as a control. Of the eight plots, two mixed fir and two sequoia plots were burned (Fig. 1).

Chemical analyses

Unfiltered samples were analyzed for pH and electrical conductivity within six hours of collection. Acid neutralizing capacity (ANC) was measured by Gran titration (Gran 1952) within 24 hours of collection. Solution pH was measured by glass combination electrode (Beckman #39833) and a Beckman pHI *pHmeter*. Specific conductance measurements were made with a YSI model 34 conductivity meter with a YSI 3402 conductance cell (cell constant = 0.1/cm). Subsamples were filtered (0.45 μm membrane) and mailed in insulated, refrigerated boxes to the National Park Service Laboratory at Michigan Tech University (MTU), Houghton, Michigan (before December, 1990) or Colorado State University (CSU), Fort Collins, CO (after December, 1990) for major anion and cation analyses. Samples were stored at MTU or CSU at 2 °C until analyses for Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}, NO_3^{-}, SO_4^{2-}, Cl^{-}, and PO_4^{3-} were performed on an automated Dionex 2020 ion chromatograph according to the methods detailed in Stottlemyer (1987). Unfiltered subsamples were acidified to pH 2 with H_2SO_4 and shipped to either Stanford University or University of California at Berkeley for H_2SO_4/HgO digestion and analysis of total kjeldahl N and P by autoanalyzer (Bremner & Mulvaney 1982).

Data analysis

Volume weighted mean (VWM) concentrations of all constituents in precipitation and throughfall were calculated as follows:

$$VWM_a = \frac{\sum_{i=1}^{n_a} C_{ai}V_i}{\sum_{i=1}^{n_a} V_i} \qquad (1)$$

where, C_{ai} is the concentration of species a in sample i, V_i is the volume of precipitation or throughfall measured for sample i, and n_a is the total number of samples for which measurement of species a was made. Volume weighted mean stream water concentrations were also calculated by Eqn. 1, where, in this case, V represents instantaneous discharge measured at the time of sampling. Arithmetic means were calculated for forest floor leachate and soil solution data because accurate assessments of sub-surface solution fluxes were not possible. The data pertaining to annual means are presented on the basis of the *hydrologic year* which is assumed to span the dates September 1–August 31.

Results and discussion

Pre-burn solution chemistry profiles

Input and output concentrations

Pre-burn (1987–1990) mean ion concentrations in wet deposition and stream water are presented in Table 2. Calcium is the predominant cation, and NO_3^- and Cl^- are the predominant anions in precipitation for means taken over all three pre-burn years. We observed strong correlations between major ions in precipitation: Ca^{2+}, Mg^{2+}, K^+, Na^+, NO_3^-, SO_4^{2-}, Cl^- and $H_2PO_4^{2-}$ exhibit pairwise correlation ($r > 0.6, p < 0.001$). Stream water concentrations of ANC (dominantly HCO_3^- alkalinity), Ca^{2+}, Mg^{2+}, and Na^+ are greatly enriched relative to precipitation whereas H^+, NH_4^+ and the strong acid anions NO_3^- and SO_4^{2-} are relatively diminished (Williams et al.1993). Calcium, Na^+ and HCO_3^- predominate in stream water. Concentrations of these ions are higher in Log Creek than in Tharp's Creek as a result of increased groundwater contributions to the perennial stream (Williams et al. 1993). These results are consistent with the input-output budget calculations of Stohlgren et al. (1991) and Williams et al. (1993) for these catchments during the years 1984–1992.

Canopy effects

Volume weighted mean (VWM) ion concentrations in wet deposition (PPT) and throughfall (TF) are presented by sampling date for the mixed fir and sequoia contol sites in Figs. 2 and 3. A log scale is used to facilitate the examination of concentration data scanning several orders of magnitude. These data indicate that variability among sampling dates is quite high, but seasonal patterns in VWM values are evident. The highest ion concentrations in both PPT and TF were encountered in summer and fall precipitation events and concentrations decline with progression of the wet winter season. Overall, TF is enriched in all major ions relative to PPT (Tables 2–3). Potassium and Ca^{2+} were consistently the dominant cations in TF, with mean K^+ concentrations higher in the fir stands and mean Ca^{2+} concentrations higher in the sequoia stands. These differences are consistent with the relative concentrations of calcium and potassium in leaf material of the two tree types (Stohlgren 1988b). Large effluxes of K^+ from plant foliage in forest ecosystems are commonly reported (Parker 1983; Lindberg et al. 1986; Johnson

Table 2. Pre burn and post burn volume weighted mean ion concentrations in precipitation (wet deposition) and stream water. Units are millimoles of charge per cubic meter. Stream water data from Williams et al. (1993) and Sequoia Watershed Research Project unpublished data.

	ANC	NO_3^-	Cl^-	SO_4^{2-}	$H_2PO_4^-$	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
	$\text{mmol}_c\ \text{m}^{-3}$										
Pre Burn (1987–1990)											
PPT	8.6	13.8	11.2	7.5	0.8	4.65	23.7	4.4	6.2	11.8	15.1
Log Ck.	322.4	0.36	15.8	5.3	0.1	0.20	238.5	41.9	150.7	24.6	1.0
Tharp's Ck.	197.8	0.05	13.9	4.9	0.0	0.23	165.3	29.5	114.2	17.7	1.6
Post Burn Year 1 (1990–1991)											
PPT	2.4	17.3	2.7	5.9	0.1	3.80	5.5	1.2	4.3	0.1	14.7
Log Ck.	238.4	0.74	11.2	7.7	0.0	0.29	168.1	24.0	116.7	22.4	0.0
Tharp's Ck.	445.8	28.13	78.4	201.6	0.0	0.15	533.9	98.6	153.3	49.6	5.8
Post Burn Year 2 (1991–1992)											
PPT	0.0	13.1	4.3	7.0	0.0	4.39	7.0	1.8	4.5	1.0	18.4
Log Ck.	233.9	0.02	11.7	6.2	0.1	0.22	200.2	43.0	155.9	24.0	0.0
Tharp's Ck.	186.8	42.31	47.6	27.4	0.0	0.11	174.7	53.9	134.6	24.2	0.0
Post Burn Year 3 (1992–1993)											
PPT	2.6	4.8	2.5	3.1	0.0	4.99	9.8	2.4	2.7	0.2	4.5
Log Ck.	240.7	0.75	14.6	9.4	0.0	0.20	140.2	37.1	121.7	19.0	0.0
Tharp's Ck.	264.4	5.76	32.7	44.8	0.0	0.13	184.9	56.9	116.0	26.6	0.0

& Lindberg 1992) reflecting the highly mobile nature of K^+ in plant tissues (Kramer & Kozlowski 1979).

Throughfall water fluxes were consistently less than or equal to PPT water fluxes as expected. For events showing lower inorganic-N concentrations in TF than PPT (e.g. winter, 1988 in Figs. 2–3) net canopy retention of NO_3^- and NH_4^+ may be inferred. Inorganic-N retention is apparently favored by a recently leached canopy and highest TF enrichments follow prolonged dry periods (Figs. 2–3). However, on an annual basis, TF fluxes of all major elements exceed quantities resulting from wet deposition alone (Table 4).

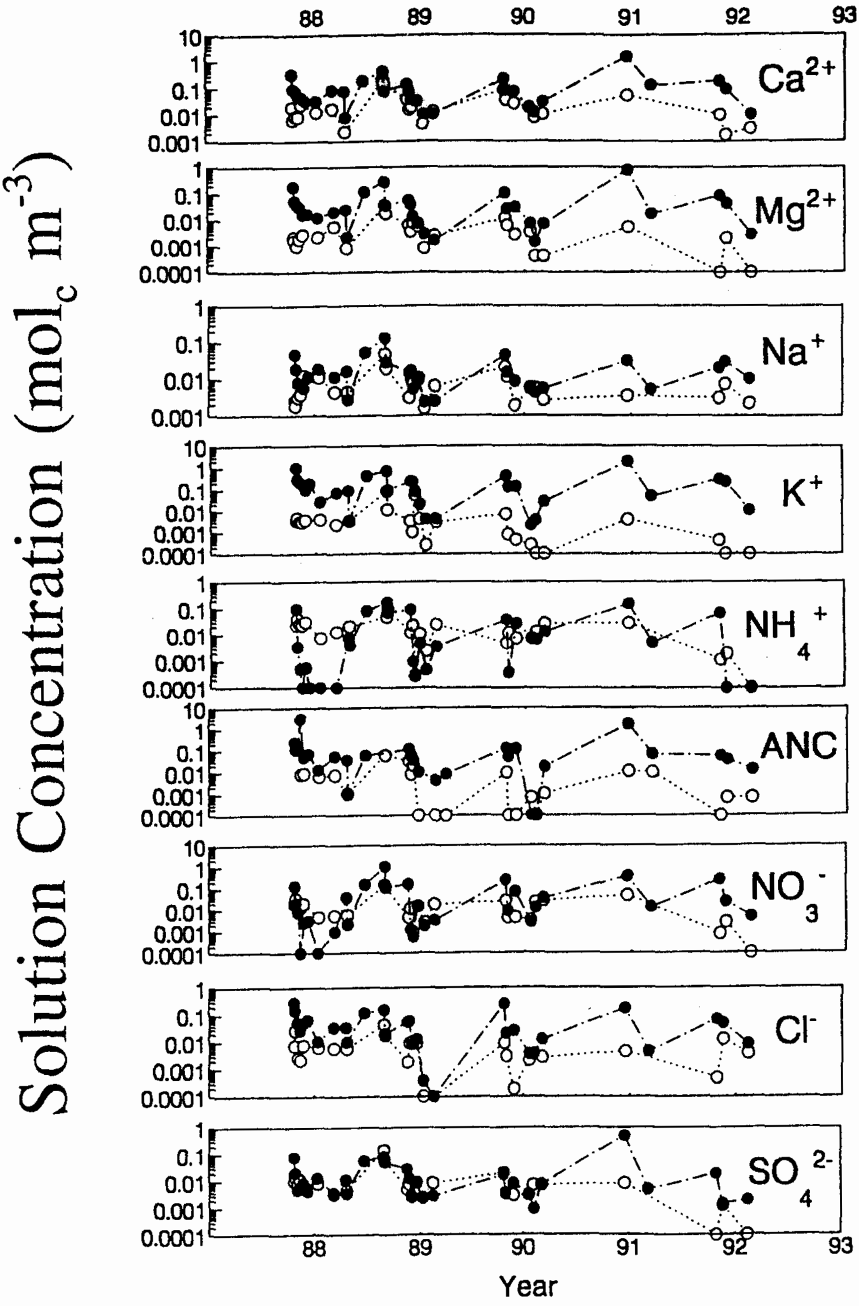

Fig. 2. Ion concentrations in wet deposition (PPT) and mixed-fir control throughfall (TF). Concentrations are presented in moles of charge per cubic meter (log scale). Symbols indicate volume weighted means by event sampling date. PPT – open circles, TF – filled circles. The same PPT data set is shown in Fig. 3.

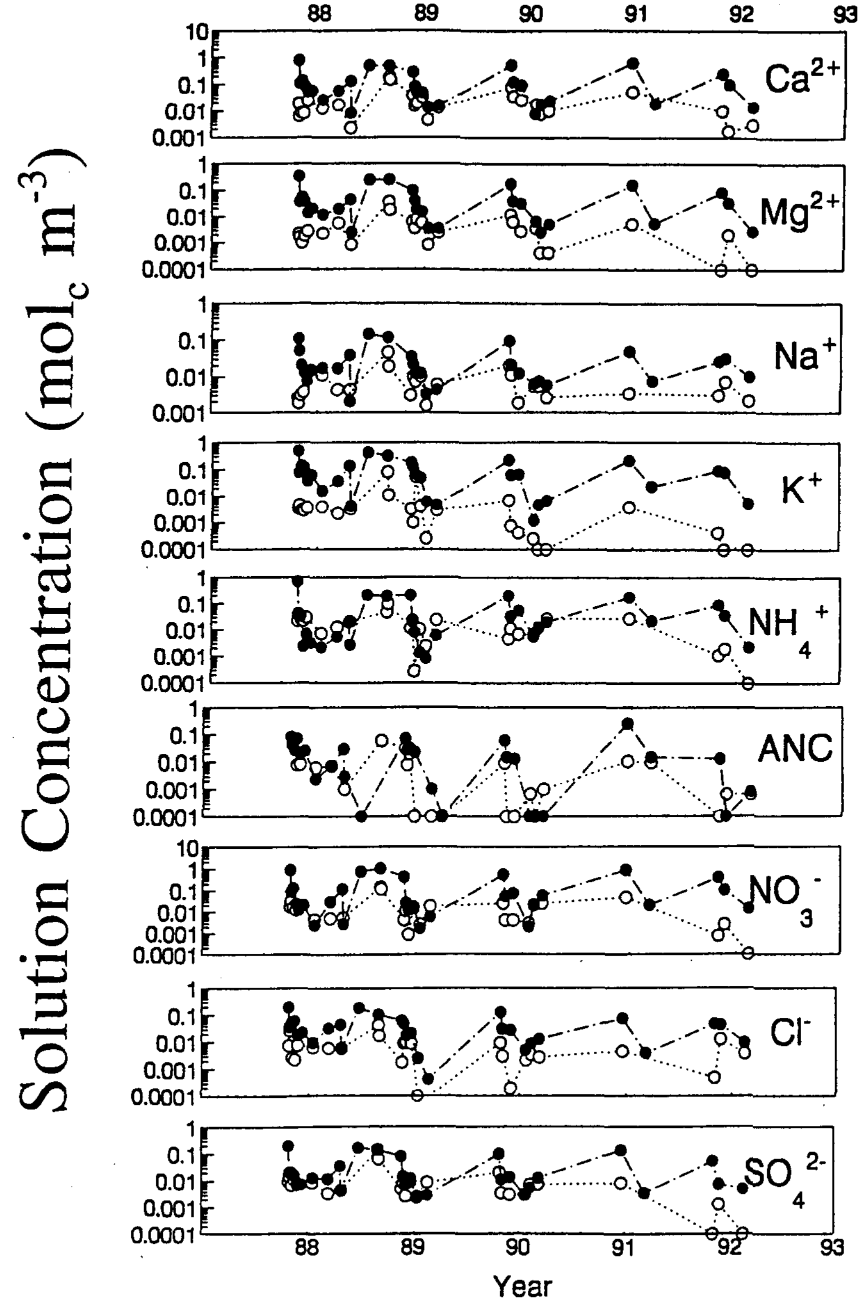

Fig. 3. Ion concentrations in wet deposition (PPT) and sequoia control throughfall (TF). Concentrations are presented in moles of charge per cubic meter (log scale). Symbols indicate volume weighted means by event sampling date. PPT – open circles, TF – filled circles. The same PPT data set is shown in Fig. 2.

Table 3. Pre-burn mean ion concentrations in throughfall (TF – volume weight), forest floor leachate (FFL) and soil solution (A and AC horizons) [1987–1990]. Fir and Sequoia Burn headings represent plots *to be burned.* Units are millimoles of charge per cubic meter.

Location	ANC	NO_3^-	Cl^-	SO_4^{2-}	$H_2PO_4^-$	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
	$\text{mmol}_c\ m^{-3}$										
						Fir Control					
TF	53.9	81.7	58.2	12.8	2.1	7.57	77.1	40.6	17.6	137.3	39.2
FFL	226.2	79.8	90.6	19.9	5.2	0.42	467.8	90.3	91.4	95.2	7.7
A	185.5	8.5	37.6	12.0	0.2	0.38	281.0	34.0	86.5	61.7	5.3
AC	157.3	0.4	14.7	13.1	0.0	0.28	210.9	27.4	102.4	43.5	16.3
						Fir Burn					
TF	169.2	45.3	37.4	10.6	7.3	3.89	68.7	29.6	11.3	137.9	20.6
FFL	204.7	183.4	50.0	23.6	0.5	0.43	490.5	91.7	62.7	115.4	5.5
A	160.8	40.6	55.1	17.9	0.4	0.37	234.6	42.5	110.3	77.4	10.9
AC	190.5	16.4	7.4	10.6	0.0	0.44	157.4	29.1	12.5	54.8	1.5
						Sequoia Control					
TF	46.7	117.2	40.3	21.9	3.2	5.52	105.8	51.1	19.6	87.5	44.1
FFL	362.9	37.6	40.0	20.6	1.7	0.44	488.4	69.3	68.0	72.2	28.2
A	395.1	11.3	28.1	17.3	0.3	0.36	394.8	54.4	75.3	66.8	2.3
AC	296.5	0.4	28.7	22.3	0.5	0.25	324.2	42.7	91.1	63.7	4.7
						Sequoia Burn					
TF	25.8	106.8	30.8	23.2	3.0	6.89	102.4	38.6	18.4	80.8	48.8
FFL	514.2	23.3	45.4	22.9	3.5	0.19	881.0	136.1	48.9	118.3	9.6
A	481.6	7.0	48.9	17.9	2.1	0.18	584.7	79.4	34.9	177.7	4.7
AC	166.3	5.0	19.6	13.0	0.0	0.30	208.9	35.8	32.8	35.2	0.8

Soil solution

Solution flux through the forest floor and soil results predominantly from snowmelt, either during winter thaws or in springtime. The temperature at the forest floor/snowpack interface is often above 1 °C. Summer and fall rainfall events rarely generate enough water to permit a wetting front to penetrate to mineral soil. Therefore, sub-surface solution data are largely confined to winter and spring months.

Forest floor leachate (FFL) exhibits the highest total solute concentration of the water chemistry profile components (Table 3). The charge deficit

Table 4. Annual mean wet deposition and throughfall fluxes (1987–1990)[1]. Units are kilograms per hectare per year, unless otherwise noted.

	Wet Deposition	Mixed-Fir Throughfall	Sequoia Throughfall
Constituent	....	kg ha^{-1} yr^{-1}	....
H^+	0.02	0.03	0.03
Ca^{2+}	2.42	6.85	10.11
Mg^{2+}	0.29	2.00	2.65
Na^+	0.77	1.57	2.12
K^+	2.62	25.28	15.98
NH_4^+-N	1.11	1.98	3.16
PO_4^{3-}-P	0.15	0.70	0.48
NO_3^-	0.94	4.18	7.62
SO_4^{2-}-S	0.66	0.88	1.76
Cl^-	2.22	7.98	6.12
Total N[2]	3.38	15.27	17.19
Total P[2]	0.35	1.52	0.92
H_2O (cm yr^{-1})[3]	74.96	67.21	69.46

[1] Solute fluxes calculated from National Atmospheric Deposition Program (NADP) water flux data for Lower Kaweah station and volume weighted mean concentrations in throughfall and precipitation.

[2] Total concentrations measured following Kjeldahl digestion.

[3] Data from NADP

(defined as sum of cation charge minus sum of anion charge) is greater in sequoia FFL than in fir FFL. This may be a result of higher concentrations of dissociated strong organic acids in the former. Organic acid concentrations may also contribute to the high ANC measured for FFL through the protonation of weak organic acids during titration, whereas stronger organic acids which remain unprotonated to very low pH (ca. pH 2) contribute to the charge deficit (Cantrell et al. 1990). The buffering capacity of the organic layer is illustrated by the 10 fold decrease in H^+ concentration as water passes through the forest floor. This horizon provides the primary sink for catchment proton inputs. Dissolved organic carbon (DOC) concentrations were not routinely measured, but the dark color observed consistently for FFL samples suggests that organic acids are an important constituent of these solutions.

Concentrations of DOC and organic strong acid charge densities may be estimated roughly from the organic N data (total kjeldahl-N minus total inorganic N) and the charge deficit. Assuming that organic N derives from soluble fulvic acids with a mean molar C to N ratio of 24 (Schnitzer & Khan

1978; Schnitzer 1985) gives preburn DOC concentrations in the range 1.3–2.0 mol m^{-3} for fir FFL and 2.7–6.2 mol m^{-3} for Sequoia FFL. Concentrations of DOC diminish with depth in the mineral soil. The charge deficit is comprised of the fraction of anionic organic functional groups not protonated during the ANC titrations. Based on our estimate of DOC and the deficit of measured solute charge, we compute charge densities of 0.1–0.3 moles of charge per mole of DOC for both fir and sequoia sites. This estimate is in agreement with measured values of carboxyl functional group concentrations for fulvic acids from cool temperate soils (Schnitzer & Khan 1978; Stevenson 1985).

Total cation and total anion concentrations decrease in the mineral soil solution (A and AC horizons) relative to FFL. Calcium and ANC dominate the charge balance in both fir and sequoia sites and the composition of these solutions approach the average chemical composition observed for stream water (Table 2). The decrease in solution Ca^{2+} and Mg^{2+} in the mineral soil underlines the significance of intrasystem cycling for these nutrients.

Effects of fire

Nearly the entire fine litter layer and a smaller portion of the large woody debris was consumed and a layer of white ash (0.05–0.3 m depth) was created by prescribed burns in the fall of 1990. This ash layer was deepest in the sequoia sites, owing to the greater litter mass under pre-burn conditions (Stohlgren 1988a). The first precipitation event to follow the fire (January, 1991) was in the form of mixed snow and rain (4 cm). Light snow in February was followed by heavy snow and rain in March. Soil solution was available for sampling from January through June, 1991. For the fir plots, the thinner ash layer vanished prior to the end of snowmelt whereas in the sequoia plots, the ash layer remained. For all burned sites, the ash layer was gone by the end of 1991.

Post-fire solution data for the control sites were similar to pre-burn results; differences may be attributed to interannual variation. However, leaching of the ash layer (represented by FFL for the burned sites in Tables 5–9) dramatically increased solute concentrations (Table 5).

Major cations

Increases in Ca^{2+}, Mg^{2+}, and K^{+} for both vegetation types were proportional to corresponding pre-burn (Table 3) and control (Table 5) solution concentrations (i.e. the relative predominance of these species was not changed). The ranking of cation concentrations in solution is the same as that in forest floor organic material (Stohlgren 1988b) and on cation exchange sites (Table 1). St. John & Rundel (1976) found that prescribed burning increased extractable

Table 5. First year post burn mean ion concentrations in throughfall (TF – volume weighted), forest floor leachate (FFL) and soil solution (A and AC horizons) [1990–1991]. (Forest floor consists of ash layer in burned sites.) Units are millimoles of charge per cubic meter.

Location	ANC	NO_3^-	Cl^-	SO_4^{2-}	$H_2PO_4^-$	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
	$mmol_c\ m^{-3}$										
	Fir Control										
TF	32.3	127.5	25.7	13.5	0.0	5.42	68.5	27.9	9.1	118.6	33.1
FFL	133.3	365.0	23.2	33.9	0.0	0.37	817.2	124.0	78.5	170.9	54.4
A	191.4	8.0	10.0	15.8	0.0	0.34	253.4	31.3	28.9	41.7	5.5
AC	323.0	0.0	11.6	78.1	0.0	0.25	266.5	40.3	24.8	65.4	0.0
	Fir Burn										
TF	318.9	93.4	38.5	97.8	0.0	0.67	401.3	158.5	10.3	405.9	36.3
FFL	358.0	1.6	21.7	186.1	0.0	0.19	814.9	100.4	22.2	76.7	46.0
A	320.1	296.1	284.1	1026.0	0.0	0.42	996.3	401.1	105.2	155.0	127.3
AC	637.5	27.2	97.2	677.8	0.0	0.20	530.4	240.7	182.7	117.1	132.8
	Sequoia Control										
TF	23.5	120.8	17.7	13.4	0.0	6.63	69.8	26.6	9.7	58.4	46.0
FFL	326.6	202.8	80.3	77.2	0.0	0.37	629.2	120.2	64.4	123.9	14.8
A	372.9	119.7	64.8	46.6	0.0	0.45	481.9	63.7	75.1	60.0	10.5
AC	210.0	15.6	77.4	44.3	0.0	0.54	305.1	35.0	32.3	50.9	0.0
	Sequoia Burn										
TF	65.3	156.4	14.3	23.7	0.0	3.90	115.7	30.6	14.0	53.3	47.0
FFL	2901.0	137.6	295.6	3611.6	0.0	0.05	5399.4	2161.0	64.7	527.2	133.0
A	3192.2	95.3	180.5	2439.7	0.0	0.04	4853.8	1305.3	52.9	383.3	103.9
AC	3199.4	93.6	140.6	1572.3	0.0	0.04	3736.4	851.2	41.2	246.1	67.6

Ca^{2+}, Mg^{2+}, and K+ for soil samples taken from Sierran mixed-conifer forests. Tomkins et al. (1991) found that extractable forest soil cation concentrations increased with fuel load and degree of combustion. The higher quantities of total cations released in burned sequoia sites is a result of both higher mass and higher nutrient concentrations of the sequoia litter.

Soil solution data (A horizon) for the burned fir and sequoia sites are plotted by sampling date in Figs. 4–5. The data are plotted on a log scale to accommodate the great range in concentrations associated with the post-burn recovery period. The dashed line in each figure denotes pre-burn mean

Table 6. Second year post burn mean ion concentrations in throughfall (TF – volume weighted), forest floor leachate (FFL) and soil solution (A and AC horizons) [1991–1992]. Ash from combusted forest floor is no longer present in burn sites. (n.a. = not available).

Location	ANC	NO_3^-	Cl^-	SO_4^{2-}	$H_2PO_4^-$	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
	....					mmol$_c$ m^{-3}	....				
						Fir Control					
TF	12.1	236.0	77.6	6.4	0.0	13.43	100.6	56.9	22.0	158.0	125.1
FFL	153.3	1.0	6.1	6.0	0.0	0.38	155.8	32.8	22.4	40.2	0.0
A	152.0	2.6	10.2	6.5	0.0	0.31	170.0	34.9	32.0	43.2	0.0
AC	114.0	2.0	6.6	8.3	0.0	0.32	160.5	28.2	54.8	91.8	0.0
						Fir Burn					
TF	37.5	126.5	44.1	9.7	0.0	5.69	106.3	50.4	18.5	192.7	31.3
FFL	—	—	—	—	—	—	—	—	—	—	—
A	320.7	148.8	33.7	109.1	0.0	0.28	493.2	161.2	50.0	131.5	41.1
AC	392.0	62.9	18.6	76.6	0.0	0.21	366.9	152.2	33.9	139.6	73.2
						Sequoia Control					
TF	12.6	179.5	39.8	17.1	0.0	9.15	121.6	53.1	20.6	103.0	52.0
FFL	300.8	2.9	18.1	9.5	0.0	0.34	544.6	124.3	34.6	105.3	0.0
A	173.9	5.2	18.6	10.2	0.9	0.54	320.9	109.2	54.5	75.4	0.0
AC	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
						Sequoia Burn					
TF	2.8	210.0	33.2	26.4	0.0	11.44	139.4	47.6	22.0	59.5	48.6
FFL	—	—	—	—	—	—	—	—	—	—	—
A	2030.9	131.8	30.1	120.9	0.0	0.05	2416.7	424.3	37.4	186.5	5.5
AC	2078.6	79.6	27.2	86.9	0.0	0.05	2077.3	292.8	30.4	140.2	10.2

concentrations for each species. The decrease in cation concentrations with time following fire (Figs. 4–5; Tables 5–8) is indicative of downward leaching and/or biotic uptake of nutrients. Nonetheless, after three years following fire, bivalent cation (Ca^{2+} and Mg^{2+}) concentrations remained higher in soil solutions of the burned sites than either control or pre-burn conditions, whereas monovalent ion concentrations (K^+, NH_4^+ and Na^+) were at or below pre-burn levels (Figs. 4–5). Differences in the depletion rates of monovalent and bivalent ions have been observed previously and may be attributed to

Table 7. Third year post burn mean ion concentrations in snowmelt (SNOW), forest floor leachate (FFL) and soil solution (A and AC horizons) [1992–1993]. (AC horizon samples were not available in sequoia sites.)

Location	ANC	NO_3^-	Cl^-	SO_4^{2-}	$H_2PO_4^-$	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
	....	....	....	....	....	$mmol_c\ m^{-3}$	....	....	....	....	....
						Fir Control					
SNOW	0.0	0.0	9.4	2.4	0.0	1.6	36.0	15.6	9.3	26.5	0.8
FFL	157.5	1.0	12.8	12.7	0.0	0.5	127.7	26.7	13.0	56.6	0.0
A	0.2	6.2	9.7	7.8	0.4	0.3	156.2	26.6	12.5	61.5	0.0
AC	76.6	0.0	8.7	8.8	0.0	0.5	140.8	22.4	11.4	52.9	0.0
						Fir Burn					
SNOW	71.0	7.7	9.0	7.2	5.9	1.4	46.7	24.7	6.3	58.1	0.0
FFL	—	—	—	—	—	—	—	—	—	—	—
A	992.7	225.4	19.4	38.8	0.0	0.2	753.3	191.3	27.8	176.7	0.0
AC	693.2	2.2	13.4	27.8	0.0	0.1	904.8	185.5	11.1	157.0	0.0
						Sequoia Control					
SNOW	0.1	0.0	11.0	8.3	0.0	1.4	44.0	20.2	7.0	50.5	7.9
FFL	378.8	0.0	22.3	37.3	0.0	0.4	473.9	93.0	58.7	84.1	0.0
A	56.7	4.0	15.3	17.9	0.0	0.6	168.0	36.3	57.8	29.8	0.0
						Sequoia Burn					
SNOW	0.0	9.0	18.5	21.1	0.0	2.6	59.7	27.7	11.4	48.3	0.0
FFL	—	—	—	—	—	—	—	—	—	—	—
A	938.5	15.0	18.7	26.0	0.0	0.1	1252.7	274.7	18.7	102.9	0.0

the higher selectivity of ion exchange sites for bivalent ions (Tomkins et al. 1991; Sposito 1989).

Ammonium and nitrate

A sharp increase in soil solution NH_4^+ was followed by its rapid decline to below pre-burn levels within a year following fire (Figs. 4–5). A similar short-term response of NH_4^+ to fire has been reported previously (St. John & Rundel 1976; Tomkins et al. 1991). Higher relative increases in NH_4^+ were observed for fir forests than for sequoia forests although both vegetation types showed an increase (Figs. 4–5). The observed behavior of NH_4^+ may be a result of thermal decomposition of organic matter or microbial activity.

Table 8. Pre-burn and post-burn mean total nitrogen and total phosphorus concentrations in precipitation (PPT – volume weighted), throughfall (TF – volume weighted), forest floor leachate (FFL), and soil solution (A and AC horizons). Ash from combusted forest floor is no longer present by post-burn year 2. (n.a. = data not available). Units are millimoles per cubic meter.

	Pre-burn		Post-burn Year 1		Post-burn Year 2	
	N	P	N	P	N	P
	mmol m^{-3}					
PPT	43.4	4.2	21.3	4.5	17.8	n.a.
			Fir Control			
TF	375.3	9.7	134.3	9.4	388.1	n.a.
FFL	166.3	7.1	37.7	1.9	58.3	n.a.
A	96.7	3.6	39.1	3.9	51.9	n.a.
AC	41.9	2.9	20.6	1.6	59.7	n.a.
			Fir Burn			
TF	159.9	14.5	105.9	8.4	211.8	n.a.
FFL	71.1	4.8	236.0	4.8	—	—
A	103.8	4.2	157.8	6.8	130.8	n.a.
AC	105.2	8.7	201.1	8.7	81.0	n.a.
			Sequoia Control			
TF	280.0	7.4	123.7	8.7	202.6	n.a.
FFL	179.1	5.8	107.3	6.8	102.3	n.a.
A	117.3	8.1	49.0	4.2	78.9	n.a.
AC	46.9	1.0	36.2	1.6	n.a.	n.a.
			Sequoia Burn			
TF	223.9	4.8	57.1	7.7	235.3	n.a.
FFL	293.5	29.4	302.1	10.3	—	—
A	211.8	24.5	229.6	9.7	92.4	n.a.
AC	53.3	0.6	123.7	7.7	73.9	n.a.

St. John & Rundel (1976) observed an increase in soil NH_4^+ immediately following fire in mixed-conifer forest and an increase in NO_3^- during the following spring. Hobbs & Schimel (1984) observed that N mineralization rates were increased (and N fixation rates were decreased) for two years following fire because of the narrower C:N ratio of incompletely combusted

Table 9. Comparison of selected ion profiles among individual plots (see Fig. 1 for plot locations).
Ca^{2+} and NO_3^- profiles shown for pre-burn period [1987–1990], Ca^{2+} and SO_4^{2+} shown for post-burn year 1 [1990–1991].
Mean ion concentrations in TF – volume weighted, FFL and soil solution (A and AC horizons).
Superscript ‘a’ denotes burned plots. Standard deviations in parenthesis. n.a. = data not available. Units are $mmol_c\ m^{-3}$.

Location	Fir 1	Fir 2	Fir 3^a	Fir 4^a	Seq. 1	Seq. 2	Seq. 3^a	Seq. 4^a
				Ca^{2+} – Pre-Burn				
TF	122 (179)	115 (109)	549 (390)	117 (120)	130 (182)	172 (149)	196 (306)	159 (141)
FFL	491 (304)	424 (198)	224 (72)	261 (59)	380 (236)	656 (370)	705 (758)	1271 (647)
A	294 (225)	239 (63)	157 (59)	281 (129)	247 (260)	1183 (832)	407 (163)	978 (629)
AC	211 (64)	n.a.	266 (72)	n.a.	316 (169)	389 (271)	210 (137)	200 (146)
				NO_3^- – Pre-Burn				
TF	136 (124)	107 (153)	222 (329)	125 (211)	127 (267)	281 (380)	247 (463)	166 (230)
FFL	92 (121)	57 (101)	48 (44)	37 (64)	38 (57)	38 (121)	27 (29)	16 (27)
A	11 (14)	2.0 (4.7)	7.3 (5.0)	10.1 (9.3)	8 (22)	32 (59)	4.8 (5.8)	12 (33)
AC	0.3 (0.6)	n.a.	16 (12)	n.a.	0.4 (0.7)	0.2 (0.8)	3.7 (4.7)	14 (18)
				Ca^{2+} – Post-Burn				
TF	135 (93)	218 (140)	187 (154)	1980 (1437)	267 (311)	259 (197)	495 (422)	371 (307)
FFL	161 (203)	817 (643)	815 (668)	n.a.	324 (261)	676 (316)	6740 (3581)	3720 (2181)
A	159 (7.5)	300 (67)	1180 (983)	680 (353)	397 (133)	550 (771)	3071 (1718)	5560 (3519)
AC	154 (87)	323 (197)	530 (34)	n.a.	404 (118)	206 (7.4)	2940 (994)	3940 (2692)
				SO_4^{2-} – Post-Burn				
TF	13 (13.4)	65 (73)	45 (38)	628 (599)	54 (82)	49 (44)	126 (124)	51 (45)
FFL	21 (17)	47 (32)	186 (56)	n.a.	37 (48)	83 (173)	5350 (6814)	2086 (4430)
A	8.5 (2.1)	19 (29)	1350 (1806)	452 (820)	63 (84)	34 (59)	2000 (5822)	2610 (4448)
AC	11.2 (4.6)	111 (152)	678 (127)	n.a.	79 (76)	9.6 (2.4)	1138 (2986)	1940 (3288)

biomass and detritus, and the increased temperature of the burned surface. Schoch & Binkley (1986) reported increased N mineralization rates during the year following prescribed fire in loblolly pine forests. They attributed the result to enhanced decomposition of partially combusted forest floor material. Adams and Attiwill (1986) noted that fire caused a large short-term increase in the net rate of N-mineralization, but rapid immobilization followed with a return to pre-fire levels of mineralization rates within 6 months.

Soil nitrate concentrations increased in the second year for the sequoia site and remained slightly high into the beginning of the third post-burn year for both vegetation types (Figs. 4–5). The increase is reflected in Tharp's Creek stream water (Table 2). Catchment NO_3^--N outputs increased from less than 0.01 kg ha^{-1} yr^{-1} during the 1987–1990 pre-burn period, to more than 0.34 kg ha^{-1} yr^{-1} in the post-burn period (Williams et al. 1993). However, even at increased stream water loading, NO_3^- outputs were less than half of wet deposition inputs (Table 4), indicating net biotic retention. Gaseous N outputs during fire were probably higher than leaching losses (Grier 1975; Richter et al. 1982; Schoch & Binkley 1986; Lobert et al. 1991) but the former were not measured in the present study.

Christensen & Muller (1975) noted low concentrations of NO_3^- before and immediately following fire in chaparral. However, with the onset of the first post fire rains, nitrate concentration rose significantly and remained higher than unburned locations for eight months. Dunn et al. (1979) also reported increased NO_3^- concentration in chaparral soils following post fire precipitation. Increased net nitrification rates are a likely result of increased NH_4^+, increased soil pH, and perhaps decreased microbial immobilization of NO_3^-. Even in the absence of increased nitrification rates, the disturbance of the major pre-burn NO_3^- sinks in the sequoia and fir stands (forest floor and surface soils) would have contributed to increased nitrate leaching. Davidson et al. (1992) showed that gross nitrification rates can be quite high in mature Sierran mixed-conifer forests even when NO_3^- pool sizes are small and net nitrification rates are low. The rapid turnover of NO_3^- is a result of microbial assimilation, which may decline after burning of the forest floor.

Total nitrogen and total phosphorus data are presented in Table 8. Mean FFL and soil solution total-N concentrations following burning exhibited very small increases although TF concentrations decreased. Mean values of soil solution total-N *decreased* for the control sites over same period. All increases in total-N are accounted for by the increase in inorganic-N. Total-P also increased slightly following burning.

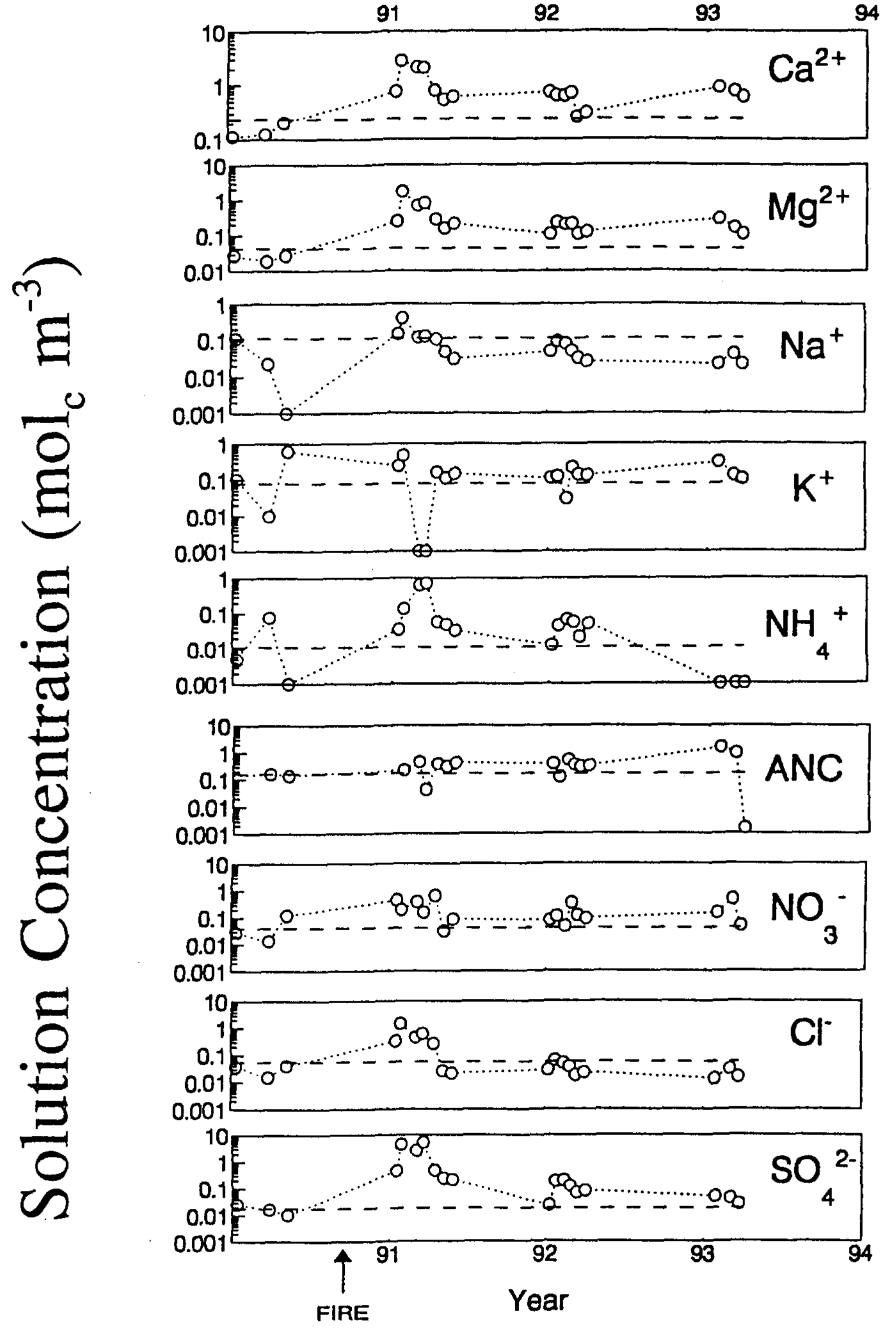

Fig. 4. Post-fire time-series of A horizon solution ion concentrations – fir burn. Means are presented by sampling date. Concentration values are presented in moles of charge per cubic meter (log scale). Dashed line in each graph represents pre-burn mean value for reference. Date of burn is indicated.

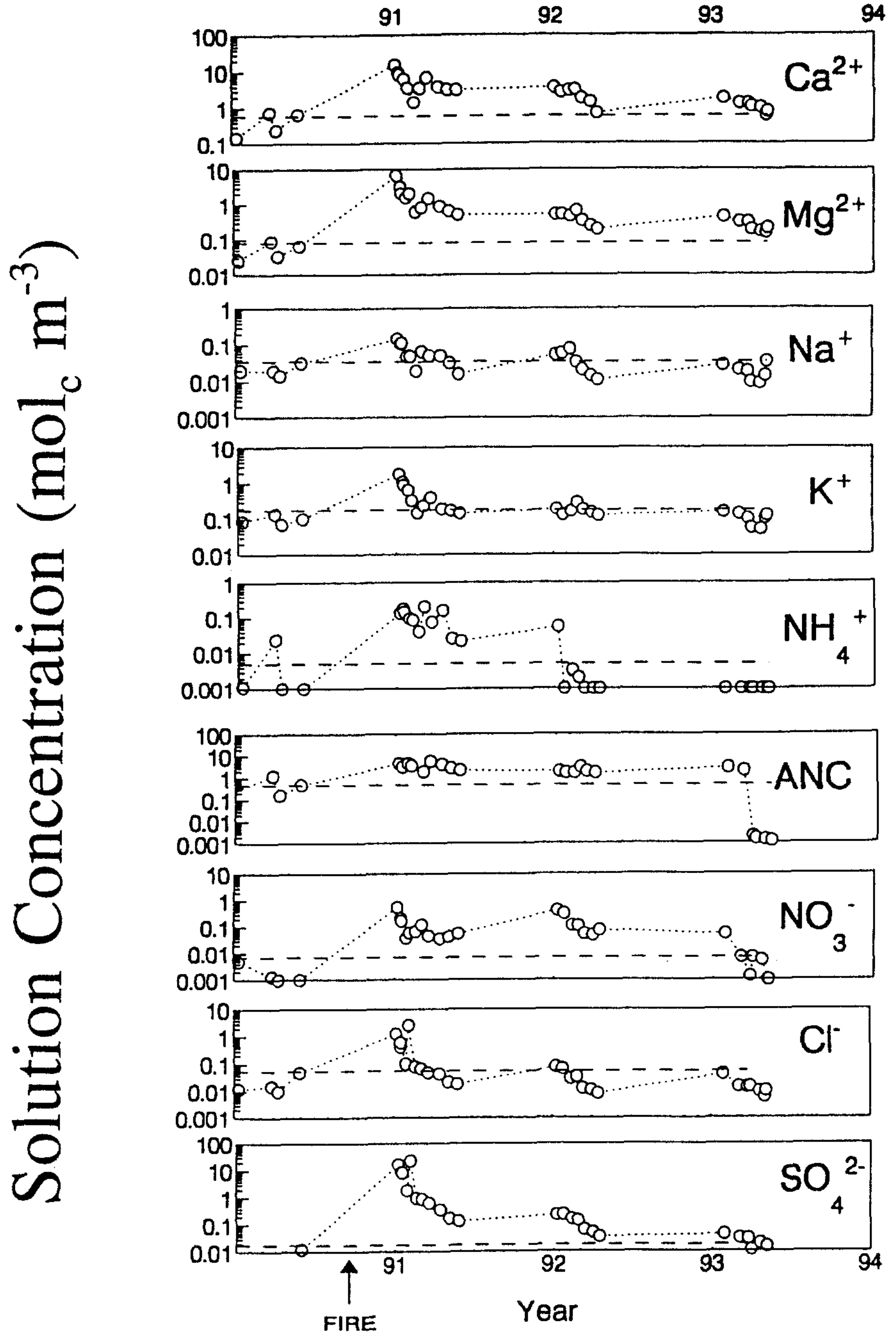

Fig. 5. Post-fire time-series of A horizon solution ion concentrations – sequoia burn. Means are presented by sampling date. Concentration values are presented in moles of charge per cubic meter (log scale). Dashed line in each graph represents pre-burn mean value for reference. Date of burn is indicated.

Sulfate and chloride

The relative predominance of anions was shifted as a result of fire. The most apparent effect was a dramatic increase in SO_4^{2-} (Table 5; Figs. 4–5). Sulfate concentrations were low in both pre-burn and control soil solutions, but increased more than 100 times, in both vegetation types, following fire. This SO_4^{2-} 'pulse' caused the large efflux of cations during the spring period immediately following the burn (Figs. 4–5) and was reflected in an increase in stream water concentrations and catchment outputs (Table 2).

Stohlgren et al. (1991) reported a net retention of SO_4^{2-} within the catchments studied here. Sulfate may be chemically immobilized by adsorption onto sesquioxides in the soil matrix (Chao et al. 1962; Parfitt 1978), but hydrous oxides were not observed in these Inceptisols (Huntington & Akeson 1987). Alternatively, SO_4^{2-} may be incorporated into organic matter by microbially mediated processes of organic S formation (Fitzgerald et al. 1982; 1988). The organic fraction is the largest S pool in most forest soils (Mitchell et al. 1991) except for those especially rich in iron and aluminum oxides and low in organic matter (Rochelle et al. 1987; Harrison et al. 1989). In the Tharp's Creek and Log Creek catchments, the organic pool comprises 95% of the total sulfur in A horizon soils (Stanko & Fitzgerald 1990). Plant and microbial demand for S regulates SO_4^{2-} mobility in sites with low S deposition rates and background SO_4^{2-} concentrations less than 40–60 $\text{mmol}_c\ m^{-3}$ (Mitchell et al. 1991; Johnson & Lindberg 1992) and the pre-burn solution concentrations encountered in the present study fall well below this range (Tables 2–3). However, a reduction in organic matter results in a reduction in the potential for organic S formation (Stanko & Fitzgerald 1990). The pulse of SO_4^{2-} through soil solution and stream water indicates that oxidation of the organic S pool, and the associated decrease in organic S formation potential, can significantly affect element transfer following fire.

The catchment budgets produced by Stohlgren et al. (1991) also indicated that Cl^- retention occurs within the catchment, but the location of the sink was unclear. It is interesting to note that Cl^- concentrations were greatly increased as a result of fire and that the time series results for this solute are very similar to those for SO_4^{2-} (Figs. 4–5). Furthermore, fluxes of Cl^- in throughfall are three to four times that of wet deposition (Table 4). These data suggest that Cl^- is retained by interaction with organic matter within the forest ecosystem, although the mechanism is unknown. Similar patterns were observed by Binkley et al. (1982) for coastal forests in British Columbia. Ulrich & Mayer (1971) reported that Cl^- was subject to intrasystem cycling within a beech forest in Germany. Our pre-burn data are consistent with the biotic uptake of Cl^- from the forest floor and A horizon, and leaching from the canopies. This pattern is supported by the post-burn Cl^- release data which shows a large increase in Cl^- leaching from the mineralized organic matter immediately following burning, followed by a gradual decline.

Bayley & Schindler (1991) observed large (ca. 300%) increases in stream water SO_4^{2-} and Cl^- concentrations following wildfire in a coniferous forest watershed in Ontario. Very few other studies have shown large increases in SO_4^{2-} and Cl^- following fire, but in most cases, data on these anions were not reported. Likens et al. (1970) reported elevated streamwater Cl^- after forest clearing. Vitousek and Reiners (1975) observed that Cl^- concentrations in streams draining aggrading ecosystems were significantly lower than those measured in drainage waters of old-growth forests. Since various forms of ecosystem development and disturbance can affect net retention or loss of Cl^-, treatment of this anion as a conservative solute in forest ecosystems is probably not justified.

Variability among individual plots

The data presented above suggest that the fir and sequoia sites differ in their Ca^{2+}, NO_3^- and SO_4^{2-} profiles. However, this assertion must be evaluated in light of the variability among the individual plots. Table 9 presents plot scale data on these ions before and after fire. The subscript ‘a’ by a column heading denotes an experimental (burn) plot. The high standard deviations reflect significant spatial and temporal variability in solution chemistry for replicate samplers within the same plot. Comparison of pre-burn mean values across a given row indicates that differences among plots within a forest type can be as large as differences between forest types. Overstory species explains some, but clearly not all, of the differences among plots. Variables such as slope position, soil depth and soil texture may be more important for undisturbed stands. However, the effects of fire distinguish the two forest types. Higher quantities of Ca^{2+} and SO_4^{2-} were leached through the soil profile in the burned sequoia plots because of the higher litter mass combusted.

Conclusions

Solution chemistry at the sub-catchment scale was studied by sampling multiple plots with internal replication. Wet deposition to southern Sierran mixed conifer forests is dominated by Ca^{2+}, NO_3^-, and Cl^-. Interaction of precipitation with the forest canopy increased mean concentrations of all measured solution constituents, with K+ exhibiting the greatest relative increase in throughfall. Mean concentrations of Ca^{2+}, Mg^{2+} and ANC were increased with passage of water through the forest floor, which also provides the primary sink for atmospherically derived H^+. Lower concentrations of solution Ca^{2+} and Mg^{2+} were observed in the mineral soil and stream water, indicating the importance of intrasystem cycling for these cationic nutrients. The increase in ANC in throughfall and forest floor leachate may be attributed to the increase in weak organic acids as water passes through the organic portion of the forest stand. Calcium and ANC dominate the charge balance of soil solution and stream water with smaller contributions from Mg^{2+}, Na^+, K^+, NO_3^-, and Cl^-. Very low solution SO_4^{2-} concentrations were observed in the undisturbed forest stands. Variations in pre-burn solute concentrations within and between plots of a given vegetation type/treatment were comparable to those observed among different forest stand types indicating the high degree of temporal and spatial heterogeneity within the watershed.

The application of prescribed fire to both vegetation types produced large and reproducible increases in soil solution ion concentrations. The chemical response to burning was greater for the sequoia site than for the fir site as a result of increased litter mass in the former. Both forests showed large increases in SO_4^{2-} and smaller increases in Cl^- concentrations following fire which indicate that S and Cl retention within these catchments is mediated by biotic uptake and subsequent retention in living and dead organic matter. The sulfate 'pulse' facilitated a large efflux of base cations in soil solution and streamwater. Mean Ca^{2+}, Mg^{2+} and K^+ concentrations in post-burn solutions increased in proportion to their pre-burn and control levels. Soil solution NH_4^+ concentrations were increased for the first year following fire, but rapidly decreased to pre-burn levels within the snowmelt season. However, increased NO_3^- concentrations in soil solution were maintained throughout the post-burn study period and stream water NO_3^- outputs remained higher than pre-burn and control levels through three years of post-burn monitoring.

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