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Effects of prescribed burning and drought on the solute chemistry of mixed-conifer forest streams of the Sierra Nevada, California

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Abstract. Solute concentrations in atmospheric deposition and stream water were measured in two mixed-conifer catchments (Tharp's and Log creeks) in the Sierra Nevada of California from 1984 through 1995, a period including a 6-year drought and a prescribed burn in one catchment. The effects of prescribed burning in the Tharp's Creek catchment significantly increased the concentrations of most solutes in stream water. In the first year after prescribed burning, the VWM (volume-weighted mean) concentrations of acid anions in stream water increased proportionally more than those of the base cations, and ANC (acid neutralizing capacity) more than doubled. Sulfate and NO_3^- increased proportionally more in stream water than any other ions after the fire, but pre- and post-burn VWM *p*H were not significantly different. VWM SO_4^{2-} and NO_3^- concentrations the first year after burning occurred were about 16- and 2,000-fold above pre-burn baselines, respectively, while that of Cl^- increased 4-fold. Net retention (precipitation inputs minus streamwater outputs) of H^+, NO_3^-, NH_4^+, SO_4^{2-} and Cl^- occurred in both catchments, except after prescribed burning of the Tharp's Creek catchment in the fall of 1990, which caused a net export of SO_4^{2-}, Cl^- and K^+ the first year after the burn. Most solutes remained above pre-disturbance concentrations by the end of the third year after burning, whereas H^+ and SiO_2 remained below. Periodic increases in the concentrations of Na^+, Ca^{2+} and SO_4^{2-}, and decreases in ANC and SiO_2 occurred during a 6-year drought monitored in the adjacent undisturbed catchment of Log Creek.

Introduction

Elemental exchange processes among atmospheric, terrestrial and aquatic compartments of watersheds are complex. Precipitation, anthropogenic pollution, soil composition, plant community structure and disturbances can affect or regulate the biogeochemical processes and chemical dynamics of watersheds. Disturbances can alter the timing, magnitude, and form of elemental fluxes to receiving waters (Likens et al. 1970; Vitousek et al. 1979; Correll et al. 1984; Meyer et al. 1988), and those which influence nutrient dynamics commonly regulate primary production, decomposition and stream community structure (Elwood et al. 1981; Peterson et al. 1985). One approach to determining the resiliency of an ecosystem to disturbances is by the systematic monitoring of atmospheric inputs and solute yields (Swank 1988; Likens & Bormann 1995).

Wildfires are a natural disturbance that occurs in the mixed-conifer forests in the Sierra Nevada, California. Prescribed burning simulates wildfires on a localized scale, and has been used over the last 20 years in Sequoia National Park to re-establish the dynamic equilibrium of mixed-conifer ecosystems that existed before fire-suppression measures were implemented early this century. The effects of fire may include erosion, solute leaching, alkalinity reduction or generation, and the nitrification of soils (Schindler et al. 1980; Bayley & Schindler 1987; Bayley et al. 1992a; Chorover et al. 1994; Williams et al. 1997); significant leaching losses can alter the chemical balance of streams and lakes (Wright 1976; Tiedemann et al. 1978; Schindler et al. 1980; Feller & Kimmins 1984; Minshall et al. 1989; Bayley & Schindler 1991; Spencer & Hauer 1991). Hence, although prescribed burning is generally used as a means of reducing fuel mass and fire severity, it can be used also to mitigate the effects of fire on the quality of receiving waters (Richter et al. 1982).

How undisturbed, mixed-conifer catchments of the Sierra Nevada regulate streamwater chemistry has been previously investigated (Stohlgren et al. 1991; Williams & Melack 1997). Other research in mixed-conifer ecosystems of the Sierra Nevada has focused on fire history and the effects of burning on biodiversity (Kilgore & Taylor 1979; Swetnam 1993; Stephens 1995). Although changes in the chemistry of soils (St. John & Rundel 1976) and the solution chemistry of soil lysimeters following prescribed burning are known (Chorover et al. 1994), the effects of prescribed burning on streamwater chemistry in mixed-conifer catchments of the Sierra Nevada are not documented.

Studies in forested catchments show that disturbances such as wildfire, windstorm, and clearcutting and slash burning generally elevate solute losses (Tiedemann et al. 1978; Schindler et al. 1980; Feller & Kimmins 1984; Bayley & Schindler 1987; Bayley et al. 1992a; b). These disturbances result in larger solute losses than prescribed burning since the latter is restricted to smaller areas and can be temporally staggered (Richter et al. 1982). Moreover, there is no scaring of the soil surface that commonly occurs during clearcutting, which promotes leaching not associated with fire (Feller & Kimmins 1984). Problems with some studies concerning the effects of fire on streamwater chemistry are the lack of pre- and post-burn data of sufficient duration to interpret chemical changes associated with interannual variability (McColl & Grigal 1975; Wright 1976), multiple disturbances (Schindler et al. 1980; Bayley & Schindler 1987), and partial-catchment manipulations (Richter et al. 1982; Feller & Kimmins 1984). Hence, the documented effects of catchment-scale prescribed burning on the export of solutes in streams are scarce. The mixed-conifer catchments of Tharp's and Log creeks include abundant *Sequoiadendron giganteum* (giant sequoia) and are part of a vegetatively unique ecosystem. Proper forest management requires a knowledge of the magnitude and duration of solute losses from burned catchments and what effects these losses have on receiving waters.

The effects of drought on the streamwater chemistry in mixed-conifer catchments of the Sierra Nevada are undocumented also. Altered climatic conditions can affect biogeochemical processes in forested catchments, and concentrating effects or increased leaching time due to low flow associated with drought can cause an increase in the levels of solutes in stream water (Braekee 1981; Swank & Waide 1988; Bayley et al. 1992b). Drier climatic conditions may lower the water table and oxidize stored sulphides, which can result in the acidification of water in these areas (Bayley & Schindler 1987).

The objectives of this paper are to document the effects of prescribed burning and drought in forested catchments on streamwater composition and ion balances. We describe the effects of prescribed burning on the chemistry of a stream by comparing the runoff chemistry of the same catchment for 7 years prior to and 5 years after a fire. Streamwater concentrations of base cations, strong acid anions, H^+ and SiO_2 prior to the fire are compared with post-burn concentrations. We examine also the effects of a 6-year drought on streamwater composition of an adjacent forested catchment without fire. The drought is bracketed by "wet" periods of 3 years each.

Site Description

The catchments reported in this study are located near the Giant Forest area of Sequoia National Park, California (36°34′N, 118°44′W; Figure 1). Hydrological monitoring and chemical sampling have been carried out since 1983. Tharp's Creek is an intermittent stream that generally 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. 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). 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-suppression 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., N. Stephenson, National Biological Service). No fires had occurred in the Tharp's and Log creeks drainages for about 80 years prior to the prescribed fire that burned the entire Tharp's Creek catchment in the fall of 1990.

Prescribed burning of the Tharp's Creek catchment – Burning of the Tharp's Creek catchment killed most of the younger trees and understory vegetation, and the larger trees were scared, but left alive. Most forest litter was combusted in the fire leaving an ash layer throughout the catchment, which remained in the litter zone under the canopies of *Sequoiadendron giganteum* until the end of 1991 (Chorover et al. 1994). Except for a 40 mm event in January 1991, precipitation was low until the last day of February 1991 when a series of large snow and rain events occurred (291 mm over 7 consecutive days at Giant Forest). After the fire, sequoia, fir and pine seedlings were visible by the end of 1991, and fern species re-established rapidly in the riparian zones.

Methods

Wet deposition – The chemical composition of wet deposition was monitored at Giant Forest (1856 m), about 4 km west of the study site (Figure 1). Samples were collected weekly from two Aerochem Metrics Model 201 samplers. Weekly precipitation depth was measured using a Belfort recording rain gauge.

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 increased by 9% to compute water balances for the Tharp's and Log creek catchments and maintain consistency with previous studies in these catchments (Stohlgren et al. 1991; Williams & Melack 1997).

Stream discharge and sampling – Stream discharge was measured using 3″ and 12″ Parshall flumes for Tharp's and Log 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%).

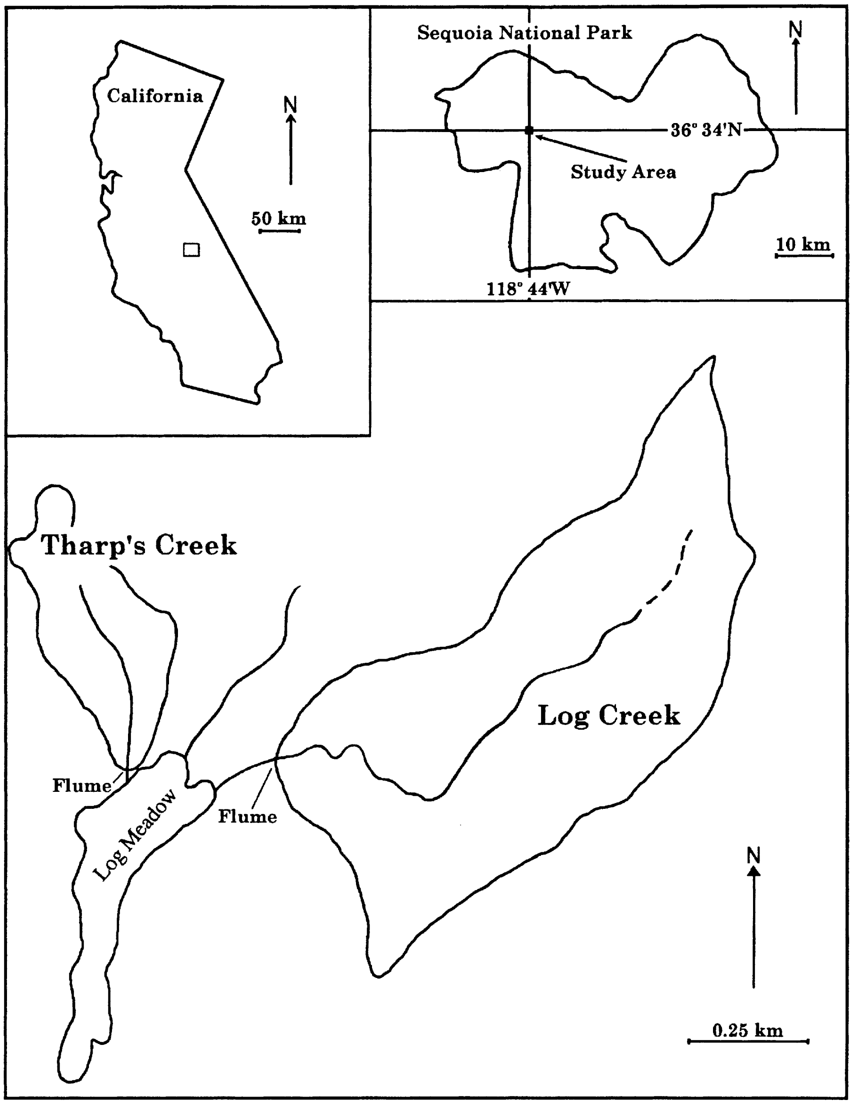

Figure 1. Map showing the locations of Sequoia National Park in the Sierra Nevada, California, and the Tharp's and Log creek catchments. The study site is located near the Giant Forest area (Stolhgren et al. 1991).

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

Chemical analyses – Unfiltered precipitation and streamwater samples were analyzed for *p*H, conductivity, and ANC (the latter was not measured in precipitation) within 6 hours of collection. An Altex model 3500 *p*H meter with Beckman glass body probe for dilute water was used from 1983 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.

Sample aliquots filtered with Gelman A/E glass fiber filters (nominal pore size of 1 μm) were stored at 4 °C prior to SiO_2, NH_4^+ and PO_4^{3-} analyses at Sequoia National Park (NPS). Filters were rinsed with at least 50 mL of deionized water prior to filtration with sample water. Filtered subsamples were analyzed colorimetrically for SiO_2 using a silicomolybdate method (Strickland & Parsons 1972), NH_4^+ by an indophenol blue method and PO_4^{3-} by a molybdate method (APHA 1981). Analyses of NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^- and SO_4^{2-} were done at Michigan Technological University (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 and Troendle (1987) and Stottlemyer (1987). Particulate N (PN) and C (PC) were determined using a modified Control Data Equipment Corp. CHN analyzer (model 2408), and particulate P (PP) was measured by high temperature combustion (Andersen 1976).

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

$$VWM = \frac{\sum_{i=1}^{n} CiVi}{\sum_{i=1}^{n} Vi} \tag{1}$$

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 Σ *V*. The same equation is used for calculating VWM concentrations in stream water, but in that case C_i = observed concentration of instantaneous stream flow *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 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 and control procedures are discussed in Williams and Melack (1997).

Results and Discussion

Precipitation and stream water – Annual precipitation amount for the Tharp's Creek area had 8 years below the long-term annual average of 1100 mm for the Giant Forest area during the study period (Williams & Melack 1997). Two years with above-average precipitation were 1986 (1345 mm) and 1993 (1404 mm), and these bracketed a 6-year drought period (6-year mean = 697 mm, SE = 44). The years with the highest (1995) and lowest (1987) precipitation measured had quantities that were 160 and 53% of the long-term average for Giant Forest. The frequency of rainfall in the wetter years was higher, and larger storms were more common compared to drier years, such as in the comparison of 1986 and 1987 (Figure 2). Storm frequency in a wetter (1995) and drier than average (1987) water year were 0.11 and 0.6 events per day, respectively.

Annual hydrographs for Tharp's and Log creeks had similar patterns, with peak discharge driven by spring snowmelt (Williams & Melack 1997). Tharp's Creek runoff ranged from 2 to 144% of that from Log Creek and had a mean of 52% (SE = 12%) for the study period. Precipitation minus stream runoff was relatively invariant the first 9 years of the study in Tharp's Creek (mean = 627 mm, SE = 33), but was proportionally larger in the large water years of 1993 (923 mm) and 1995 (881 mm). Runoff increased proportionally more in the Tharp's Creek catchment the first year after burning compared to the Log Creek catchment (Table 1), and the post-burn average ratio of annual runoff in Tharp's Creek to Log Creek was higher (mean = 0.74, SE = 0.20, n = 5) than the pre-burn average (mean = 0.37, SE = 0.11, n = 7). Runoff coefficients for both creeks were highest in the water years 1986 and 1993, and the highest daily discharge rates recorded in both streams occurred during snowmelt of 1986 with mean daily flows of 34 and 189 L s^{-1} for Tharp's and Log creeks, respectively.

Disturbances did not change the similarity in the seasonal variation of streamwater solute concentrations in either catchment. The major ions had their annual concentration maximum in the beginning snowmelt period of

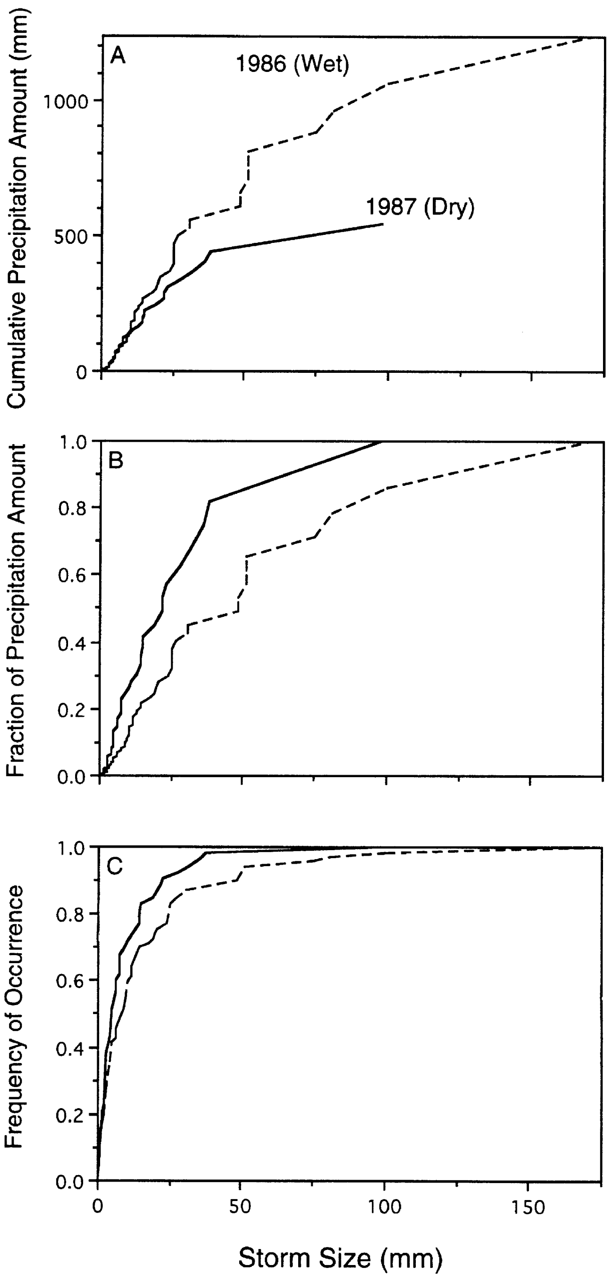

Figure 2. Frequency of occurrence for rain in the Giant Forest area for the water years of 1986 (wetter than average) and 1987 (drier than average). These two years represent the general patterns observed in wet versus dry water years in this study.

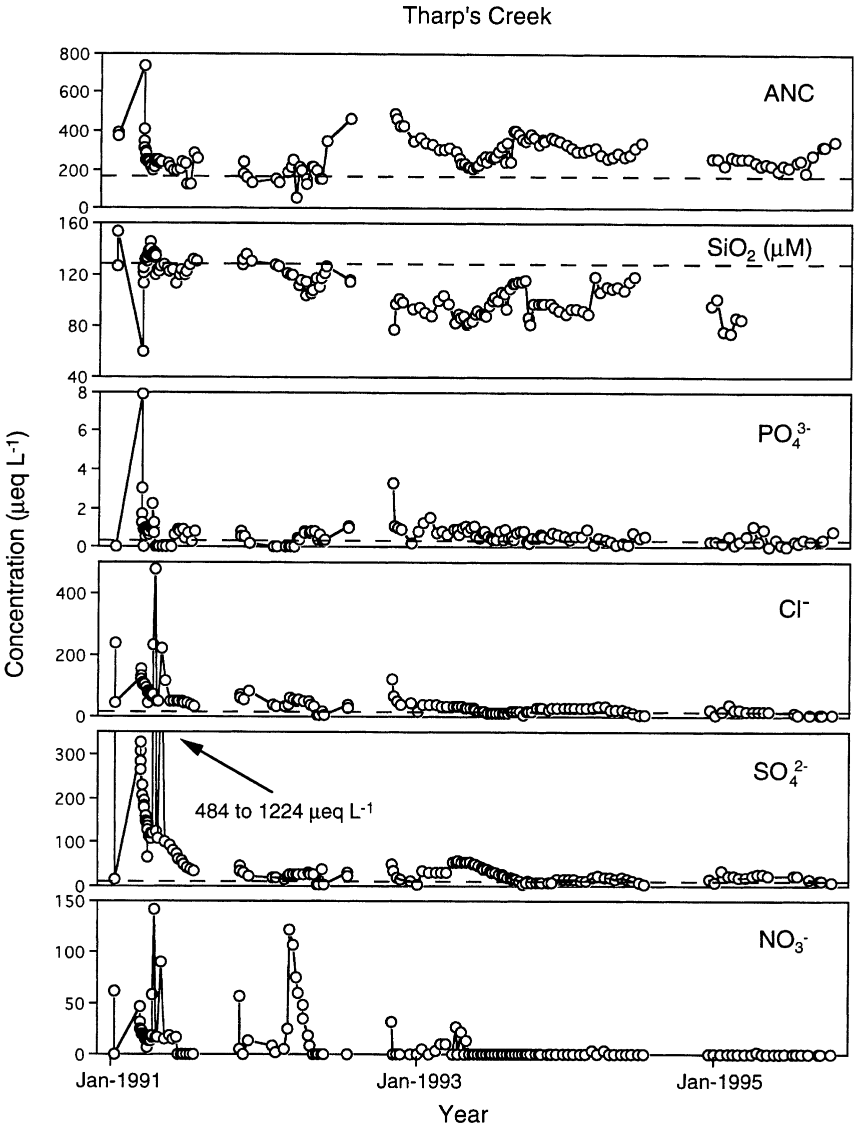

Figure 3a. Time series of selected solutes for Tharp's Creek after prescribed burning of the catchment in October 1990. Breaks in the record indicate periods with no baseflow. VWM baseline concentrations of stream water for the 7-year pre-fire monitoring period are indicated by dashed lines, except for solutes with concentrations at the limits of detection.

March-April (Figures 3a, b and 4a, b). The concentration maximum for most ions roughly preceded the annual discharge maximum in May or June. In contrast, SO_4^{2-} commonly had an annual concentration maximum coincid-

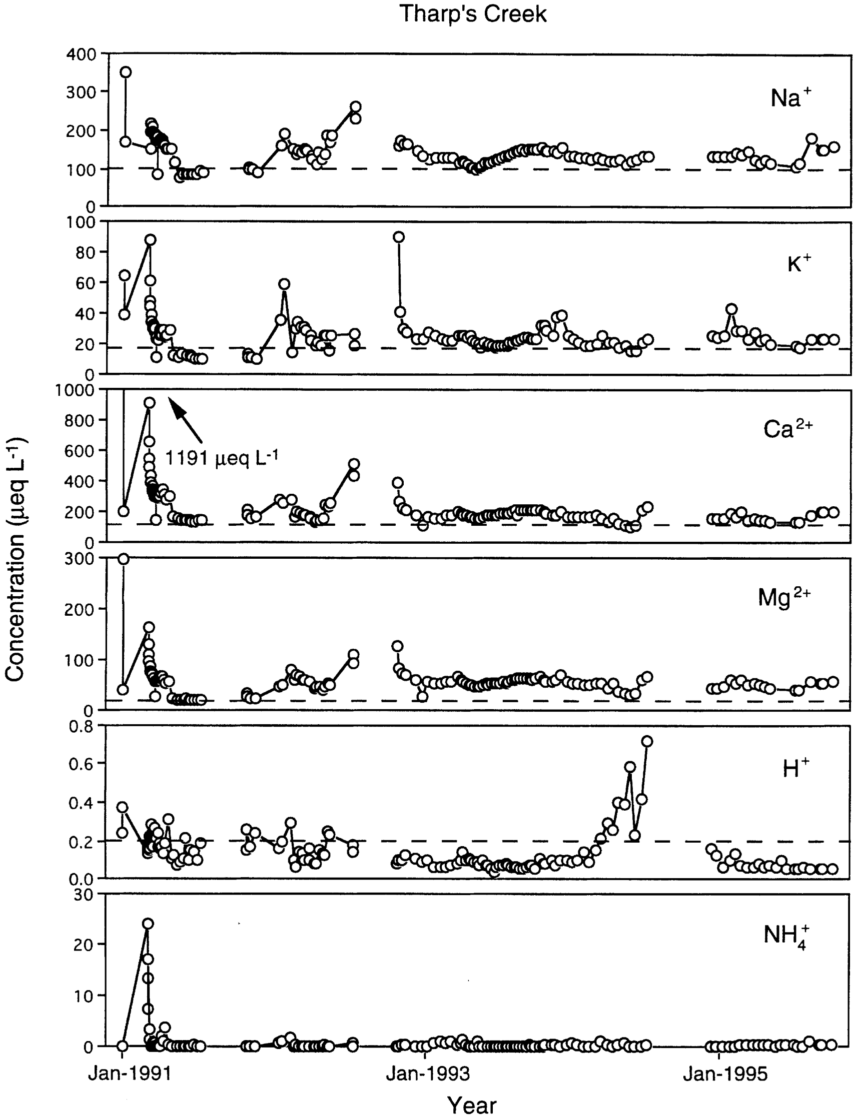

Figure 3b. Time series of selected solutes for Tharp's Creek after prescribed burning of the catchment in October 1990. Breaks in the record indicate periods with no baseflow. VWM baseline concentrations of stream water for the 7-year pre-fire monitoring period are indicated by dashed lines, except for solutes with concentrations at the limits of detection.

ing with maximum discharge, although there was no significant discharge-concentration relationship in Tharp's Creek streamwater in the 1991 water year due to large SO_4^{2-} fluxes prompted by the fire.

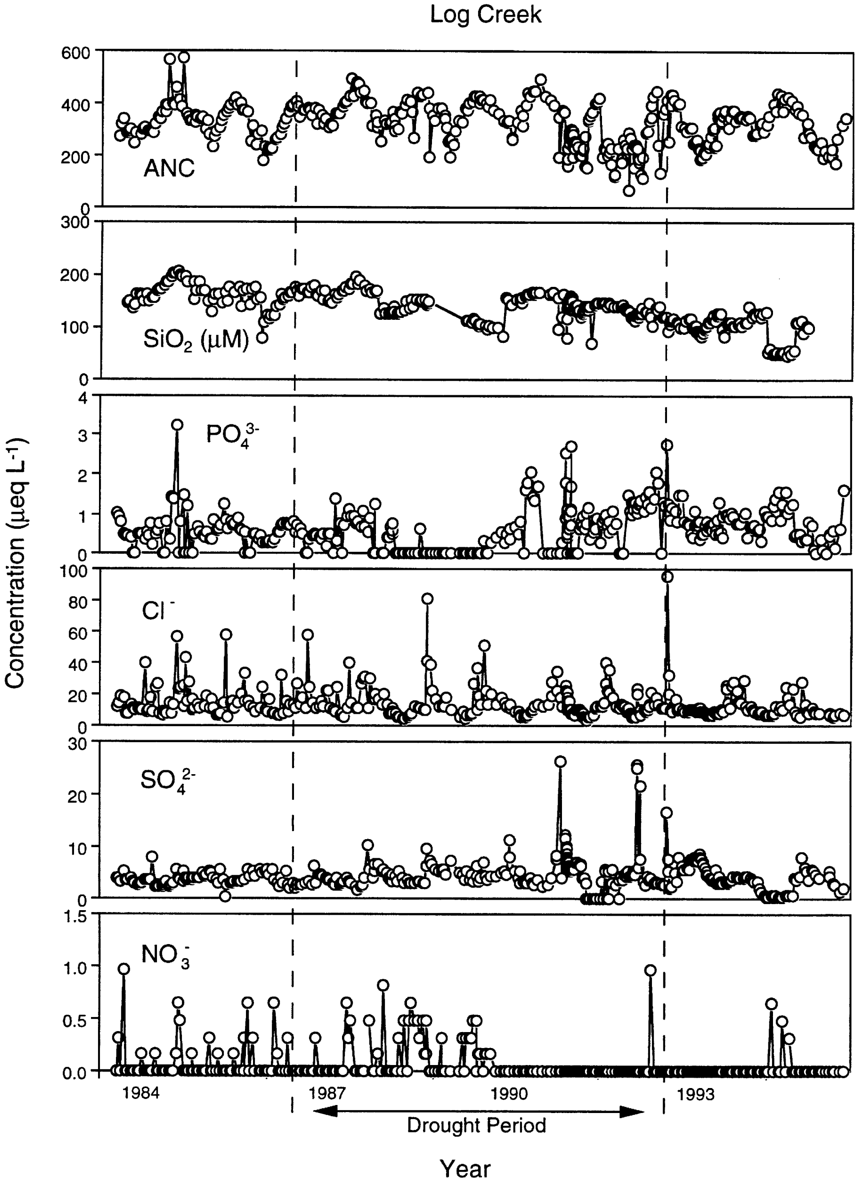

Figure 4a. Time series of selected solutes for Log Creek. The 6-year drought from 1987 to 1992 is bracketed by 3 pre- and post-drought water years.

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

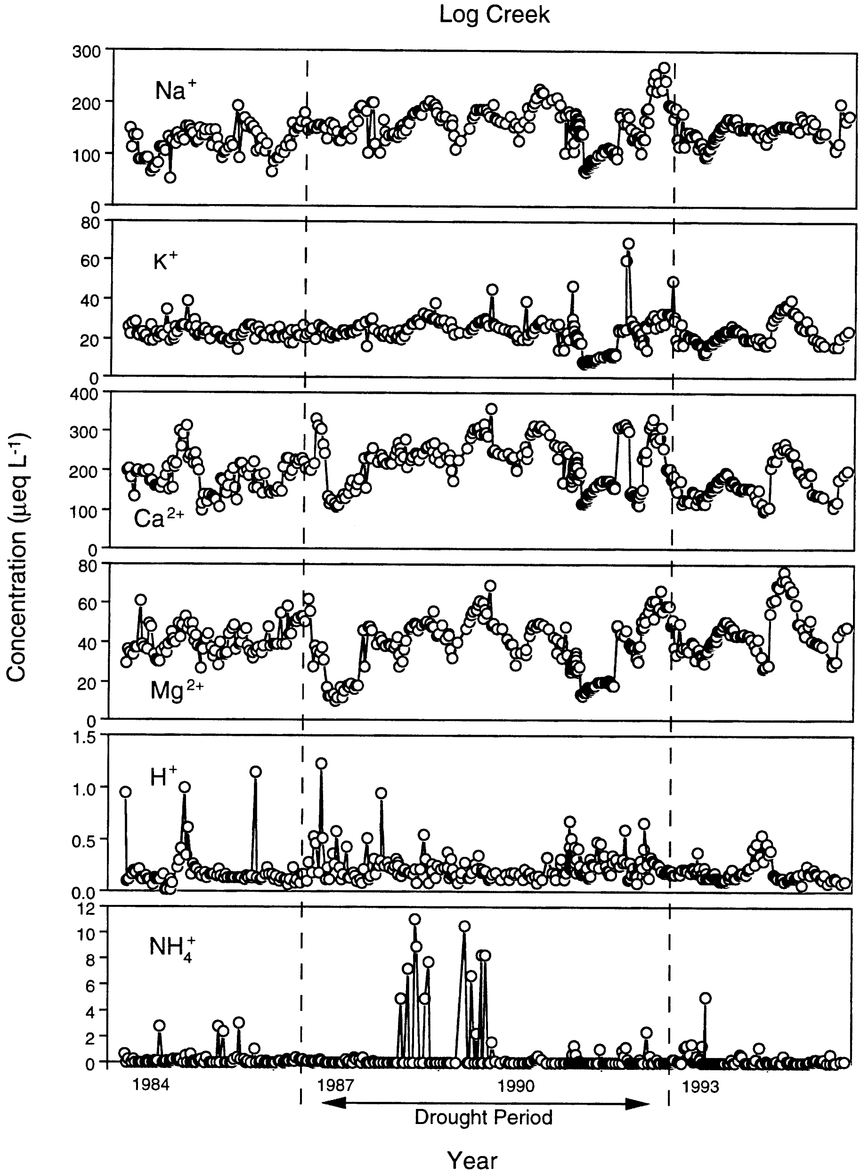

Figure 4b. Time series of selected solutes for Log Creek. The 6-year drought from 1987 to 1992 is bracketed by 3 pre- and post-drought water years.

Tharp’s Creek. VWM *p*H was not significantly different in pre- and post-burn Tharp’s Creek (6.7 and 6.9, respectively), although variability increased in the first two years after the burn (Figure 3b). The annual [VWM] of non-

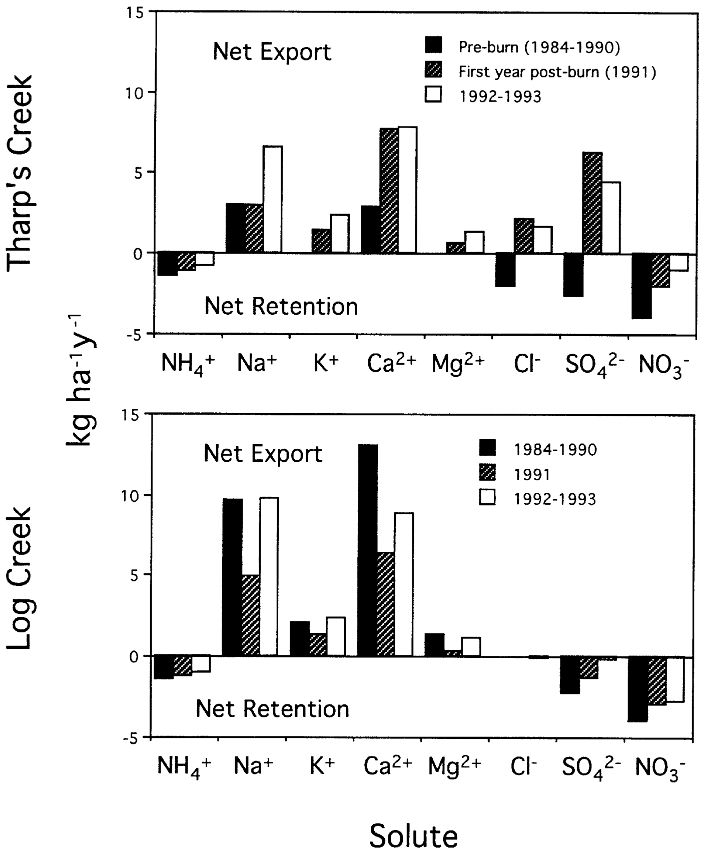

Figure 5. Net-retention and net-export characteristics of solutes in Tharp's and Log creeks for pre- and post-burn periods of the study. Values were calculated as wet-deposition inputs minus streamwater outputs in kg ha^{-1} yr^{-1}; positive values indicate net retention and negative values indicate net export occurred.

conservative solutes showed no significant correlation with annual discharge, and pre-burn annual [VWM] of the base cations, ANC and SiO_2were higher in Log Creek than Tharp's Creek.

The magnitude of net retention and export changed after the fire in Tharp's Creek. However, mass balances comparing atmospheric inputs to fluvial outputs in Log Creek and pre-fire Tharp's Creek commonly showed net retention of acid anions, NH_4^+, PO_4^{3-} and H^+ (PO_4^{3-} and H^+ are not shown because net retention is 0.06 kg ha^{-1} yr^{-1} for both ions (Williams & Melack 1997)), and net export of ANC, SiO_2 and the base cations (Figure 5). 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 burning the Tharp's Creek catchment.

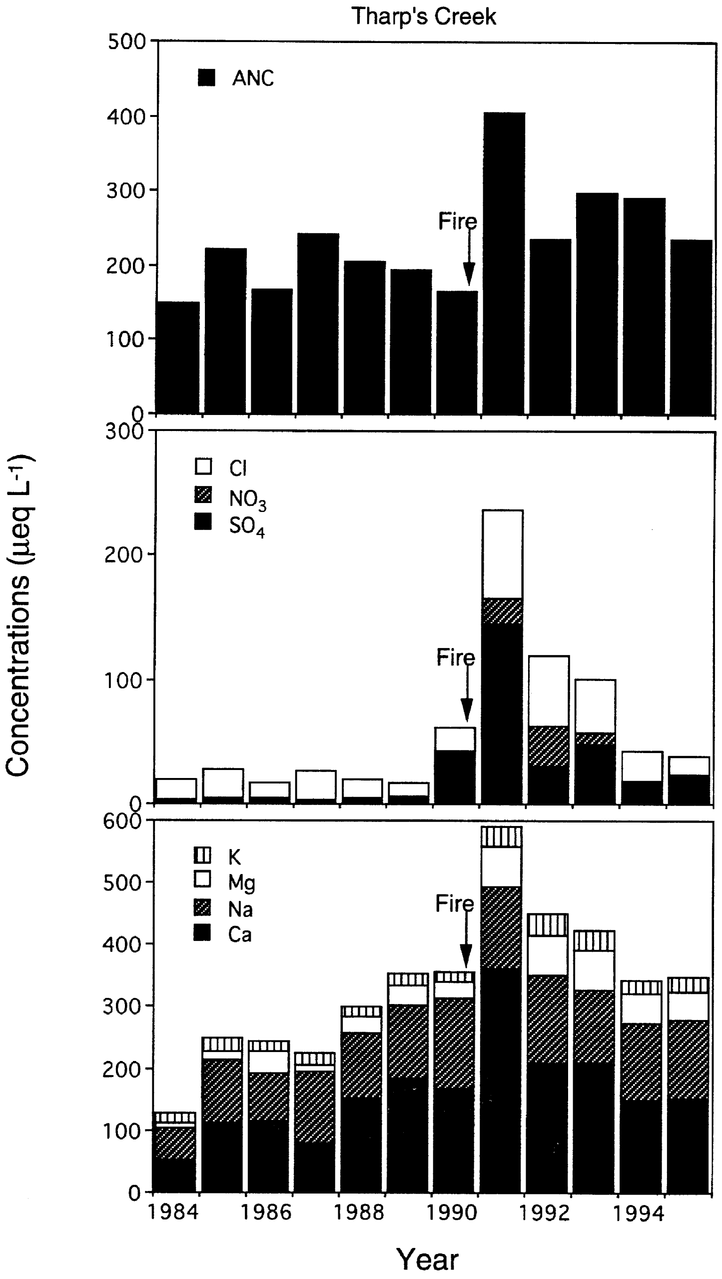

Figure 6a. VWM concentrations for anions and cations in stream water of Tharp's Creek for the period of study.

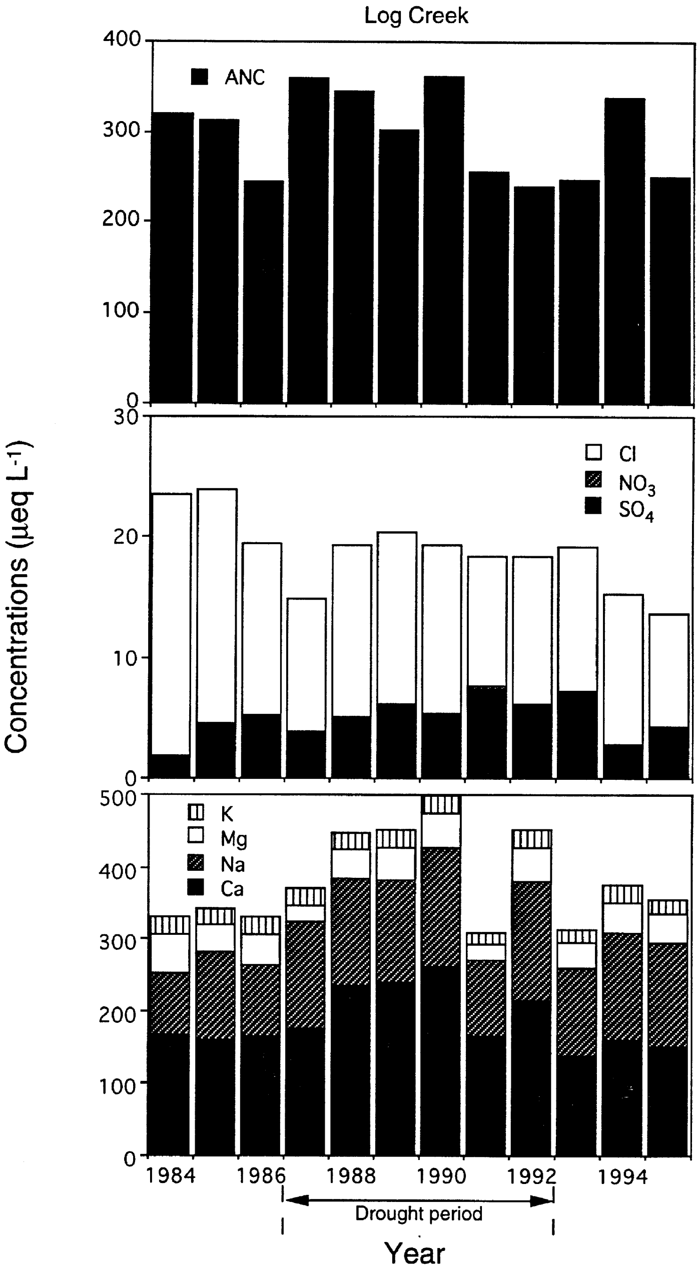

Figure 6b. VWM concentrations for anions and cations in stream water of Log Creek for the period of study.

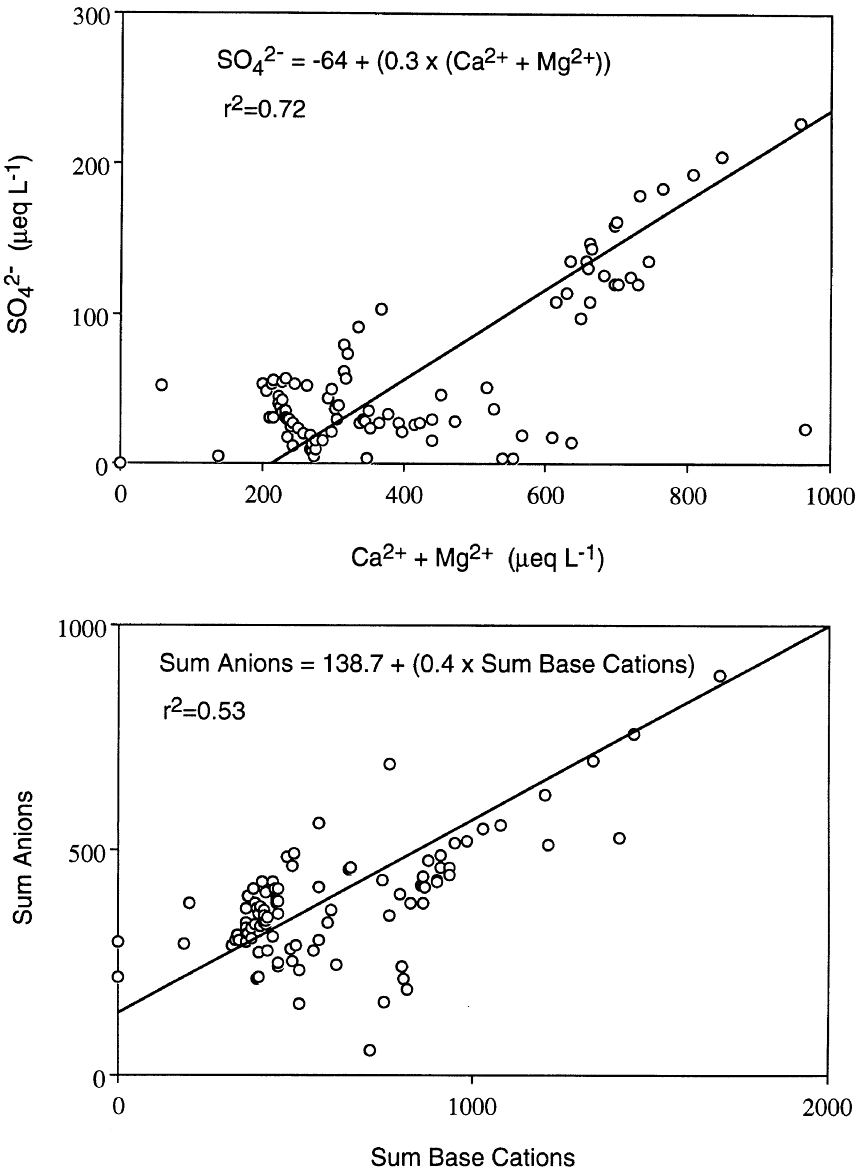

Figure 7. Concentrations of SO_4^{2-} versus the sum of Ca^{2+} and Mg^{2+}, and the sum of base cations versus the sum of anions in Tharp's Creek the first three years after prescribed burning.

Knight et al. (1985) and Likens and Bormann (1995) report cation losses similar in ranking to those for Tharp's and Log creeks ($Ca^{2+} \gg Na^{+} > Mg^{2+}$ and K^{+}).

Low concentrations of strong mineral acid anions were commonly measured in the stream water of both catchments compared to precipitation. Williams and Melack (1997) determined that anthropogenic inputs of NO_3^- and SO_4^{2-} were usually incorporated, transformed or consumed by watershed processes, and that these catchments have a large capacity for neutralizing atmospheric acid inputs. 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.

Effects of prescribed burning – Comparisons of the solute concentrations of post-fire stream water with those of pre-burn baselines in Tharp's Creek and the adjacent unburned catchment of Log Creek show that fire increased most solute concentrations in Tharp's Creek (Figures 3a, b). Gross solute yields increased also after fire, although net fluxes showed retention of H^+, NO_3^-, NH_4^+ and PO_4^{3-}, and export Na^+, Ca^{2+}, Mg^{2+}, ANC and SiO_2, which are similar to pre-fire export characteristics. Exceptions were post-burn solute fluxes of SO_4^{2-}, Cl^- and K^+, which shifted from net retention to net export (Figure 5).

Tharp's Creek had large increases in the concentrations of strong acid anions compared to those of Log Creek after burning (Figures 6a, b), and movement of these anions was associated with the flux of base cations in soils to stream water (Chorover et al. 1994). Mean annual base cation concentrations in Tharp's Creek prior to the 1990 fire were variable, partially due to annual streamwater runoff from 1983–1990 that ranged from 3 to 880 mm (Table 1). Nevertheless, streamwater concentrations of base cations increased after the fire as expected (Tiedemann et al. 1978; Feller & Kimmins 1984; Bayley et al. 1992b). VWM concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} in Tharp's Creek increased by factors of 1.3, 1.8, 3.0 and 2.9, respectively, in the first year after the burn compared to pre-fire means. Concentrations of base cations in Tharp's Creek had not yet returned to pre-fire levels by the end of the study. In contrast to most other solutes, VWM SiO_2 concentrations significantly decreased from an average of 127 μM in pre-burn to 98 μM in post-burn stream water (Figure 3a). Comparatively large, short duration increases in PO_4^{3-} and NH_4^+ occurred (Figures 3a, b).

Our study showed that small and insignificant decreases in $[H^+]$ occurred in the first two years after burning the Tharp's Creek catchment. In contrast, Bayley et al. (1992b) and Nakane et al. (1983) documented slight increases in H^+ concentrations after fire. Most other studies of burning do not cite any change in *p*H, primarily because the *p*H was not measured. In contrast to *p*H, VWM ANC concentration increased by about 190 μeq L^{-1} the first year after the fire compared to the average pre-fire value.

Sulfate – The sum of strong acid anion concentrations in Tharp's Creek increased proportionally more than base cations, which was due mostly to increases in SO_4^{2-} and Cl^- (Figures 3a and 6a). Before the fire, VWM annual SO_4^{2-} concentrations in Tharp's Creek were low, averaging 9.2 μeq L^{-1}, compared to a mean of 4.4 μeq L^{-1} in Log Creek (1984 to 1990). In the first year after the fire, VWM SO_4^{2-} concentrations in Tharp's Creek increased about 16 times, compared to an increase of only 2 μeq L^{-1} in Log Creek, and the increase in Tharp's Creek stream water was commensurate with the increase of SO_4^{2-} in soil solutions. Chorover et al. (1994) found that $[SO_4^{2-}]$ in soil solutions of the Tharp's Creek catchment are typically low (< 25 μM), but that $[SO_4^{2-}]$ increased over 100 times after prescribed burning occurred. The slight increase in $[SO_4^{2-}]$ in stream water of the control catchment was possibly due to carry-over effects of combustion products from burning in the Tharp's Creek catchment. The maximum concentration of SO_4^{2-} in stream water reached 1,224 μeq L^{-1} in March 1991, and this pulse was associated with a large efflux of other solutes in stream water (Figures 3a, b and 6a, b). The VWM SO_4^{2-} concentration in Tharp's Creek in the fifth year after the fire remained over 2 times higher than the pre-fire baseline. Gross SO_4^{2-} yields slightly decreased in Log Creek the first year after burning the Tharp's Creek catchment, whereas the latter showed a 7-fold increase. Large increases in streamwater SO_4^{2-} concentrations were observed also by Bayley and Schindler (1991) after a wildfire burned a coniferous forest in Ontario. In contrast, Feller and Kimmins (1984) observed a decrease in SO_4^{2-} concentration due to cutting, and a subsequent increase after burning that was < 15 μeq L^{-1} compared to the pre-disturbance baseline.

The retention of S in mineral soils appears to be a function of the degree of mineral weathering and the amount of iron and aluminum oxides (Chao et al. 1964), although other factors such as deposition history (Johnson et al. 1986), *p*H (Nodvin et al. 1986), and the extent of soil flushing (Williams & Melack 1997) appear to be important. Since there are few sesquioxides in the soil matrix of these catchments (Huntington & Akeson 1987), SO_4^{2-} may be incorporated into soil organic matter by microbially mediated processes (Fitzgerald et al. 1982; 1988). Soil contains most of the S in some forested ecosystems, with soil organic matter acting as the main sink (Johnson et al. 1986). For example, in the Tharp's and Log creek catchments, 95% of the total S in A-horizon soils is organic (Stanko & Fitzgerald 1990). Since background SO_4^{2-} concentrations and deposition of S are both low in the Tharp's and Log creek catchments, SO_4^{2-} mobility may be regulated by plant and microbial demand for S (Mitchell et al. 1991). Indeed, both catchment streams showed large increases in SO_4^{2-} and smaller increases in Cl^- concentrations after fire, which supports the contention that SO_4^{2-} and Cl^- are regulated by biotic uptake and retention in living and dead organic matter. Fire probably increased SO_4^{2-} mobilization via the oxidation of organic matter. Exhaustion, biotic uptake and organic S formation after burning were likely responsible for the decline in concentration after the initial pulse in the winter of 1991.

Inorganic nitrogen – Increased organic matter mineralization and a subsequent state of rapid nitrification were probably responsible for the large pulses of NO_3^- in stream water that were observed after burning the Tharp's Creek catchment (Figure 3a). Concentrations of inorganic N in the Tharp's Creek catchment were likely influenced also by runoff. Prescribed burning contributed to a 40-fold increase in runoff over the preceding year, whereas runoff of Log Creek increased by a factor of 1.5 (Table 1). Similar to NO_3^-, Tharp's Creek stream water showed rapid increases in NH_4^+ after the burn. Ammonium increased to about 25 μeq L^{-1} immediately after burning occurred, but decreased to the pre-burn baseline several months later, albeit with more variability until the end of the study than prior to the disturbance. The maximum concentration of NO_3^- briefly exceeded 60 μeq L^{-1} in January 1991, the first month of streamwater runoff after the burn, while in March 1991, NO_3^- concentrations exceeded 140 μeq L^{-1}. Nitrate concentrations increased above 120 μeq L^{-1} the following spring (1992), and persisted above 60 μeq L^{-1} for several weeks (Figure 3a). In contrast, pre-fire concentrations seldom exceeded 0.5 μeq L^{-1}.

Many studies of disturbance have documented an increase in NO_3^- concentrations in streams (Tiedemann et al. 1978; Feller & Kimmins 1984; Swank 1988; Likens & Bormann 1995). Likens et al. (1969) showed that disturbance enhanced nitrification released large amounts of NO_3^- to stream water, which resulted in streamwater acidification. In boreal forest ecosystems, the export of NO_3^- appears to be minimal and increased acidity is associated with an increase in SO_4^{2-} concentration. Although large amounts of NO_3^- were not released in the streams of the Experimental Lakes Area (Bayley et al. 1992a), they observed enhanced nitrification since high concentrations of NH_4^+ in soil water were detected immediately after fire, which declined rapidly with a small increase in NO_3^-. Nitrate was probably not released by fire in large quantities because boreal forests are N-poor environments (Foster & Morrison 1976; Gosz 1981). Shallow soils did not allow NO_3^- to leach below the rooting zone, and most NO_3^- was probably retained by vegetation (Raison 1979; Bayley et al. 1992a). In the Tharp's Creek catchment, Chorover et al. (1994) detected high concentrations of NO_3^- and NH_4^+ in A-horizon soil water in sequoia and fir stands immediately after fire. In the third year after the burn, NH_4^+ declined below, while NO_3^- remained above pre-burn baselines. Chorover et al. (1994) attributed the behavior of NH_4^+ to the thermal decomposition of organic matter or microbial activity.

Gross NO_3^- export in Tharp's Creek increased from an annual average of less than 0.03 kg ha^{-1} yr^{-1} during the 7-year pre-burn period to 1.6 kg ha^{-1} yr^{-1} in the first three years after the burn (Williams & Melack 1997). Still, streamwater outputs did not exceed atmospheric inputs in the post-burn period, with net retention averaging 2.4 kg ha^{-1} yr^{-1} the first three years after the burn (Figure 5). Because this estimate does not include dry deposition inputs to these catchments, net retention is probably somewhat larger. For example, Williams and Melack (1997) estimated that NO_3^- inputs from dry deposition were about 20% of those attributed to wet deposition. Streamwater NO_3^- remained above pre-burn baselines until the middle of the third year after burning, indicating the forest-soil processes controlling NO_3^- concentrations in stream water were recovering by this time. Since increased nitrification rates may occur from increased $[NH_4^+]$ and soil *p*H, similar increases in the Tharp's Creek catchment indicate that nitrification was responsible for at least part of the increase in streamwater NO_3^- concentrations. It is likely that the disturbance of the major pre-burn NO_3^- sinks in the sequoia and fir stands (forest floor and surface soils) contributed also to elevated NO_3^- in stream water of Tharp's Creek. A decrease in nitrification and an increase in terrestrial denitrification and biological uptake were probably factors responsible for the steady return of streamwater NO_3^- concentrations to pre-burn baselines toward the end of the third year of the study.

Chloride – Chloride concentrations were elevated immediately after the fire, and remained elevated for 3 years (Figure 3a). Chloride concentrations during this 3-year post-burn period were 4.2 times higher than baseline levels during the fire year, and was probably released from burned vegetation. Although Cl^- concentrations increased in smaller proportion compared to either SO_4^{2-} or NO_3^- the first year after the fire in Tharp's Creek, large concentration increases in stream water suggest that there is considerable Cl^- retention within this catchment. Both Likens et al. (1970) and Swank (1988) observed increases in Cl^- concentrations in stream water after cutting and herbicide treatment, and harvesting experiments, respectively. Similarly, Bayley and Schindler (1991) observed elevated Cl^- export after a wildfire in a coniferous forest. Chorover et al. (1994) argue that Cl^- retention in the Tharp's and Log creek catchments occurs through interactions with organic matter, although they do not provide a mechanism. Evidence suggests that previous assumptions about

Table 1. Comparison of annual precipitation (wet deposition) and streamwater runoff. Precipitation depth from the Giant Forest area was increased by 9% to account for orographic differences in precipitation at the Tharp’s Creek study area. Water years are from October 1 to September 30. Runoff coefficients (the ratio of runoff to precipitation listed as percent) are in parentheses.

	YEAR												12-YEAR
SOURCE	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	MEAN
Precipitation Depth (mm):	1063	767	1345	588	679	831	601	788	692	1404	796	1765	943
Tharp’s Creek Runoff (mm):	372	163	880	52	25	45	3	121	49	481	105	884	265
	(35)	(21)	(65)	(9)	(4)	(5)	(1)	(15)	(7)	(34)	(13)	(50)	(22)
Log Creek Runoff (mm):	457	372	1240	228	175	198	157	227	156	515	218	612	380
	(43)	(49)	(92)	(39)	(26)	(24)	(26)	(29)	(23)	(37)	(27)	(35)	(38)

the conservative behavior of Cl^- are inadequate to explain the apparent sinks that exist in these catchments.

Base cations – The inputs of the strong mineral acids in precipitation after burning likely contributed to cation leaching and increased stream water concentrations of most solutes. Although soil alkalinity was moderately high and both catchments continuously exported ANC, cations in soils can become mobilized from H^+ derived from strong mineral acids in precipitation and snowmelt. Without forest leaf litter acting as an effective acid neutralizer after burning, soils were prone to experience higher leaching effects. However, most of the increase in cation concentrations in stream water is due to the formation of soluble oxides of alkaline earth cations resulting from the combustion of organic matter (Viro 1974). The leaching of this ash generally increases the concentration of base cations in solution. Hence precipitation, snowmelt and fire-related pulses of strong acid anions were associated with the terrestrial transport of base cations to Tharp's Creek, which had higher variability for at about three years after burning and elevated concentrations compared to pre-burn means throughout the remainder of the study (viz. the bivalent cations, Figure 3b).

Increased export of K^+ after disturbance has been more consistently detected than increases in other base cations (Bayley & Schindler 1991). However, in this study, VWM concentrations of both Ca^{2+} and Mg^{2+} in Tharp's Creek increased by a factor of about 3 in the first year after the fire compared to pre-fire baselines, whereas K^+ increased by about a factor of 2 and Na^+ increased by a factor slightly > 1 (Figure 3b). Despite differences in the proportional increases in base cations after burning, the ranking of cation species was invariant for most years of the study (i.e. $Ca^{2+} > Na^+ > Mg^{2+} > K^+$).

The slow decrease in base cation concentrations subsequent to an immediate increase after a disturbance generally results from the exhaustion of exchangeable ions in soils and a reduction in organic matter. Biological uptake may also be responsible for the decrease, for example, in the case of K^+, which is an essential nutrient in plant growth and maintenance. Chorover et al. (1994) observed that 3 years after the fire, bivalent cation concentrations remained higher in soil solutions of the burned sites than either those of the control catchment or pre-burn baselines, whereas monovalent ions were at or below their pre-burn levels. In contrast, at the end of this study, stream water had higher concentrations of all the base cations compared to pre-burn baselines, with Ca^{2+} and Mg^{2+} having decreased proportionally more than the monovalent cations since their initial increases after the fire.

With the large increase in anion concentrations after the fire, maintenance of the ion balance required an equivalent release of cations. We found that there was a significant relationship ($p < 0.05$, $r^2 = 0.53$) between the sum of base cation versus the sum of anion concentrations in post-fire Tharp's Creek (Figure 7), which was similar to the relationships between SO_4^{2-} ($r^2 = 0.72$) and NO_3^- ($r^2 = 0.61$, not shown) versus Ca^{2+} and Mg^{2+}, respectively. This analysis indicates that the export of anions is balanced by the export of base cations from soils to the stream in the Tharp's Creek catchment after burning, and that SO_4^{2-} is probably the most influential in maintaining this balance compared to other strong acid anions. The increase in the export of strong acid anions was associated with a slight decrease in streamwater $[H^+]$. In contrast to our study, Likens et al. (1970) observed the acidification of stream water due to nitrification, and increased NO_3^- export balanced that of the base cations after clearcutting. Bayley et al. (1992b) observed a similar relationship between strong acid anions and base cations as in our study, albeit with an associated decrease in ANC and an increase in streamwater $[H^+]$.

Despite the strong relationship between anions and cations in this study, base cation export after fire in the Tharp's Creek catchment was not balanced by measured anion export on an equivalent basis. The average anion deficit (Σ base cations – Σ anions) for stream water in the unburned Log Creek catchment was 9% of the sum of base cations, whereas that for Tharp's Creek in the pre-fire period was 11%. Anion deficit in Tharp's Creek typically was slightly lower during the 5 years after the burn (9%). We attribute the anion deficits to organic acids, which were not measured in this study.

Augmented sediment export – Fluxes of sediment and particulate N (PN), P (PP), and C (PC) increased in Tharp's Creek after burning compared to those of Log Creek. Tharp's Creek was influenced by runoff from a series of storm events (291 mm total) from February 28 to March 5, 1991 that increased the concentration of PN to above 1.8 mg L^{-1}. In contrast, about 20 μg L^{-1} PN was observed in the Log Creek and pre-burn concentrations in Tharp's Creek. The succession of storm events was responsible for a qualitatively different streamwater solute composition than that which occurred during other storms. The magnitude of overland flow caused large quantities of soil and particulates to be suspended and large increases in the concentrations of most solutes (Figures 3a, b). Fluxes in Tharp's Creek the first year after burning were 76, 0.5, 0.4 and 1.6 kg ha^{-1} yr^{-1} for sediment, PN, PP and PC, respectively. In comparison, losses from the unburned Log Creek control catchment were 5.0, 0.1, 0.1 and 0.5 kg ha^{-1} yr^{-1}, respectively (Figure 8). Unlike solute concentrations, particulate removal rapidly returned to pre-burn

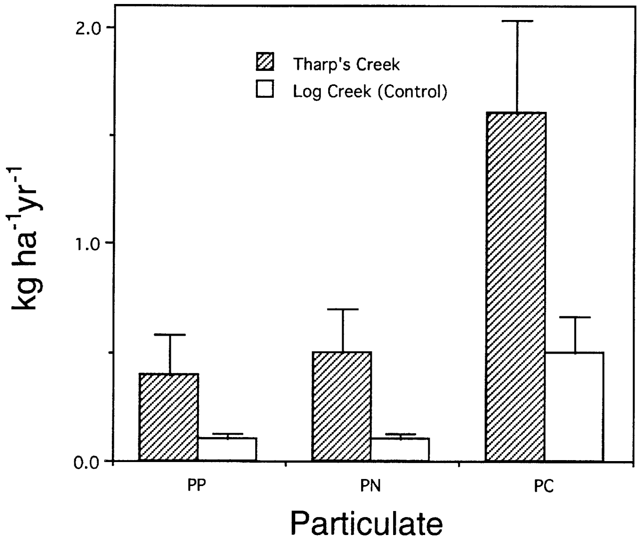

Figure 8. Particulate P, N and C from Tharp’s and Log creeks the first year after burning in the Tharp’s Creek catchment.

levels as catchment vegetation became reestablished, particularly along the small riparian meadow bordering Tharp’s Creek.

Effects of drought – A drought spanning 6 years (1987 to 1992) resulted in quantities of precipitation as low as 53% (1987) of the long-term average for the Giant Forest area (1100 mm). Mean precipitation for the Log Creek area was 697 mm during the drought period. Drought can produce an increase in the concentration of ions in water due to evaporative concentration and increased residence time in soils (Braekee 1981; Swank & Waide 1988). Bayley et al. (1992b) observed an increase in SO_4^{2-}, base cations and H^+ in stream water after a 3-week drought period. Williams and Melack (1997) observed that the beginning of snowmelt runoff after antecedent dry periods commonly produced elevated concentrations of ANC and base cations, but most solute concentrations in Log Creek stream water during the 6-year drought period did not correlate with annual precipitation amount. Increasing trends were apparent for VWM concentrations of Na^+ and Ca^{2+} in the first 4 years of the drought (Figure 6b), and SO_4^{2-} generally increased throughout the drought period, whereas SiO_2 (Figure 4a) decreased. Annual VWM concentrations of ANC generally decreased from the beginning of the drought in 1987 to 1993, although the low VWM concentration in the wet years of 1993 and 1995 suggest that this decreasing trend was not a ramification of drought (Figure 6b). Mean $[H^+]$ in the Log Creek catchment increased slightly in stream water during the drought years compared to years with above average precipitation (pH = 6.7 and 7.0, respectively). However, the largest increase in $[H^+]$ was from about 0.1 to 0.6 μeq L^{-1} (pH of 7.0 to 6.2) and occurred during the decreasing discharge limb of the hydrograph in the 1994 water year (dry year bracketed by wet years). The increase was observed in both catchments, although similar trends in $[H^+]$ were not observed during the 6-year drought period. Phosphate in Log Creek generally increased throughout the last three years of the drought, then decreased after the second wettest year of the study (1993; Figure 4a). Although the increases in PO_4^{3-} concentrations were small, a similar increasing trend was not apparent in the stream water of Log Creek at any other time of the study and did not occur in Tharp's Creek.

We observed trends in Tharp's Creek before burning the catchment in 1990 that were similar to those observed in Log Creek. Tharp's Creek stream water showed an increase in VWM concentrations of SO_4^{2-}, Ca^{2+} and Mg^{2+} (unlike Log Creek), a decrease in [ANC] the first three years of the drought, and a continual decrease in $[SiO_2]$. Despite some trends during the drought period, only VWM $[Ca^{2+}]$ in the Log Creek catchment was significantly higher ($p = 0.01$) during the drought period than during the other 6 years of the study using a t-test. The slightly higher concentrations of SO_4^{2-} and Na^+ during the drought period were moderately significant ($p = 0.08$ and 0.06, respectively). Correlation analysis of annual precipitation amount to VWM concentrations in Log Creek stream water showed significance ($p < 0.05$) for ANC ($r = -0.63$) and Ca^{2+} ($r = -0.59$). Sodium concentration in stream water was the only solute that was significantly correlated to annual runoff ($r = -0.59$). Although a concentrating effect was observed for Ca^{2+}, Na^+ and SO_4^{2-} in Log Creek, concentration increases were inconsistent among solutes and years and may not be related entirely to drought conditions. For example, $[SiO_2]$ decreased in concentration, presumably a result of suppressed weathering related to reduced soil moisture during the drought. However, this does not explain the continual decrease in $[SiO_2]$ after the drought had ended in 1993. The lack of strong correlations between precipitation amount and streamwater solute concentrations indicates that the regulatory mechanisms that influence solute concentrations in stream water were relatively unaffected by the drought.

Conclusions

After burning the Tharp's Creek catchment, we observed increased runoff and streamwater solute concentrations compared to pre-cut baselines and those of an adjacent undisturbed catchment. Strong acid anion concentrations increased proportionally more after the fire than the base cations, and our study indicates that SO_4^{2-} oxidation is responsible for balancing the export of base cations more than other strong acid anions in the post-fire environment. The increase of strong acid anions in solution was not associated with a significant change in streamwater *p*H, which indicates that the role of forest litter as a source of terrestrial buffering capacity is not as important as soils in mixed-conifer catchments. Retention and large increases of $[Cl^-]$ in streamwater after fire indicate that there is a terrestrial Cl^- sink. The efflux of solutes and particulates in post-burn stream water was accentuated by a succession of large snow and rain events 4 months after burning. Below average precipitation the subsequent year to burning indicates that solute and particulate losses after fire in wetter than average years would be much higher. Following the initial increases after burning, most streamwater solute concentrations generally diminished throughout the 3-year post-burn period, while the base cations remained above pre-burn baselines until the end of the study. Our study indicates that the affects of fire on non-conservative ions lasts approximately 3 years in these catchments, whereas base cations may be elevated above pre-fire levels for more than 5 years.

Silicate concentrations in Log Creek decreased during the drought period, presumably a result of suppressed weathering related to reduced soil moisture under drought conditions. However, $[SiO_2]$ in the 3-year post-drought period continued to decrease below concentrations observed during most of the drought, and a similar trend was observed in the Tharp's Creek catchment. Further investigation is required to provide a mechanism for the steady decrease in $[SiO_2]$ in these catchments over the last decade. Temporary increases in the concentrations of Na^+, Ca^{2+} and SO_4^{2-}, and decreases in ANC occurred during the drought period in the Log Creek catchment, but only $[Ca^{2+}]$ was significantly higher during the drought compared to the other years of the study.

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