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Similarities between Climatic Warming and Acidic Precipitation

Author(s): S. E. Bayley, D. W. Schindler, B. R. Parker, M. P. Stainton, K. G. Beaty

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## Effects of forest fire and drought on acidity of a base-poor boreal forest stream: similarities between climatic warming and acidic precipitation

S. E. BAYLEY<sup>1</sup>, D. W. SCHINDLER<sup>2</sup>, B. R. PARKER<sup>2</sup>,  
M. P. STANTON & K. G. BEATY

*Department of Fisheries and Oceans, Freshwater Institute, 501 University Crescent, Winnipeg, Manitoba, R3T 2N6 Canada; <sup>1</sup> Department of Botany, University of Alberta, Edmonton, Alberta, T6G 2E9 Canada; <sup>2</sup> Department of Zoology and Botany, University of Alberta, Edmonton, Alberta, T6G 2E9 Canada*

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**Abstract.** In a boreal forest catchment in the Experimental Lakes Area in northwestern Ontario, wildfire caused an increase in the concentrations of strong acid anions and base cations of the stream. In the naturally base-poor Northwest (NW) Subbasin, a 1980 wildfire caused exports of strong acid anions to increase more than export of base cations, causing a 2.5 fold increase in the acidity of the stream. Mean annual stream pH declined from 5.15 prior to fire to 4.76 two years after fire. Acid-neutralizing capacity (ANC), calculated as the difference between total base cations and strong acid anions, decreased to 20% of pre-fire values. Sulfate and chloride were the strong acid anions responsible for the decline in ANC, increasing four-fold. While nitrate increased eleven-fold, concentrations were too low to significantly affect ANC. There was a significant correlation between weekly sulfate concentration and base cation concentration ( $r^2 = 0.83$ ) in the two years after fire. Recovery of ANC was caused by the more rapid decline in concentration of sulfate than by changes in base cations. Drought produced a similar but weaker response than fire, with increased sulfate concentrations and decreased stream pH. Climatic warming that increases drought and fire frequency would have effects that mimic the impacts of acidic precipitation (i.e. higher sulfate concentrations and acidic stream waters). Areas which have higher concentrations of stored S from past acid precipitation or have large areas of peatlands in the watershed may have aggravated losses of S and H<sup>+</sup> after drought and fire.

### Introduction

Aggrading forest vegetation is known to take up more base cations than strong acid anions from terrestrial soils, causing runoff from catchments containing such forests to be more acidic than they would be if forests were at steady-state or degrading (Bormann & Likens 1979; Brinkley & Richter 1987). This differential uptake of cations vs anions has led some

investigators (Krug & Frink 1983; Rosenqvist 1978) to believe that soils and freshwaters in aggrading watersheds of the eastern USA and Scandinavia are becoming more acidic in the 20th century because they are reforesting after earlier land disturbance. Forest fires have been thought to cause a decrease in the acidity of runoff by releasing base cations from burned vegetation and soils (Beaton 1959; Grier 1975; Raison 1979; Smith 1970; Tarrant 1956; Viro 1974). It has even been suggested that acidification of lakes and streams in the 20th century has been caused by suppression of natural fires that previously replenished buffering of soils and streams by returning base cations to them (Brown 1984).

Base cation exports in streams have been studied after a variety of disturbances including clearcutting, slash burning, control burning and forest fires (Feller & Kimmins 1984; Johnson & Swank 1973; Likens et al. 1970; Nakane et al. 1983; Richter et al. 1982; Swank 1988; Tiedemann et al. 1978). Increased export of potassium after disturbance appears to be more consistently detected than increases in other base cations (Bayley & Schindler 1991).

Disturbance of vegetation or soils in forest ecosystems causes increased nitrate concentrations in soils and streams (Bayley et al. 1992; Likens et al. 1970; Likens et al. 1977; Schindler et al. 1980; Swank 1988; Vitousek et al. 1979; Wiklander 1981). It has been suggested that more fertile ecosystems lose more nitrate after disturbance than do the more infertile ones (Vitousek et al. 1979). Some studies of fire show increased nitrate losses after burning (Feller & Kimmins 1984; Tiedemann et al. 1978), while other studies have not documented increased nitrate losses (Wright 1976). Studies documenting the effect of fire on the export of strong acid anions (sulfate and chloride) in streams are rare (Bayley & Schindler 1987; Schindler et al. 1980). Disturbance such as clearcutting and herbicide experiments at Hubbard Brook in New Hampshire caused a decrease in the export of sulfate and an increase in the export of chloride (Likens et al. 1970; Nodvin et al. 1988).

The objectives of this paper are to document the effects of a wildfire in a forested catchment on the pH and acid-neutralizing capacity (ANC) of a stream in the naturally base-poor Canadian Shield. Here we describe the effects of forest fire and regrowth of the forest on the chemistry of a stream for an eighteen year period. We compare the runoff chemistry of the same basin for nine years prior to the wildfire to the nine years after the fire. The stream concentrations of base cations, strong acid anions and  $H^+$  prior to wildfire are compared with concentrations after the wildfire. In addition, the effects of drought (without wildfire) are compared to the effects of wildfire on stream chemistry.

## Site description

The upland watershed reported in this study is a part of the drainage of Lake 239 at the Experimental Lakes Area (ELA) located on the Precambrian Shield in northwestern Ontario, Canada (49°40'N, 93°44'W). Hydrological monitoring and chemical sampling have been carried out since 1971 on the stream in the Northwest (NW) Watershed (56.4 ha). At the time our studies began, there had been no fires in the catchment for several decades, and the vegetation was near climax. The vegetation and soils in the ELA region are described in Schindler et al. (1980) and in Brunskill & Schindler (1971). Generally the watershed has thin discontinuous deposits of granitic, sandy till on the valley slopes and in the valley. On the valley slopes the deposits are generally less than 1 m thick, while deposits in the lowland areas are deeper. Most areas were overlain by a thin organic mat prior to the fires. The underlying bedrock is granite and granodiorite. Approximately 18% of the NW watershed is barren rock outcrop. The average side slopes in the NW basin are 11% and the maximum relief is 59 m. The NW stream is a primary headwater stream with an average annual discharge of  $0.004 \text{ m}^3 \text{ sec}^{-1}$ .

Prior to the 1980 fire the dominant vegetation was ~100 year old *Pinus banksiana* (jack pine) with some *Picea mariana* (black spruce), *Betula papyrifera* (paper birch), and *Populus tremuloides* (trembling aspen). The fire killed most of the trees and shrubs, but left the standing dead trees. After the fire, the terrestrial areas re-vegetated rapidly with small jack pine, black spruce, poplar, birch, black alder (*Alnus nigra*), balsam poplar (*Populus balsamifera*) and pin cherry (*Prunus pennsylvanica*). Herbaceous vegetation was dense for several years following the fire and was dominated by *Epilobium angustifolium*, *Polygonum convolutus*, *Rubus strigosus*, and *Vaccinium* spp. Details of the fire and vegetation are reported in Bayley et al. (1992).

## Methods

Hydrological monitoring started in June 1971 with installation of a weir on the NW stream. The near-surface flows and surface runoff were collected in the short stream channel and monitored by the 120° V-notch weir prior to entering Lake 239. The weir captured almost all of the water leaving the subbasin (Newbury & Beaty 1980). Deep groundwater movement of water in the watershed was very low (Newbury & Beaty 1980; Bottomley 1974). Continuous measurement of the stream flow has occurred since 1971. Details of the hydrologic monitoring are described in Beaty (1981) and Newburg and Beaty (1980). Samples for chemical analysis

were collected weekly during the ice free season, except during spring melt when sampling was more frequent. All stream chemistry data are reported as volume weighted mean annual concentration. Volume-weighted mean annual concentrations were calculated by estimating daily chemical concentrations and multiplying by daily discharge; the daily fluxes are then summed and divided by total discharge (Bayley et al. 1992). Interannual variations in streamflow were less important than the fire in affecting streamwater solute concentrations (i.e. in Fig. 1 the 1984 stream flow was 84,473 m<sup>3</sup> while in 1985 it was 185,068 m<sup>3</sup>). The prefire period from June 1971–June 1980 was compared to the post fire years using the student-*t* test. If the post fire mean annual concentration is different from the prefire mean (and its 95% confidence interval), then the post fire year is considered significantly different from the prefire years (at  $\alpha = 0.05$ ).

Water samples were analyzed for pH, dissolved inorganic carbon (DIC), NO<sub>3</sub>-N, base cations, SO<sub>4</sub><sup>-</sup>, and Cl<sup>-</sup>. ANC is calculated as the difference between the sum of base cations (Ca<sup>++</sup>, K<sup>+</sup>, Mg<sup>++</sup>, Na<sup>+</sup>) minus the sum of strong acid anions (SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub>-N. The methods of Stainton et al. (1977) were used for analysis of all ions except SO<sub>4</sub><sup>-</sup>. The SO<sub>4</sub><sup>-</sup> was measured from 1974–1979 with the ion exchange technique (Stainton et al. 1977). This method is now known to measure SO<sub>4</sub><sup>-</sup> plus organic anions (Kerekes et al. 1984). Starting in 1980 Dionex ion chromatography was used. To correct the 1974–1979 SO<sub>4</sub><sup>-</sup> data, the ion exchange technique and ion chromatography techniques were intercalibrated by measuring all samples with both methods for two years. In addition, the SO<sub>4</sub><sup>-</sup> data from 1983–1987 were incorporated into the SO<sub>4</sub><sup>-</sup> regression by assuming that the Dionex ion chromatographic SO<sub>4</sub><sup>-</sup> plus the organic anion measured on the Dionex is the same as the ion exchange SO<sub>4</sub><sup>-</sup>. With this regression, samples analyzed with the ion exchange method were adjusted to correspond to the ion chromatographic method. The regression for the NW subbasin SO<sub>4</sub><sup>-</sup> intercalibrations showed good agreement between the methods ( $r^2 = 0.81$ ). No SO<sub>4</sub><sup>-</sup> values are reported for 1971–1973 since the data are unreliable. More details of the chemical and hydrological techniques are reported in Schindler et al. (1980) and Bayley et al. (1992). NH<sub>4</sub><sup>+</sup> exports are excluded here because they do not contribute significantly to the base cation exports (see Bayley et al. 1992).

## Results and discussion

### *Chemical concentrations in stream after fire*

Hydrogen ion concentrations in outflow from the Northwest Subbasin

increased several-fold after fire, with the highest mean annual  $H^+$  concentration in 1982 (Fig. 1). The mean annual pH prior to the fire (1971–80) was 5.15 ( $7.1 \text{ ueq L}^{-1} H^+$ ). The pH during the growing season was even higher (5.45). After the 1980 fire, the mean annual pH was 4.92 in 1981 and 4.76 ( $17.4 \text{ ueq L}^{-1}$ ) in 1982 (Fig. 1). The pH during the growing season in 1982 was 4.95, a 3.2 fold increase over the prefire growing season acidity. A similar increase in acidity occurred after a wildfire in a Japanese forest although the study compared adjacent burned and unburned basins (Nakane et al. 1983). Most other studies of wildfire do not cite any change in pH, primarily because the response has been variable or the pH was not measured.

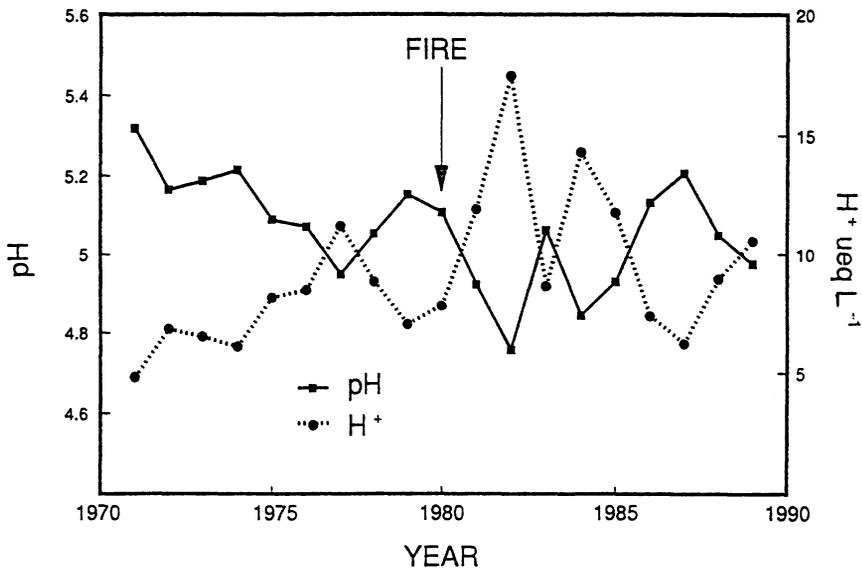


Fig. 1. Mean annual pH and mean annual hydrogen ion concentration in the NW stream at the Experimental Lakes Area before and after wildfire (1971–1989).

Calculated mean annual ANC of the NW stream showed a sharp decrease for two years after the fire (Fig. 2a). Since ANC is calculated as the difference between the sum of base cation and strong acid anions, the decrease in ANC was associated more with an increase in acid anions than an increase in base cations. The ANC decreased by  $76 \text{ ueq L}^{-1}$  the first year after the fire compared to the average prefire ANC value.

Mean annual base cation concentrations in the NW stream prior to the 1980 fire were fairly constant, even though the discharge from 1971–80 ranged from 0 to  $0.187 \text{ m}^3 \text{ s}^{-1}$ . Stream concentrations of base cations

increased after the fire as expected from the literature (Feller & Kimmins 1984; Tiedemann et al. 1978; Wright 1976). Concentrations of  $K^+$ ,  $Ca^{++}$ ,  $Mg^{++}$ , and  $Na^+$ , in the NW stream increased by a factor of 3.08, 1.89, 1.89, and 1.74 respectively (Fig. 2b) in the first year after the fire compared to the pre fire mean values. The sum of base cations showed the sharp increase in concentration in 1980 and 1981 and a decline in subsequent years. Concentrations of base cations in the stream have not yet returned to prefire levels even nine years after the fire (Fig. 2b).

The sum of strong acid anion concentrations in the NW stream increased even more than base cations, tripling in the two years after the 1980 fire (Fig. 2c). Most of the increases in strong acid anions were due to increases in sulfate and chloride, not to nitrate increases. Before the fire, volume-weighted mean annual  $SO_4^-$  concentrations in the NW stream averaged  $59.7 \text{ ueq L}^{-1}$ . For two years after the fire,  $SO_4^-$  concentrations averaged  $229 \text{ ueq L}^{-1}$ , a 3.8 fold increase. The maximum concentration of  $SO_4^-$  in streamwater reached  $634 \text{ ueq L}^{-1}$  in July 1980. Annual average concentrations remained 3.1 times higher than pre-fire values for five years after the fire and were still elevated nine years after burning (Fig. 2c). Thus, Brown's (1984) hypothesis that stream and lake acidification is caused by the depletion of base cations due to fire suppression in forested regions is not supported by our findings that increased acidity is associated with elevated strong acid anions. Export of  $SO_4^-$  appears to be due to oxidation of the organic S contained in the forest vegetation and soil by fire and leaching of the released  $SO_4^-$  via streamflow. Clearcutting (and herbicide application) would presumably release S contained in the dead debris but the appearance of  $SO_4^-$  in streams is mediated by soil absorption which varies widely in North America (Rochelle & Church 1987).

Chloride and nitrate concentrations in stream water also increased after the fire (Fig. 2c). Chloride concentrations were elevated immediately after the fire, and remained elevated for the fire year and one year after the fire. The elevated  $Cl^-$  concentrations were 3.9 times higher than background levels during the fire year. It is likely that  $Cl^-$  was released from the vegetation by burning, especially from the moss mat. We have measured  $Cl^-$  uptake by *Sphagnum* moss in a nearby bog (Bayley, unpub. data). Likens et al. (1970) observed a 1.6 fold increase in  $Cl^-$  concentrations in stream water at Hubbard Brook after clearcutting and herbicide application. Swank (1988) also reported an increase in  $Cl^-$  concentrations in the stream draining the most severely harvested watershed (W6) at Coweeta forest.

In the weeks immediately after the fire, maximum concentrations of  $NO_3-N$  occasionally reached  $48 \text{ ueq L}^{-1}$ , while in the following spring (1981) concentrations of  $70 \text{ ueq L}^{-1}$  persisted for over a month. In this

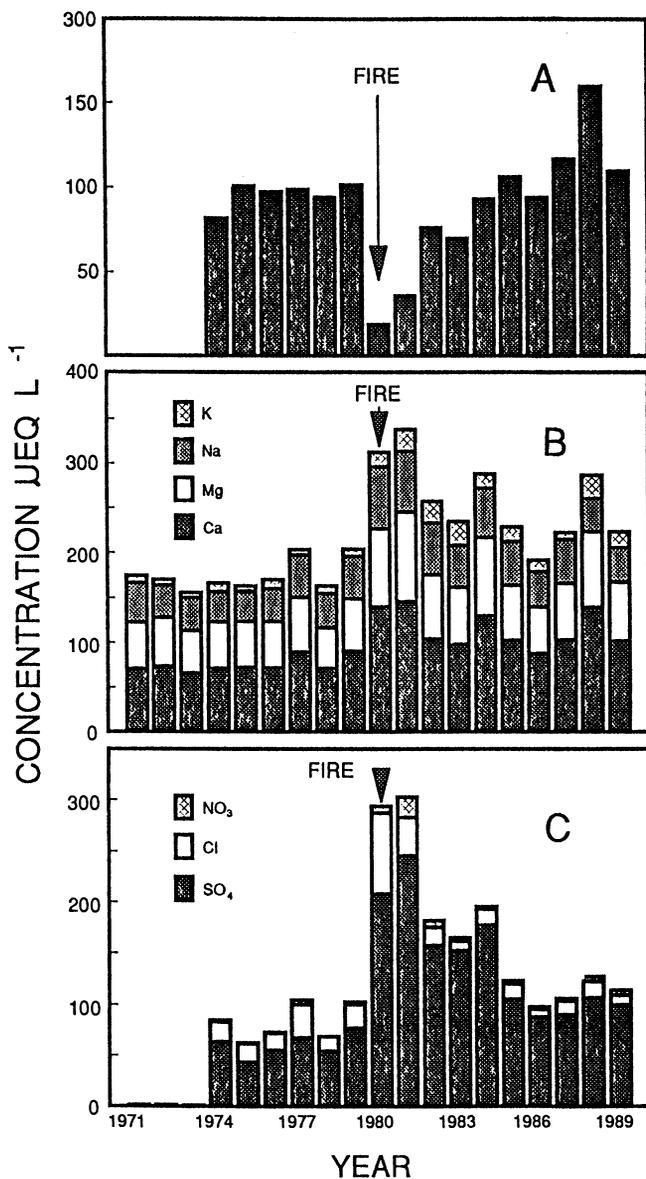


Fig. 2. a) Mean annual acid neutralizing capacity (ANC) in the NW stream at the Experimental Lakes Area from 1974–1989. ANC is calculated as the difference between the sum of base cations and strong acid anions. Data are in  $\text{ueq L}^{-1}$ . b) Mean annual concentrations of base cations in the NW stream at the Experimental Lakes Area from 1971–1989. Data are in  $\text{ueq L}^{-1}$ . c) Mean annual concentrations of strong acid anions in the NWS stream at the Experimental Lakes Area from 1974–1989. Data are in  $\text{ueq L}^{-1}$ .

nitrogen poor ecosystem, prefire concentrations had seldom exceeded 5  $\mu\text{eq L}^{-1}$ . Many studies of disturbance have documented an increase in  $\text{NO}_3^-$  concentration in streams (Feller & Kimmins 1984; Likens et al. 1969; Swank 1988; Tiedemann et al. 1978). Likens et al. (1969) showed that disturbance enhanced nitrification, releasing large amounts of  $\text{NO}_3^-$  to the stream. Although large amounts of  $\text{NO}_3^-$  were not released in the ELA streams (Bayley et al. 1992), nitrification was probably enhanced. Schindler (unpublished data) detected high concentrations of  $\text{NH}_4^+$  in soil water immediately after the fire which declined rapidly concurrent with the small increase in nitrate. Large amounts of N were probably not released by fire because boreal forests are nutrient poor environments particularly low in N (Foster & Morrison 1976; Gosz 1981). In general the soils are too shallow to allow  $\text{NO}_3^-$  to leach below the rooting zone, and most nitrate released was probably retained by the newly growing vegetation (Bayley et al. 1992).

With the large increase in strong acid anions after the fire, maintenance of the ion balance required an equivalent release of cations. We found that there was a significant relationship ( $r^2 = 0.83$ ) between  $\text{Ca}^{++}$  plus  $\text{Mg}^{++}$  versus  $\text{SO}_4^{--}$  concentrations in the NW stream in 1980–1981 (Fig. 3).

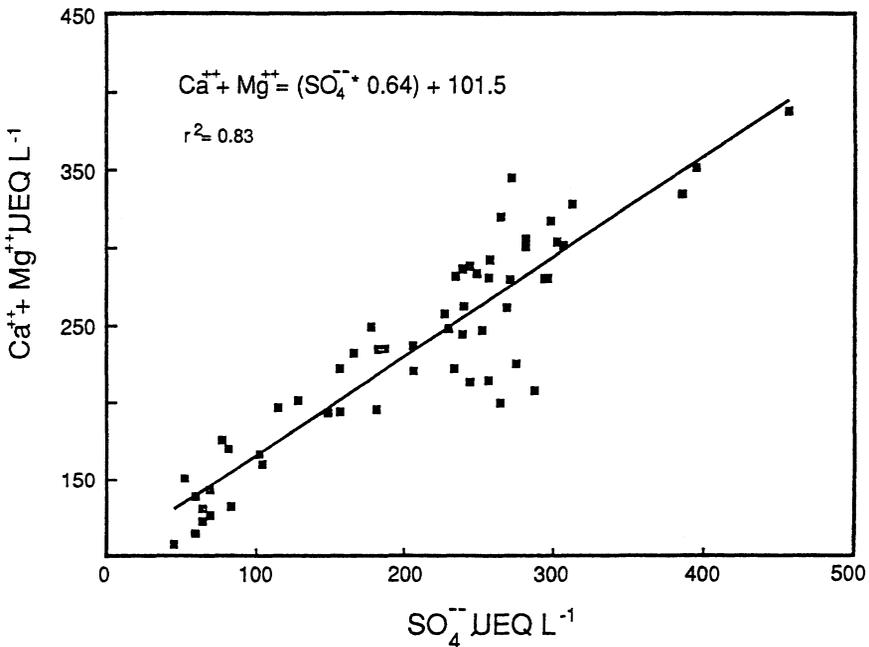


Fig. 3. Concentrations of sulfate versus the sum of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  in the NW stream in the two years after the wildfire.

This indicates that the base cation export after fire was balanced by the sulfate concentration, not by the nitrate concentration as was observed by Likens et al. (1970) after clearcutting. In the more nutrient-rich watersheds of Hubbard Brook, Likens et al. (1969) detected increased acidification of streams associated with nitrification and nitrate export. In the nitrogen-deficient boreal forest ecosystem at ELA, export of nitrate appears to be minimal and increased acidity is associated with the increase in sulfate concentration.

#### *Effects of drought versus wildfire*

Drought can also produce an increase in concentration of ions in water due to evaporative concentration and slow flow through the soil (increased leaching time) (Brakke 1981; Schindler et al. 1991; Swank & Waide 1988). The first rains after a drought produced elevated concentrations of  $\text{SO}_4^-$ ,  $\text{H}^+$  and base cations, but the concentrations after drought were much lower and of shorter duration than were observed after the wildfire. The effect of the 1974 drought (prior to the wildfire) on weekly sulfate concentrations in the NW stream is shown in Fig. 4. A similar response to drought and fire was observed for base cation concentrations (Fig. 4). Weekly  $\text{H}^+$  concentrations in the NW stream (Fig. 4) showed an increase in  $\text{H}^+$  after the drought although the response after the fire was greater (Fig. 4).

#### *Similarities between climate warming and acidic precipitation*

Drought and fire cause increased concentrations of  $\text{SO}_4^-$ , base cations and  $\text{H}^+$  (Fig. 4) as acid precipitation does. Climate warming with increased numbers and duration of droughts and fires can cause higher  $\text{H}^+$  export and may enhance acidification of streams in some of the naturally base-poor areas of the Canadian Shield. Acid precipitation also causes increased storage of sulfur in wetlands of the Precambrian Shield, increasing the potential acidification should the sulfur be reoxidized during drought or fire (Bayley et al. 1986).

#### *Recovery of chemical concentrations in stream*

Recovery of the forest-soil processes controlling nitrate was rapid, with stream nitrate concentrations remaining elevated for only three years after the fire, and then only in the spring and autumn (Bayley et al. 1992; Schindler et al. 1980). The nutrients may be regulated primarily by uptake by the herbs, shrubs and young trees which grew rapidly after the fire.

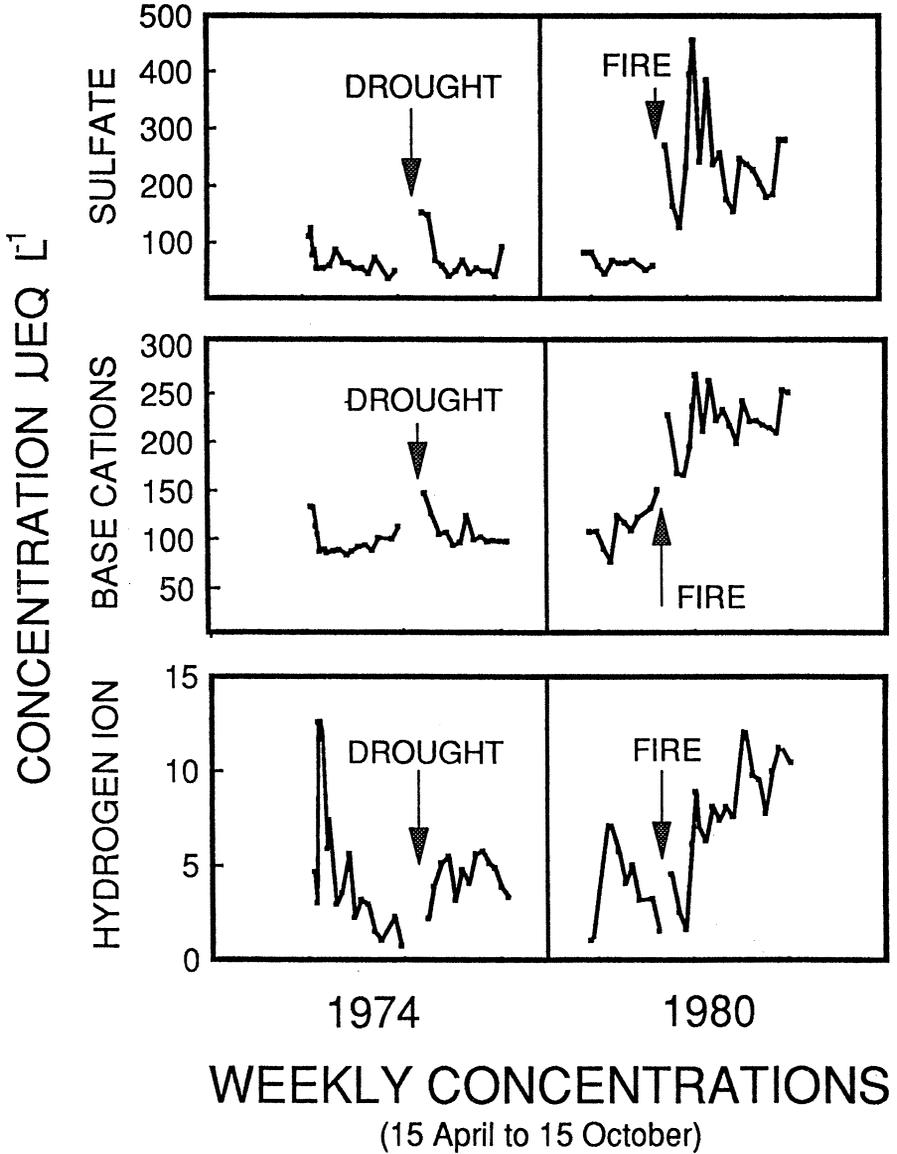


Fig. 4. Comparison of the effects of drought and fire on ion concentrations in the NW stream. Weekly concentrations of ions in 1974 prior to the wildfire are compared to weekly concentrations of ions in 1980 after the fire. Drought and fire are noted with arrows. Data in  $\mu\text{eq L}^{-1}$ . Note the differences in scale for the concentrations of sulfate, sum of base cations and hydrogen ion.

The recovery of the mature forest ground cover with its thin organic mat covered by *Sphagnum* and lichen species has been slow. The organic layer and moss mat in the mature boreal forest ecosystem may regulate the base cation,  $H^+$  and strong acid anions by both ion exchange and adsorption. The slow recovery of concentrations of base cations (especially  $Ca^{++}$  and  $Mg^{++}$ ) and  $SO_4^{--}$  in the stream may be due to the lack of the organic layer and moss mat in the young forest.  $Ca^{++}$  and  $Mg^{++}$  concentrations in the stream were still higher than prefire concentrations nine years after the fire. Recovery of  $SO_4^{--}$  and  $H^+$  concentrations has been faster than recovery of base cations.

Most studies have shown that the soil contains most of the sulfur in forest ecosystems, with soil organic matter the main repository (Johnson et al. 1986). Retention of S in mineral soils appears to be a function of the degree of mineral weathering and the amount of iron and aluminium oxide (Chao et al. 1964), although other factors such as deposition history (Johnson et al. 1986) and pH appear to be important (Nodvin et al. 1986). In mineral soils in the northeastern United States, decreasing pH of soil has caused an increase in the ability of the soil to retain sulfate (Nodvin et al. 1986, 1988). In the unweathered podsoles of ELA, retention of S in the mineral soil is likely quite low and recovery is partially a function of the development of the organic soil layer.

## Summary

Wildfire caused an increase in acidity in stream outflow by about 0.39 pH units or a 2.45 fold increase in  $H^+$  for two years after the fire. Drought in a mature forest can also cause an increase in stream acidity but the effects are more muted than the effects of wildfire. The decreased pH was associated with a decrease in ANC of the stream after the fire. The low ANC was due to the large increase in concentration of  $SO_4^{--}$  in the stream which was probably produced by oxidization of organic matter in the fire. Base cation concentrations increased after the fire but not to the extent that acid anions increased. The sulfate oxidation may be the driving mechanism controlling base cation release and  $H^+$  increase. The recovery of the stream pH and ANC generally occurred within three years after the fire.

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