

Water quality of two streams near Yellowstone Park, Wyoming, following the 1988 Clover-Mist wildfire

P. J. Gerla · J. M. Galloway

Abstract In 1988, wildfire burned over 50% of the Jones Creek watershed near Yellowstone Park, Wyoming. Crow Creek, an adjacent watershed, was unburned. Water quality data collected from 1989–1993 may show the fire's effect on weathering and nutrient transport. Jones Creek had 25–75% larger concentrations of dissolved solids than Crow Creek during the sampling period. Both streams revealed molar ratios consistent with the stoichiometry of andesine and pyroxene hydrolysis in the trachyandesites that underlie the basins. During 1989, nitrate transported from the unburned Crow Creek basin peaked at $2 \text{ mmol ha}^{-1} \text{ s}^{-1}$. This was twice as much as Jones Creek, possibly indicating a source from ash fallout. By 1992 these rates diminished to $0.1 \text{ mmol ha}^{-1} \text{ s}^{-1}$ in Crow Creek and increased to $1.8 \text{ mmol ha}^{-1} \text{ s}^{-1}$ in Jones Creek, suggesting later nitrate mobilization in the burned watershed. Phosphorus transported from Jones Creek basin averaged $0.011 \text{ mmol ha}^{-1} \text{ s}^{-1}$ during summer 1989, but fell to $0.004 \text{ mg ha}^{-1} \text{ s}^{-1}$ in subsequent years.

Key words Surface water quality · Nutrients · Fire · Chemical weathering · Equilibria

Introduction

In the summer of 1988, wildfires throughout Yellowstone National Park and the surrounding areas burned nearly 325 000 ha. The Clover-Mist Fire burned for several weeks, destroying about 160 000 ha of forest in northeastern Yellowstone Park and adjoining areas. A cooperative study by several agencies, including the US Geological

Survey, began in 1989 and focused on the effects the fires had on stream chemistry, runoff, sedimentation, and biological activity. Crow and Jones Creeks, two streams near the east-central boundary of Yellowstone National Park, Wyoming, with similar hypsometry, slope, aspect, and geology, were chosen to compare between a basin that was severely burned to one essentially unaffected by the fire. Over 50% of the Jones Creek watershed was burned by the Clover-Mist Fire, while Crow Creek experienced fire in less than 2% of its basin. The objective of the work was to examine the US Geological Survey's 1989–1993 analytical data for the two streams to identify temporal differences, changes, and patterns in water quality. This report compares the chemical erosion and nutrient flux processes in the two basins.

Methods

In 1989, the year following the fire, two temporary sampling stations were established by the US Geological Survey and US Department of Agriculture, Shoshone National Forest, on Jones and Crow Creeks. These stations were a short distance above the confluence of the creeks with the North Fork of the Shoshone River. During the times when the sites were accessible (generally from mid to late March until mid November), stream waters were sampled through the summer of 1993 on either a weekly, biweekly, or monthly basis using the procedures described in Fishman and Friedman (1989). Temperature, pH, and alkalinity were measured directly in the field at the time of sampling. Discharge for each stream was estimated for each sampling round using a current meter at normal flow or indirect measurements and hydrograph analysis when the channels were inaccessible during spring runoff (Rantz 1982). Water samples were submitted to the US Geological Survey National Water Quality Laboratory in Denver, Colorado for analysis of a large range of parameters, including major and minor elements, trace elements, nutrients, and turbidity. Analyses were performed using the procedures described in Fishman and Friedman (1989). Only the major elements and nutrient analyses and their interpretation are described herein; complete data are available on request from the first author.

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Description of the watersheds

Physiography

Jones and Crow Creeks, tributaries to the North Fork of the Shoshone River, lie in the North Absaroka Wilderness, adjacent to the east boundary of Yellowstone Park and immediately north of US Highway 14/20 (Fig. 1). The basins of Jones Creek (6423 ha) and Crow Creek (4946 ha) lie at an elevation that ranges from 2075 m to about 3300 m. The basins have a similar hypsometry and slope distribution (Fig. 2; M. Smith pers. comm., 1996).

Geology

Volcanic rocks of the Thorofare Creek and Sunlight Groups underlie most of the region to the east of Yellowstone Park. Within the two stream basins, the Langford Formation (Thorofare Group) crops out at lower elevations and consists of a thick section of mostly light-colored pyroxene andesite volcanoclastic strata and lava flows. The Trout Creek Formation (Sunlight Group) occurs at higher elevations and includes a sequence of trachyandesite and trachybasalt lava flows. Radiometric dates indicate a Middle to Late Eocene age for both formations (44–49 my bp; Smedes and Prostka 1972). Although the composition of the rock units in the region is reported by Miller and Drever (1977) and Nelson and Pierce (1968), the chemical composition of most primary igneous minerals have not been determined. The trachyandesite and trachybasalt flows of the region consist of dominantly andesine plagioclase (An_{38}) and augitic pyroxene (Smedes and Prostka 1972). Rapid physical erosion and limited soil development have occurred in the region. Field sampling and mineralogical

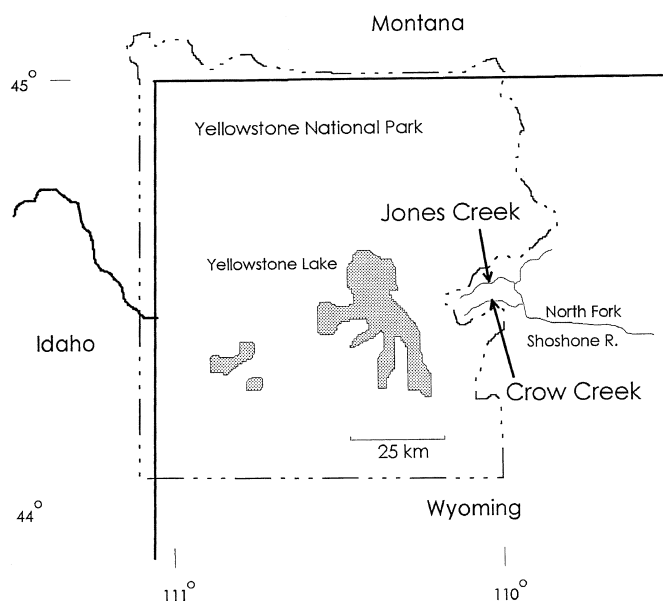


Fig. 1

Location of Jones and Crow Creek basins, northwestern Wyoming

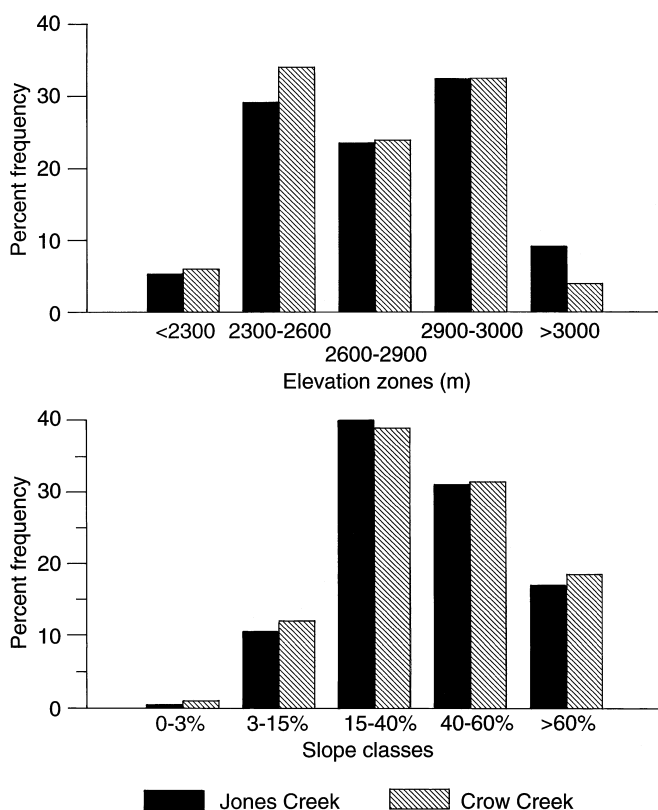


Fig. 2

Distribution of elevation zones and slope classes for Jones (stippled) and Crow (hatched) Creeks

analysis of soils in the North Fork Shoshone River basin by Miller and Drever (1977) revealed an overall abundance of Ca-montmorillonite (smectite) and sporadic minor occurrence of kaolinite, illite, and chlorite in soils. Surface water composition and mass balance considerations led Miller and Drever (1977) to postulate a kinetic rather than equilibrium control of weathering. They suggested that the composition of surface waters in the region was determined not by reactions in the soil zone, but by slight alteration of large volumes of volcanic rock.

Description of the water quality data set

Surface water in the two basins following the 1989 fires had very low concentrations of dissolved constituents. Total dissolved solids ranged from < 50 mg/l to approximately 100 mg/l. The waters can be classed as Ca-Mg bicarbonate type. Generally, the greatest concentrations of all constituents occurred during the late spring and early summer months; this time corresponds to the period of spring runoff and greatest seasonal rainfall (Fig. 3). The raw analytical data were converted to millimoles per hectare per second in most of the figures that follow to indi-

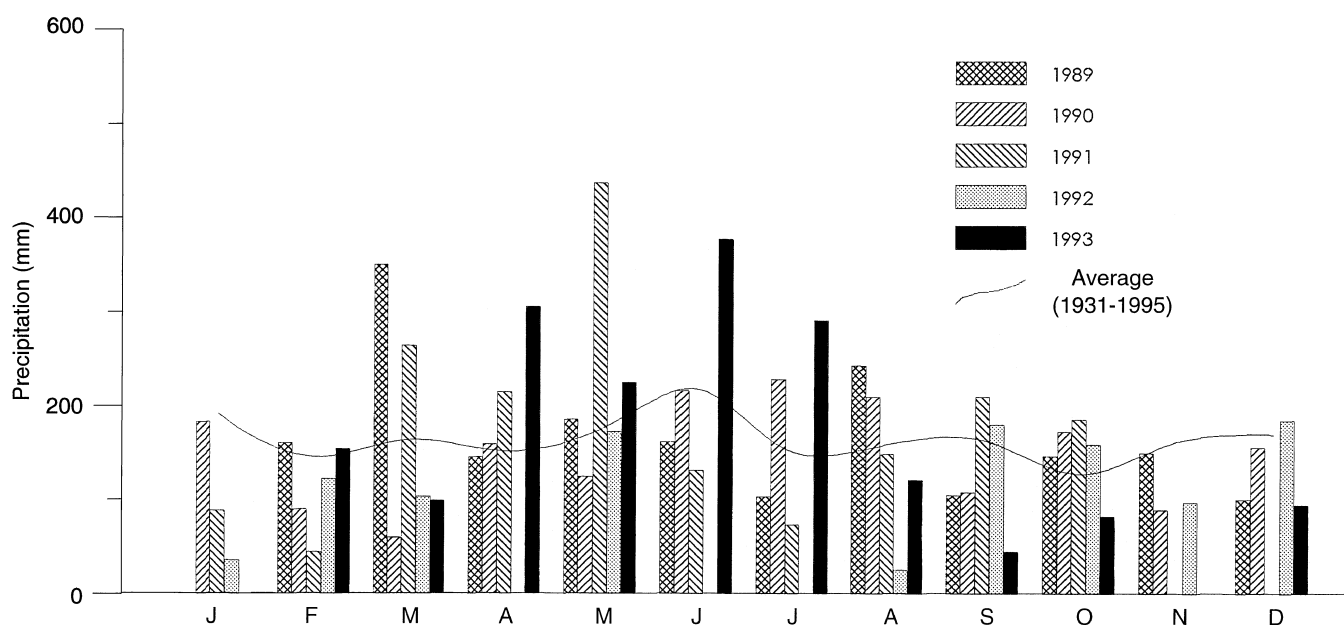


Fig. 3

Precipitation records for the NOAA weather station at Lake Yellowstone, approximately 35 km west of Jones and Crow Creek basins and at a similar elevation

cate the amount of transport from the two drainage basins. Although discharge for the two basins was similar, the transport of dissolved load from the burned Jones Creek basin ranged from 25% to 50% more (Fig. 4). During May 1991, precipitation was almost double the aver-

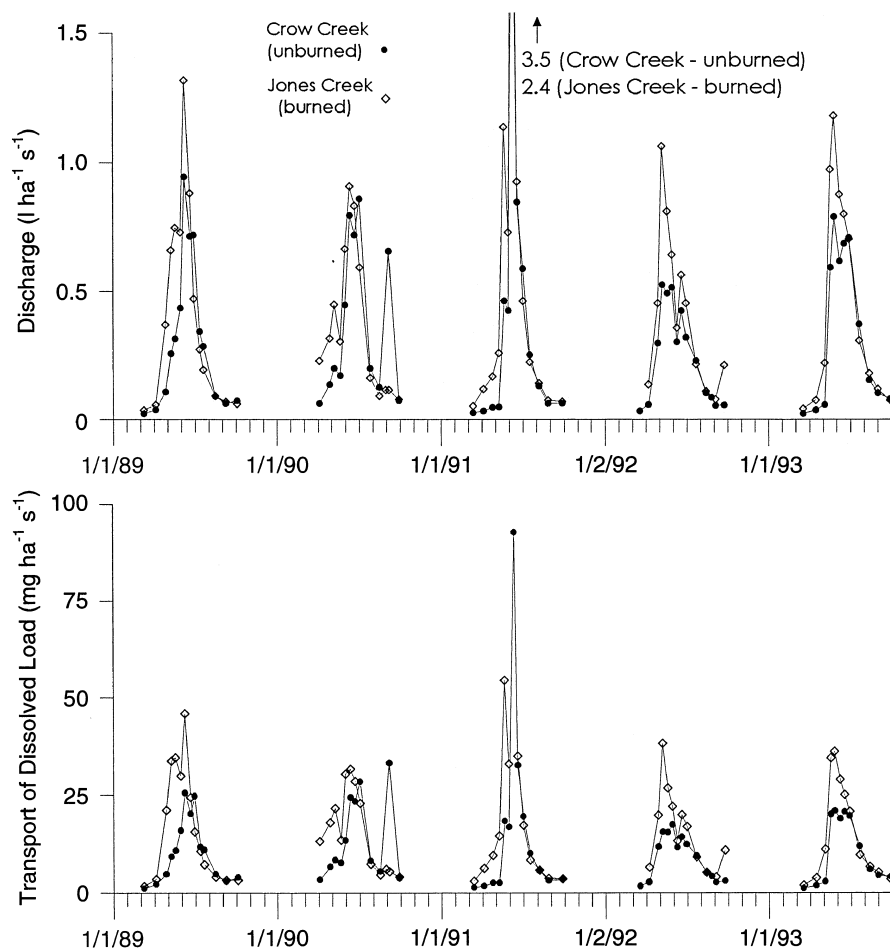


Fig. 4

Discharge and dissolved load transport rates for Jones and Crow Creeks (filled circles Crow Creek; open diamonds Jones Creek)

Table 1
Turbidity and suspended organic carbon

	Basin	Turbidity (NTUs)	Suspended organic carbon (mg/l)
Maximum	Jones	90	3.3
	Crow	85	0.6
Minimum	Jones	1.2	0.1
	Crow	0.3	<0.1
Average	Jones	10.0	0.65
	Crow	5.2	0.25
Standard deviation	Jones	14.9	0.87
	Crow	11.4	0.20
Samples	Jones	62	13
	Crow	62	11

age (Fig. 3); a large storm resulted in unusually large discharges for both streams (Fig. 4).

Turbidity and suspended organic carbon averaged about twice as much in Jones Creek (burned) as in Crow Creek (unburned; Table 1). Similarly, the sample standard deviation indicates more variability in the Jones Creek samples. The low values of turbidity and suspended organic carbon in both streams, however, suggests minimal transport of particulates.

Effects of persistence on the uncertainty of correlation estimates

Assuming conservative transport of dissolved constituents, one factor that may reveal the correlation between chemical weathering in the basin and surface water composition is the relationship between molar concentrations of major elements involved in the hydrolysis of rock-forming minerals. The similar ratio and pattern of major cations and silica are shown in Fig. 5.

Sample autocorrelation coefficients [$R1(x)$] were computed for each parameter of the water quality analyses. The significance for autocorrelation was tested using

$$|R1(x)| > R1^*$$

$R1^*$ equals $2/N^{1/2}$, where N is the number of samples. If this relationship is true, then there is less than a 5% chance that the actual autocorrelation for the population equals zero (Haan 1977).

Results (not shown) indicated that most parameters had a high degree of autocorrelation, except for turbidity, ammonium + organic nitrogen, and total phosphorus in the burned watershed of Jones Creek. In addition to these parameters, dissolved oxygen, nitrate, and orthophosphate showed insignificant autocorrelation in the unburned Crow Creek watershed.

Persistence, the tendency for a time series variable to be high following high values and low following low values, can be identified through sample autocorrelation coefficients. If two time series variables have persistence, then they will appear to be more highly correlated than they actually are.

The influence of persistence on time series sample correlation coefficients between calcium, silica, discharge and the other parameters was tested using effective sample size $N_{\text{eff-R}}$ and R^{*} :

$$N_{\text{eff-R}} = \frac{N}{1 + 2R1(x)R1(y)} \quad R^{*} = 1.96(N_{\text{eff-R}} - 3)^{1/2}$$

(Yevjevich 1972; Dingman 1994)

After correction for persistence, parameter time series showed significant linear correlation among most parameters, except specific conductance, dissolved oxygen, pH, ammonium + organic N, nitrate, and alkalinity (Table 2). Correlation coefficients between major inorganic cations (calcium, magnesium, sodium, and potassium) and three selected parameters, discharge, calcium, and silica, were very high; each exceeded 0.94. These results suggest that the hydrolysis of rock-forming silicate minerals control the major cation composition of the stream waters.

Weathering, mass balance, and equilibria

Background

The composition of water in Jones and Crow Creeks results from the reaction of infiltrated precipitation with soil and volcanic rock, biogeochemical processes in stream channels and soils, and mixing with snowmelt and direct runoff. The major ion composition of the waters can be roughly explained by a mass balance model involving dissolution of primary igneous minerals and equilibrium with phases precipitated during weathering. The earliest work using this approach was described in a benchmark paper by Garrels and Mackenzie (1967) on spring waters in the Sierra Nevada. The composition of springs was shown to be consistent with a closed-system model in which the primary rock-forming silicates are altered to form soil minerals plus a solution in steady-state equilibrium with these secondary minerals.

In contrast to the results by Garrels and Mackenzie (1967), Miller and Drever (1977) suggested that slight alteration of large volumes of rock rather than equilibration of water with soil clay minerals was the principal source of dissolved constituents of surface water in the North Shoshone basin. The composition of water results from the kinetics of plagioclase and pyroxene weathering rather than equilibration with clay minerals. This observation was partly supported by Miller and Drever's (1977) inability to develop a reasonable mass balance expression for the average water composition of the basin. The following reaction only appears consistent with mineralogy and surface water composition (Drever 1988):

Fig. 5

Transport rates for dissolved calcium, magnesium, sodium, and silica (*filled circles* Crow Creek; *open diamonds* Jones Creek)

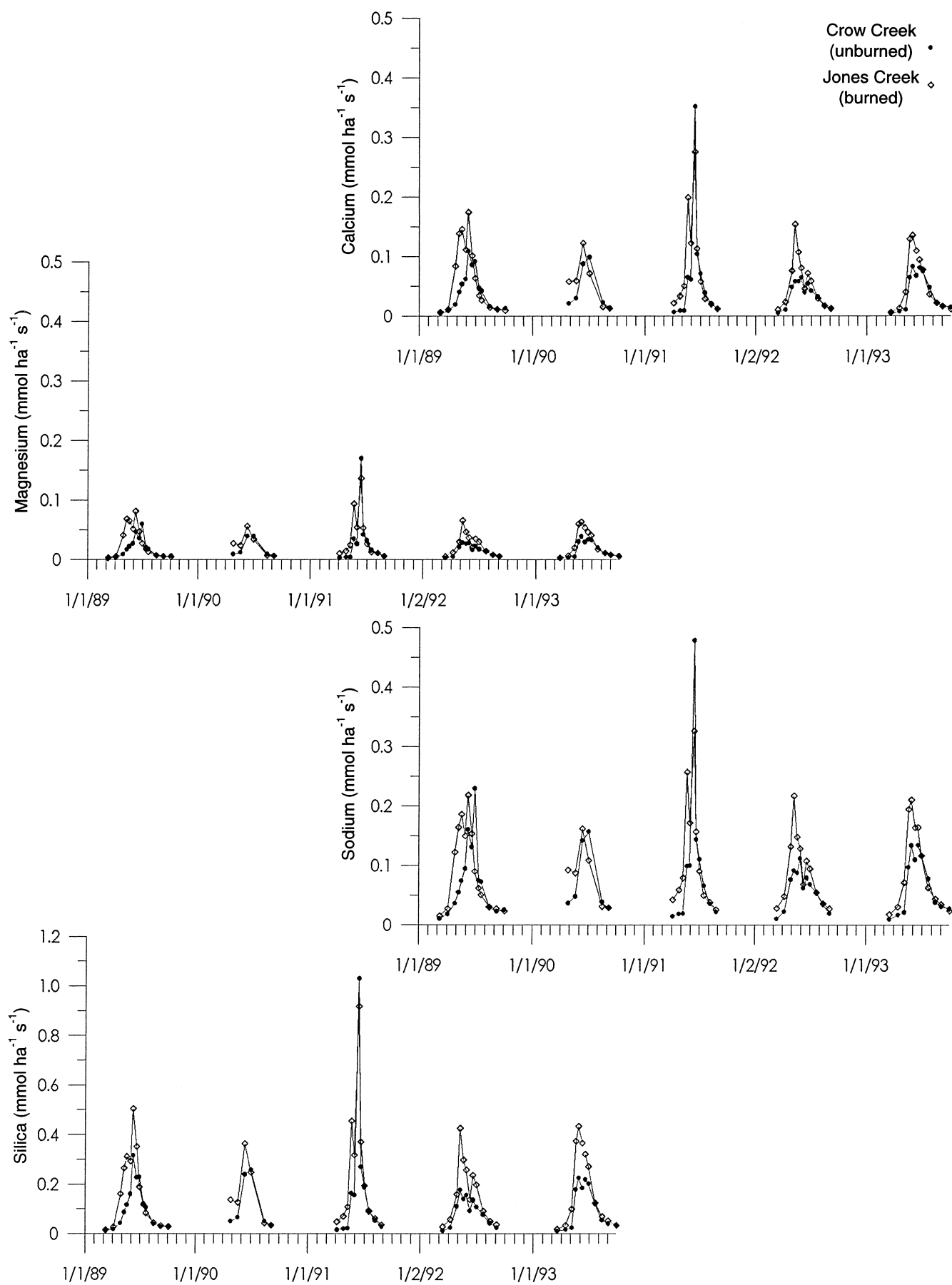
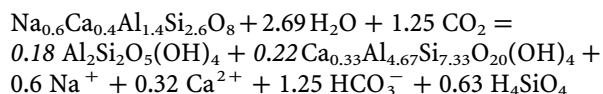


Table 2
Linear correlation coefficients among water quality parameters

	Jones Creek (burned)			Crow Creek (unburned)		
	Discharge	Calcium	Silica	Discharge	Calcium	Silica
Discharge	—	0.97	1.00	—	1.00	1.00
Specific conductance	−0.63	−0.46	−0.59	−0.63	−0.66	−0.64
Dissolved oxygen	0.04	0.07	0.04	−0.06	−0.06	−0.06
pH	−0.24	−0.30	−0.28	−0.09	−0.11	−0.11
NH ₄ ⁺ organic nitrogen	0.36	0.34	0.34	0.19	0.19	0.20
Nitrate	0.79	0.79	0.79	0.09	0.08	0.06
Total phosphorus	0.43	0.48	0.42	0.88	0.86	0.87
Organic carbon	0.62	0.51	0.60	0.92	0.89	0.92
Calcium	0.97	—	0.97	1.00	—	1.00
Magnesium	0.97	1.00	0.97	0.99	0.99	0.99
Sodium	0.97	0.99	0.97	0.97	0.98	0.98
Potassium	0.98	0.94	0.98	0.96	0.96	0.97
Sulfate	0.72	0.83	0.74	0.64	0.66	0.68
Silica	1.00	0.97	—	1.00	1.00	—



Abundant Ca-montmorillonite, but only trace quantities of kaolinite, if any, were observed in the soils of the basin (Miller and Drever 1977). However, the mass balance relationship given above suggests that kaolinite and Ca-montmorillonite occur in nearly equal molar proportions, as indicated by the reaction stoichiometry (italicized). Note that pyroxene, an important rock-forming mineral in the volcanic rock of the basins, was not included in the mass balance computation. Additional net geochemical mass balance reactions that are consistent with the US Geological Survey's Crow Creek and Jones Creek water quality data can be obtained with further analysis.

Assumptions

Several assumptions are required for the mass balance analysis:

1. The composition of water in the streams result from the interaction of infiltrating precipitation and the volcanic rock of the basins. Ideally, mass balance analysis requires chemical evolution along a single flow path, but in this application multiple flow paths with similar evolution lead to an average integrated mass balance for each basin. The composition of snow reported by Miller and Drever (1977) was used as the initial solution.
2. Evolution of the water's composition generally occurs following infiltration of precipitation, but prior to discharge to the surface water course. Although soil and ground water discharged into the stream probably mixed with variable amounts of direct melt and runoff, this mixing was not considered in the model because of a lack of detailed hydrological data.
3. Minerals precipitated during the weathering reactions must be in equilibrium with stream waters. Similarly, primary igneous minerals dissolved must remain unsatu-

rated along the entire pathline. WATEQ4 (Ball and others 1987) was used to demonstrate these relationships.

4. Aluminum was assumed to be conserved between reactant and product mineral phases, hence, dissolved aluminum was not accounted for in mass balance. (Aluminum averaged about 30 ppb in streamwater analyses).

5. Small increases in chloride and sulfur were modeled as dissolution of halite and gypsum. These phases are unlikely to occur as discrete minerals, but may roughly correspond to authigenic solutions trapped as inclusions in the volcanic rock.

The US Geological Survey's NETPATH computer code (Plummer and others 1991) was used to vary constraints and phases in the mass balance model. In this application, constraints are defined as chemical elements. Phases are any minerals or gases that can enter or leave the aqueous solution along the flow path. Fifty-seven water analyses were modeled: 27 from Crow Creek and 30 from Jones Creek. Table 3 shows the phases, constraints, and stoichiometry used in the model.

In addition to intermediate plagioclase (An₃₈) as the reactant mineral and Ca-montmorillonite and kaolinite as products, augitic pyroxene was included as a reactant and chlorite, illite, quartz added as phases that might be precipitated. Only calcium, magnesium, and silicon were included in the mass balance computation for pyroxene; the small concentrations of aluminum in volcanic augitic pyroxene (Deer and others 1978) had little to no effect on mass balance results. Also, neither electron transfer as a constraint nor iron as a component were considered in the mass balance analysis.

Results

Results of the modeling, as might be expected, were generally nonunique; several sets of phases could explain the observed water compositions. Only two sets appeared consistent with the mineralogic composition of the volcanic rocks and soils in the basin:

Table 3
Phases, constraints, and stoichiometry used in mass balance computations

Phases	Constraints (elements) and moles per phase							
	Ca	Mg	Na	Al	Si	C	S	Cl
Plagioclase (An ₃₈)	0.380	0	0.620	1.380	2.620	0	0	0
Pyroxene	1	1	0	0	2	0	0	0
Chlorite	0	5	0	2	3	0	0	0
Kaolinite	0	0	0	2	2	0	0	0
Ca-montmorillonite	0.167	0	0	2.330	3.670	0	0	0
Calcite	1	0	0	0	0	1	0	0
Gypsum	1	0	0	0	0	0	1	0
Halite	0	0	1	0	0	0	0	1
Quartz	0	0	0	0	1	0	0	0
CO ₂ -gas	0	0	0	0	0	1	0	0

plagioclase + pyroxene + CO₂ + (Na⁺ Cl⁻) + (Ca²⁺ SO₄²⁻) + initial solution = Ca-montmorillonite + kaolinite + calcite + final solution (Reaction 1)

plagioclase + pyroxene + CO₂ + (Na⁺ Cl⁻) + (Ca²⁺ SO₄²⁻) + initial solution = Ca-montmorillonite + chlorite + calcite + final solution (Reaction 2)

Figures 6 and 7 summarize the results of the mass balance computation. In Figs. 6 and 7, the moles of pyroxene dissolved (per kilogram of H₂O) are plotted against moles of dissolved plagioclase for each water analysis. For both kaolinite (Fig. 6; Reaction 1) and chlorite (Fig. 7; Reaction 2) precipitation, about 4–6 times more plagioclase than pyroxene weathers. The stoichiometry of the

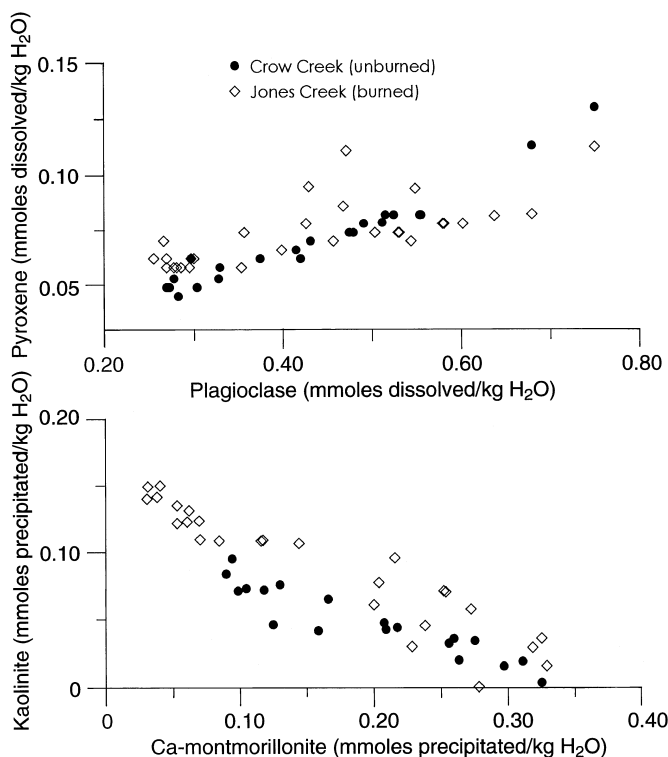


Fig. 6
Relationship between the moles of pyroxene and plagioclase dissolved per kilogram H₂O (upper plot) for each of the streamwater analyses; the lower plot shows the corresponding moles of kaolinite and Ca-montmorillonite precipitated, as required by mass balance for reaction 1 (filled circles Crow Creek; open diamonds Jones Creek)

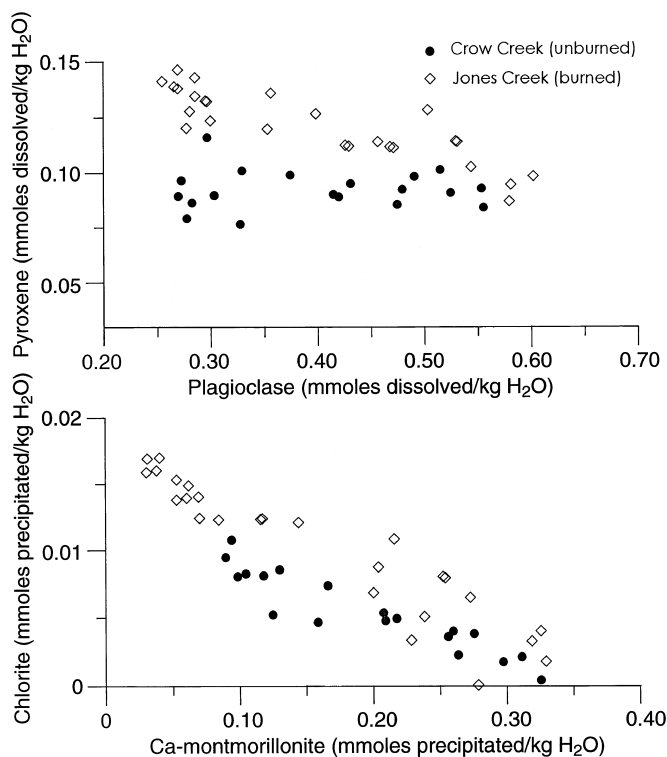


Fig. 7
Relationship between the moles of pyroxene and plagioclase dissolved per kilogram H₂O (upper plot) for each of the streamwater analyses; the lower plot shows the corresponding moles of chlorite and Ca-montmorillonite precipitated, as required by mass balance for reaction 2 (filled circles Crow Creek; open diamonds Jones Creek)

weathering reactions leads to the linearity between Ca-montmorillonite precipitated and the moles of either kaolinite and chlorite precipitated. This is revealed by the identical lower scatterplot with different scales (Figs. 6 and 7).

The molar ratio of Ca-montmorillonite to kaolinite or chlorite in the weathered product varies greatly (Figs. 6 and 7), but only a few of the analyses indicate that a greater amount of kaolinite than Ca-montmorillonite precipitated during weathering. All of the analyses indicate that at least twice as much Ca-montmorillonite as chlorite precipitated, consistent with Miller and Drever's (1977) observation that soils in the North Shoshone basin contain mostly Ca-montmorillonite with occasional small amounts of kaolinite and chlorite. Various linear combinations of the two mass balance reactions given above support the possibility that stream waters are in steady-state equilibrium with minerals precipitated during weathering.

Subtle, but significant differences exist between the unburned Crow Creek (filled circles) and burned Jones Creek (open diamonds) basins (Figs. 6 and 7). Generally greater concentration of dissolved SiO_2 was observed in Jones Creek (Fig. 5). Using the mass balance model, Jones Creek appears to have a greater pyroxene/plagioclase weathering ratio than Crow Creek. Furthermore, greater amounts of Ca-montmorillonite, and especially more chlorite and kaolinite, may have precipitated during accelerated weathering in Jones Creek basin. Unfortunately, water compositions from Jones Creek prior to the fire are not available to confirm if this difference can be attributed to the fire.

As noted by Drever (1988), dilution by direct mixing of soil and groundwater discharge with snowmelt and runoff would lead to an apparent increase in the relative amount of kaolinite precipitated, thus analysis of surface water at times when the streams carried the greatest percentage of baseflow provides for the best model of weathering mass balance.

Apparent effects of the fire on nutrients

Description

Following the fire, nutrient flux in the streams varied significantly. Nitrate in the unburned Crow Creek basin during spring runoff increased to a level approximately ten times greater than concentrations recorded five years after the fire (Fig. 8a). A rapid return to apparently normal transport rates occurred following the 1990 summer season (Fig. 8a).

Nitrate concentrations in Jones Creek in 1989, the year following the fire, appeared to be similar to the low levels exhibited by Crow Creek five years after the fire, but rose to a peak in the summer 1991 when over 1.5 mmoles $\text{ha}^{-1}\text{s}^{-1}$ were transported from the basin. Following 1991,

nitrate levels appeared to be slowly returning to possibly normal seasonal maximum concentrations of about 0.2 mmoles $\text{ha}^{-1}\text{s}^{-1}$ (Fig. 8a).

Total phosphorus transported from the two basins was generally similar for the years 1990–1993 (approximately 0.003 mmol $\text{ha}^{-1}\text{s}^{-1}$), although transport from the burned basin was slightly greater in 1990 and 1992. In the summer season immediately following the fire (1989), greater rates of phosphorus transport (averaging 0.011 mmol $\text{ha}^{-1}\text{s}^{-1}$) punctuated the water quality record for Jones Creek (Fig. 8b).

The incomplete record for ammonium and organic nitrogen showed no obvious changes or pattern during the 5 years following the fire (Fig. 8c), although the record for Jones Creek appears to parallel the trend in nitrate transport.

Possible interpretation

During fires, nutrients are lost through atmospheric transport of gases and particulates (although these losses may be added as deposition elsewhere) and, for longer periods following the fire, through increased erosion and runoff (Clayton 1976; Waring and Schlesinger 1985).

Losses often follow the trend $\text{N} > \text{K} > \text{Mg} > \text{Ca} > \text{P}$. Losses of N are particularly important because little N is derived from rock weathering. For example, Grier (1975) reported a 40% loss of soil N following an intense Washington State wildfire.

Nitrogen-fixing microbial activity following a fire can have a significant effect on the nitrogen cycle in several different ways:

1. Decomposition of partially burned wood and forest debris may take two or three years before reaching a maximum rate. The delayed leaching of nitrogen compounds formed in this process may have led to the broad 1990–1993 rise and fall in nitrate concentration for Jones Creek (Fig. 8a).
2. Slash burning has been shown to stimulate germination of *Ceanothus velutinus* (buckthorn), which may provide important N replacement by symbiotic fixation (Youngberg and Wollum 1976). This common brushy species thrives in forests opened by wildfire and ranges from the Pacific Ocean into the mountains of western Wyoming.
3. The greater rates of nitrate transport from the unburned Crow Creek basin during 1989 and 1990 may have resulted from atmospheric fallout of ash. Nitrogen released from ash by microbial activity occurs soon after fires and ash deposition (Mroz and others 1980). In addition, physical processes have been shown to affect nitrogen cycling. The time lag observed in the transport of nitrate from Jones Creek basin (Fig. 8a) may be related to slow leaching of N. Volatile forms of N can be driven to greater depth in the soil horizon during a fire; oxidation and slow leaching can occur over a period of several years following the fire. Losses of N from surface soils have been overestimated by failure to recognize increases of N in the lower soil profile (Mroz and others 1980). Fewer studies have examined the changes forest fires

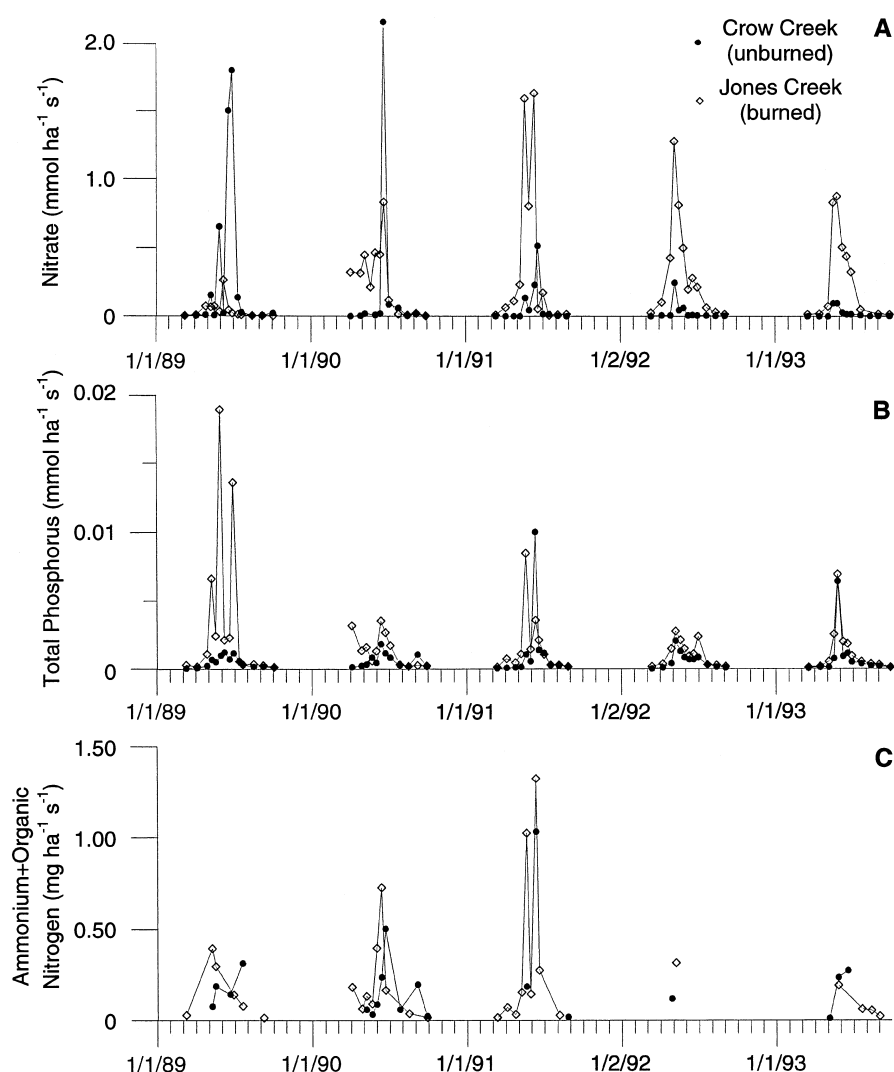


Fig. 8 Transport rates for **a** nitrate, **b** total phosphorus, and **c** ammonium + organic nitrogen (filled circles Crow Creek; open diamonds Jones Creek)

have on the phosphorus cycle. Wright (1976) noted a significant increase in phosphorus and potassium transport out of a burned Minnesota forest. Transport was greatest in the first 2 years following the fire, but less P was lost than transport from mature forests in the third year, presumably due to new growth. Apparently, phosphorus was readily transported from the burned Jones Creek basin the summer following the fire (1989; Fig. 8b), but not 2 years later, presumably due to uptake by newly established vegetation.

Conclusions

1. Jones Creek, which drains the burned watershed, generally showed a specific discharge similar to that of Crow Creek during the post-fire sampling period, but the flux of total dissolved solids was about 25–50% greater. A similar difference in turbidity and suspended organic carbon was also observed. Most of the major cation concentrations showed a very close correlation throughout the

year, both within and between the two basins. Dissolved silica was generally greater in Jones Creek.

2. Models of mass balance and comparison to existing data on the soils and lithology of the basins suggest that stream waters may be in equilibrium with Ca-montmorillonite, kaolinite, and chlorite. Mass balance indicates that plagioclase and pyroxene react to form mostly Ca-montmorillonite with much smaller amounts of kaolinite and chlorite. Equilibration of infiltrated precipitation with minerals formed through weathering of trachyandesite may explain the observed water composition in both Jones and Crow Creek, contrary to the results of an earlier study in the North Fork Shoshone River basin (Miller and Drever 1977). Weathering reactants and products are generally similar for the two basins, except that Jones Creek appears to have a greater pyroxene to plagioclase weathering ratio. It is unknown if this is related to the fire.

3. Nutrient flux (nitrate, ammonium + organic nitrogen, and total phosphorus) shows more variability and much less correlation than major ions. Transport of nitrate from the unburned Crow Creek basin for the 2 years fol-

lowing the fire peaked at levels about 4–5 times greater than in later years. This may be related to bacterially mediated nitrogen fixation during the degradation of ash.

4. A delayed peak in nitrate flux from Jones Creek may have resulted from nitrogen fixed by post-fire establishment of *Ceanothus*, gradual biological breakdown of charred wood, slow leaching of volatile nitrogen that had been driven to greater depth in soils during the fire, or a combination of these processes. Jones Creek experienced erratic peaks in phosphorus flux the first year following the fire, and then an apparently rapid return to levels similar to Crow Creek during later years.

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