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Soil solution chemistry in lodgepole pine (*Pinus contorta* ssp. *latifolia*) ecosystems, southeastern Wyoming, USA

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Abstract. Concentrations of the principal inorganic and organic solutes in the soil root-zone were measured in six contrasting lodgepole pine (*Pinus contorta* ssp. *latifolia*) forest ecosystems for five years (1979–1983). Consistent temporal changes in the principal inorganic solutes (Ca, Mg, K, Na, SO_4, Cl) were observed in all the forest stands and years of study: high concentrations at the initiation of snowmelt in the spring were followed by rapid declines to rather constant values in the mid to late stages of snowmelt. Except for K, concentrations of these solutes differed significantly between sites and between years. Sulfate was the principal mobile anion in the root-zone soil solutions, but contributions of bicarbonate and organic anions also were important.

The pH of root-zone solutions was relatively high (6.0), did not change significantly as snowmelt proceeded, and was significantly lower in high-clay soils. No consistent trends in bicarbonate alkalinity were observed and soil atmosphere CO_2 concentrations were only about 10 to 20 times above atmospheric levels, peaking at the end of the snowmelt interval. Concurrent changes in the concentrations of dissolved organic carbon, non-volatile acid-neutralizing capacity, and total Al and Fe indicated that these soil-forming metals were transported vertically in the soil as organic complexes. Precipitation of these complexes was more rapid and more complete in the soils with high clay content than in the coarser soils. Moreover, organic anions comprised up to 30% of the total anionic charge in the coarse-textured soils but less than 10% in the fine soils.

Little seasonal or spatial variation of inorganic N and P concentrations was observed in root-zone solutions, probably as a result of high biotic demand for these limiting nutrients. Flux of N and P in these ecosystems was predominately via organic forms so that losses of these nutrients was strongly linked to the mobility of dissolved organic carbon. However, a two-fold increase in the organic N:P and C:P ratios was observed during passage of melt water from the forest floor to mineral soil, evidence of more rapid mineralization of organic P.

Introduction

The soil solution serves the important functions of providing nutrient elements available for root uptake, mediating "weathering" reactions of the soil solid phase, and transporting solutes beneath the tree rooting zone to groundwater and streams. Although surveys using collecting lysimeters have advanced our understanding of the factors controlling soil solution chemistry (e.g. Ugolini et al. 1977), the information available is limited in many regards. The present study was undertaken to provide a better understanding of the factors controlling soil solution chemistry in lodgepole pine (*Pinus contorta* ssp. *latifolia*) ecosystems in southeastern Wyoming. These forests dominate the upper montane and lower subalpine landscape throughout the central and northern Rocky Mountains under many combinations of topographic position and slope aspect, soil type, and geologic substrate (Peet 1981). In these lodgepole pine forests water flux through the tree rooting zone occurs only during the 4–6 week snowmelt drainage interval, so that detailed information on within-season patterns is needed to characterize the leaching process. Few analyses of within-season patterns of forest soil solution chemistry have been reported (Feller 1977; Sollins & McCorison 1980).

Cation flux in soil solution often is regulated by the supply and mobility of anions (Nye & Greenland 1960), and three principal classes of anions have been identified: strong-acid anions (NO_3, SO_4, Cl), bicarbonate, and organic anions. Although usually only one or two of these classes is important at any particular site (Johnson & Cole 1980), all three anion classes could be abundant in soil solutions in our sites because of:

- SO_4 and Cl supplied by wet and dry precipitation (Fahey et al. in press);
- organic anions from forest floor leachate (Yavitt & Fahey 1986); and
- bicarbonate alkalinity resulting from the relatively high solution pH values (Johnson et al. 1977).

The mobility and proportional importance of each of these anion classes was expected to vary among lodgepole pine stands because of differences in biological activity (productivity, respiration, decomposition), topography and climate, and especially soil physical and chemical properties (Fahey & Knight 1986). Finally, high annual variation was not anticipated because of the regularity of the annual climatic and hydrologic pattern.

Study area

All the study sites were located in the Medicine Bow National Forest, southeastern Wyoming. The climate is cold and continental, with about two-thirds of the annual precipitation of about 60 cm coming in the form of snow from October to May. The surface geology of the Medicine Bow Mountains is rather complex. The vicinity of the major peaks was glaciated during the Pleistocene and mixed glacial tills form a surface mantle in many areas. The forest history of the region has been marked by extensive fires

Table 1. Some physical and chemical characteristics of soils in six lodgepole pine stands, southeastern Wyoming.

Stand	Depth	(% by volume)		(% of < 2 mm fraction)	(g/cm^3)	(% of < 2 mm fraction)		mg/g dry mass					
		Stones	Gravel	Clay	Bulk density	Volatile matter	pH	Ca	Mg	K	Na	Fe	Mn
Nash	root-zone	19.7	31.7	15.4	1.40	5.4	5.56	0.91	0.100	0.130	0.008	0.06	0.08
Fork	sub-soil	18.0	47.1	15.9	1.70	2.1	5.59	0.73	0.150	0.040	0.006	0.01	0.01
French	root-zone	18.8	19.0	23.9	1.22	7.1	5.20	1.53	0.240	0.100	0.009	0.02	0.16
Creek	sub-soil	18.1	54.0	21.1	1.44	2.6	4.88	1.20	0.260	0.035	0.003	0.01	0.01
Albany	root-zone	0.3	55.6	12.6	1.33	5.0	5.40	0.82	0.098	0.070	0.006	0.023	0.017
	sub-soil (50 cm)	0	72.4	8.4	2.40	2.5	5.61	1.15	0.183	0.056	0.005	0.006	0.009
Dry	root-zone	5.5	63.0	12.0	1.43	5.5	5.55	1.33	0.145	0.126	0.010	0.030	0.047
Park	sub-soil	6.6	41.0	11.5	1.74	2.3	5.65	2.75	0.431	0.089	0.010	0.012	0.003
Chimney	root-zone	nd[1]	nd	nd	nd	4.3	5.67	0.72	0.110	0.124	0.010	0.054	0.058
Park	sub-soil	nd	nd	nd	nd	1.9	6.06	1.25	0.202	0.021	0.008	0.008	0.005
Rock	root-zone	4.4	1.9	39.3	0.91	nd	nd	nd	nd	nd	nd	nd	nd
Creek	sub-soil	19.3	24.1	27.7	1.35	nd	nd	nd	nd	nd	nd	nd	nd

[1] nd = not determined

which destroyed pre-existing forests, and more recently, logging activity has created a patchwork of clear-cuts within this matrix of mature forest. We chose for intensive study a series of six contrasting sites, all dominated by stands of lodgepole pine, in order to sample a range of biogeochemical conditions within this forest type.

Nash Fork. This site is typical of many upland stands in the lodgepole pine forest of the central Rocky Mountains. Located at 2,900 m, the forest was initiated following a stand replacement fire in about 1875 and currently has a basal area of 65 m^2/ha and leaf area index (LAI, all surfaces) of 9.9. The soil, a typic Cryoboralf, was derived from a bouldery glacial moraine (Pleistocene) composed predominately of gneiss fragments and including less than 2% carbonates (dolomite and calcite). The soil was a gravelly loam with very weak profile development, well-drained during snowmelt. Illite and chlorite, probably derived from metasediments in the glacial source area, were present throughout the profile, whereas the autogenic clay mineral fraction was dominated by kaolinite to about 0.6 m depth and by smectite at greater depths in the profile (J. Drever, pers. commun.). Slight depletion of oxalate-extractable and citrate/dithionate-extractable Fe and Al was evident in the surface mineral soil (0–2 cm depth). For most chemical features the soil at Nash Fork was intermediate among the sites (Table 1), but organic matter and nutrient accumulation in the forest floor was higher, probably reflecting in part the higher primary productivity of this site (Pearson et al. 1984).

French Creek. The forest at this site, on the west slope of the Medicine Bow Mountains at 2,950 m, was older than the others with some trees exceeding 250 years. The stand had low stem density, basal area (37 m^2/ha) and LAI (4.5). The typic Cryoboralf soil was derived from a Pleistocene moraine composed mostly of quartzite, with a small quantity of metagabbro and no detectable carbonates. The soil was rich in the clay fraction (20 to 25%), with consequent impedance to snowmelt drainage inducing small amounts of overland flow in most years. Clay mineralogy of this soil resembled that at Nash Fork, but organic matter and extractable bases were in much higher supply at the French Creek site. Forest floor organic matter and nutrient accumulation were relatively low in this stand, probably reflecting low productivity and high decomposition rates (Fahey 1983).

Dry Park. This stand (2,800 m) apparently was initiated by fire in the same year as the Nash Fork stand. Basal area (42 m^2/ha) and LAI (7.3) were intermediate in comparison with the other sites and stem density in different parts of the stand ranged from 2,000 to 14,000 stems/ha. Surprisingly, none of the measurements made to date has differed between areas of the stand with differing density. The Cryochrept soil developed from fluvial deposits of Pleistocene age, dominated by quartzofeldspathic gneiss and with no evidence of carbonates. Soils were very gravelly (over 60% of soil volume was fragments 0.2–4.0 cm diameter) and freely-drained near the surface, but a perched water table rose to the surface at the end of the snowmelt period. Most soil chemical features resembled Nash Fork (Table 1), but forest floor biomass was significantly lower at Dry Park (Fahey 1983).

Rock Creek. A fire in about 1910 destroyed a mixed coniferous forest at 3,050 m elevation and initiated this younger stand. The forest had moderately low density and basal area (26 m^2/ha), but high LAI (9.0). The typic Cryoboralf soil developed on a Pleistocene moraine dominated by quartzite, and high surface clay content (38% of < 2 mm fraction) impeded drainage; overland flow of melting snow dominated the hydrologic regime. Organic matter and nutrient accumulation in the forest floor was lower than the other sites, partly reflecting the younger age of the stand, and decaying wood inherited from the previous forest generation was the largest detrital compartment (Fahey 1983).

Albany. This uneven-aged stand of low density (1,920 stems/ha) basal area (20 m^2/ha) and LAI (3.9) was located at 2,850 m near Albany, Wyoming and was the driest and most well-drained of the study areas. The lithic Cryochrept soil was derived from deeply-weathered Sherman granite (K-feldspar, quartz, plagioclase, horneblende). Kaolinite was present throughout the profile, and vermiculite, formed from alteration of biotite in the Sherman granite, peaked at about 20 cm depth. Smectite became prominent at greater depths (> 60 cm) in the soil/regolith, and micas were apparent throughout the profile. Because of the coarse nature of the parent material and soil (60% gravel; 70% sand in fine fraction), drainage at this site was very rapid and waterholding capacity very low (Knight et al. 1985). Soil extractions indicated lower availability of base cations (Table 1), and forest floor mass was low and spatially variable, with little or no detrital accumulation in areas between trees where the canopy was open.

Chimney Park. This low elevation site (2,800 m) was situated in a topographic depression on soils derived from high-grade metamorphics with quartzofeldspathic gneiss and metagabbro. The forest stand was similar in most respects (age, basal area, LAI) to Nash Fork and Dry Park, and stem density was high (9,700 stems/ha). As at the Dry Park stand, a local perched water table reached the surface towards the end of the snowmelt period each year, and based on observations of topography and surface geology, this stand received sub-surface flow from adjacent forested areas. Except for relatively low Ca levels, soil chemical features were similar to the other sites (Table 1), and forest floor accumulation was similar to that at Dry Park.

Methods

Soil analysis

Soil samples were collected at a total of twelve random points and four depths from the faces of four soil pits excavated by back-hoe in summer 1980 in each stand. Samples were wet sieved to remove the gravel fraction, and the fine fraction was dried to constant mass at 80 °C. Percent sand, silt, and clay was determined by a combination of dry-sieving and hydrometer analysis (Day 1965) by the Soil Testing Laboratory, University of Wyoming. Organic matter was estimated as loss-on-ignition for 4 h at 600 °C. Soil pH was determined by glass electrode on a 1:1 soil–water slurry. Cations (Ca, Mg, K, Na, Fe, Mn) were extracted with 0.1 N ammonium acetate, with element determinations by atomic absorption spectrophotometry. Finally, adsorption and desorption of organic carbon were measured on the Nash Fork and French Creek soils by shaking soil samples with natural forest floor leachate of varying dissolved organic carbon (DOC) concentrations, measuring initial and final DOC levels in solution, and calculating the concentration at which organic solutes were neither adsorbed nor desorbed (the equilibrium concentration) (McDowell & Wood 1984). Four concentrations of DOC (2, 6, 12, and 24 mg/L) were prepared by dilution of natural forest floor leachate, and equilibrium concentrations were calculated for several incubation intervals ranging from 5 min to 4 h.

Collection and analysis of soil solutions

Six to twelve porous cup lysimeters (5 cm diameter) were installed at about 0.4 m depth (below about 90% of tree roots; Pearson et al. 1984) in each stand in summer and fall 1978. Access holes were power-augered using a 6 cm diameter bit, the lysimeters imbedded in powdered silica sand, and the holes firmly backfilled with soil. Samples were collected under tension (10–12 kPa) at 3- to 7-day intervals throughout the snowmelt drainage period in 1979–1983. The total water volume collected from a lysimeter during the season typically corresponded to a 10–15 cm diameter cylinder of the snowpack (i.e. 3 to 6 L), so that the soil volume exploited for solution collection was not excessive.

Samples were sealed in plastic bottles with minimal head space, except early and late in the snowmelt drainage period when sample volume was small. Samples always were transported to the laboratory on the day of collection and were analyzed for pH using glass and reference electrode, nearly always on the same day. For years 1979–1981 total alkalinity was estimated by titration to pH 4.5 with carefully standardized HCl (Golterman et al. 1978). In 1982 and 1983 a more detailed titration procedure was employed. Samples were titrated to pH 3.5 in a N_2 atmosphere using an automatic titrator (Radiometer, Inc.), and the total alkalinity end point was estimated by a Gran plot interpolation procedure (Stumm & Morgan 1981). Samples were purged of CO_2 with N_2, and to estimate nonvolatile alkalinity each sample was titrated (under N_2) from the total alkalinity end point to the original pH with standardized NaOH. Total acidity was estimated by titration (under N_2) to pH 8.3 with NaOH, and separate CO_2-purged samples were also titrated to measure non-volatile acidity.

Samples were stored at 4 ± 2 °C for up to 3 days (usually less than 24 h) before being analyzed colorimetrically for NH_4, NO_3 (cadmium reduction) and ortho-phosphate (molybdate) on a continuous flow analyzer (CFA; Scientific Instruments, Inc.). The phenol-hypochlorite method for NH_4 was adapted to prevent hydrolysis of organic N, as prescribed by White & Gosz (1981). In 1979, NH_4 and ortho-P were analyzed with similar methods, but colorimetric determinations were made with a Beckman uv/vis spectrophotometer equipped with a 5 cm cuvette. Cross comparison of these methods indicated insignificant differences in analytical results. Nitrate was not analyzed in 1979.

In 1982 and 1983, samples were analyzed for dissolved Al, Fe and Si following filtration through a 0.1 um membrane filter. Aluminum was measured by the pyrocatechol violet method of Dougan and Wilson (1974) and dissolved iron by the ferrozine method of Stookey (1970). Dissolved silica was measured by a colorimetric method on the continuous-flow analyzer (Fanning & Pilson 1973).

Samples were stored at 4 ± 2 °C for up to 12 weeks (usually less than 4 weeks) before being analyzed for the remaining dissolved constituents. Metal cations (Ca, Mg, K, Na, Mn) were measured by atomic absorption spectrophotometry on a Perkin-Elmer model 560, with 1% lanthanum added to prevent interferences in Ca and Mg analysis. In 1979, sulfate was measured by a turbidimetric method (Rand 1976) on the Beckman spectrophotometer, whereas in 1980–1983 a methyl-thymol blue method was employed on the CFA (Anon. 1971). To prevent interference from coloured organic compounds (Cronan 1979), samples were autoclaved for 2 h in the presence of 1% H_2O_2; thus, these sulfate data include some hydrolyzed organic sulfur (probably less than 3% of SO_4), and direct comparison of SO_4 values in 1979 with those for 1980–1983 may be problematic. Chloride was determined with a specific ion electrode (Orion, Inc.) in 1979–80, whereas a colorimetric method (Zall et. al. 1956) was employed on the CFA in 1981–1983. Cross-comparison of these methods indicated good agreement. In 1982 and 1983, dissolved organic carbon (DOC) was measured by coulometric titration (Coulometrics, Inc.), following sealed ampule persulfate digestion (Huffman 1977).

Concentrations of CO_2 in the gaseous phase of the soil were determined in two stands (Nash Fork and Albany) by direct sampling at 2–4 week intervals during 1982–1983 (less frequently in winter). Samples were collected at 25 cm depth by forcing a 10 mm diameter probe into the soil from the surface or from the face of soil pits. Immediately after removing the probe, a specially constructed gas-tight syringe (5 mL), equipped with a side-port needle, was inserted into the soil at the end of the void created. Soil atmosphere samples were injected into field-evacuated, gas sampling vials (10 ml) and returned to the laboratory. Repeated resampling showed that diffusion/convection from the atmosphere was not a problem. Concentration of CO_2 was measured within 48 h (usually the same day) by in-line injection into a Beckman infrared gas analyzer, and fresh standards were prepared in the field by dilution of pure CO_2 for each analysis. This method could not be used when soils were near saturation or frozen.

Statistical analysis

Because of spatial variation in the timing of snowmelt within stands, caused by drifting of snow and varying radiation loads at the snow surface, the lysimeters did not all begin collecting soil water on the same date in a particular year. Furthermore, plots of element concentrations in root-zone solutions collected by individual lysimeters indicated that concentrations of many dissolved constituents declined steadily as snowmelt proceeded, reaching rather constant levels in mid-to-late stages of snowmelt. This temporal variation dictated that a special approach was needed to quantify the sources of variation in soil solution chemistry during snowmelt drainage in these lodgepole pine ecosystems.

For each lysimeter, solute, and year of collection, the most significant linear regression of concentration against time (days since first collection) was calculated, and the slope and intercept from these regressions were used in subsequent analysis of variance. The number of points in the regressions ranged from 3 to 8, and the slope was set equal to zero if the regressions were not significant ($p > .01$) with the intercept defined as the mean concentration for all collections. The ANOVA quantified variation from three sources: within stands, among stands, and among years. If the ANOVA indicated significant variation among stands or years, pair-wise comparisons were made using Duncan's test. One additional parameter from the regressions was chosen to characterize the soil solution composition for each solute, stand, and year; i.e. the constant minimum concentration reached following the early-season decline. This was determined from the mean of all collections after the last point in the declining phase (as defined by the best linear regression, above) and also was included in the ANOVA. To permit comparison of element behavior, significant differences among solutes in the relative slope (i.e. slope/concentration) during the phase of concentration decline were analyzed in the same manner as outlined earlier.

For pH, NH_4, NO_3 and ortho-P, significant seasonal trends were uncommon and the usual ANOVA was applied without modification. Seasonal trends were observed for bicarbonate, organic anions, DOC, and Al, but a mid-season peak in concentration often confounded the use of the previous method so that we applied ANOVA without the modifications.

Results

Acidity and alkalinity

The pH values of root zone soil solutions in these lodgepole pine ecosystems were relatively high in comparison with other cool-temperate, coniferous forests, with an overall mean of nearly 6.0 for all sites, lysimeters, and years (Table 2). Time trends in pH as snowmelt proceeded usually were small and not statistically significant (Fig. 1). The lowest pH values were observed in the two high-elevation sites (French Creek, Rock Creek), both of which also exhibited high clay contents in the upper mineral soil and lacked carbonate minerals. The highest soil solution pH values occurred at the Chimney Park site in soils derived from high-grade metamorphic rocks and at Dry Park where soils were derived from fluvial deposits dominated by gneiss (Table 2).

As expected, bicarbonate alkalinity also varied significantly among sites (Table 2) and was negatively correlated with H^+ concentration ($r = 0.55$, $n = 1800$). Low CO_2 concentrations were observed in the lodgepole pine rooting zone (0.3–0.6% by volume) and, surprisingly, the highest concentrations occurred at the end of the snowmelt period. Finally, no consistent within-season trends were observed for HCO_3 (Fig. 1).

Table 2. Solute concentrations in the root zone solution of six lodgepole pine ecosystems, southeastern, Wyoming. In columns, values with the same letter are not significantly different ($p > 0.05$).

Stand	pH	m Eq-litre^{-1}	ug-litre^{-1}				mg-litre^{-1}		mg-litre^{-1}			
		Titratable alkalinity	NH_4-N	NO_3-N	ortho-P	organic P	organic N	DOC	C:N	Fe	Al	Si
Nash Fork	5.80^{a}	0.160^{b}	23^{a}	3^{a}	10	19^{b}	0.51^{b}	16.5^{b}	32	0.323^{c}	0.235^{b}	13.2
French Creek	5.69^{a}	0.106^{a}	21^{a}	20^{b}	7	3^{a}	0.17^{a}	4.5^{a}	26	0.021^{a}	0.056^{a}	13.9
Albany	5.88^{a,b}	0.109^{a}	25^{a}	7^{a}	7	10^{b}	0.30^{b}	8.5^{b}	28	0.074^{b}	0.118^{b}	10.1
Dry Park	6.09^{b}	0.248^{c}	21^{a}	3^{a}	11	13^{b}	0.35^{b}	nd	nd	nd	nd	nd
Chimney Park	6.27^{c}	0.307^{d}	15^{a}	8^{a}	9	18^{b}	0.36^{b}	nd	nd	nd	nd	nd
Rock Creek	5.90^{a}	0.138^{a,b}	10^{b}	3^{a}	6	8^{b}	0.20^{a,b}	nd	nd	nd	nd	nd

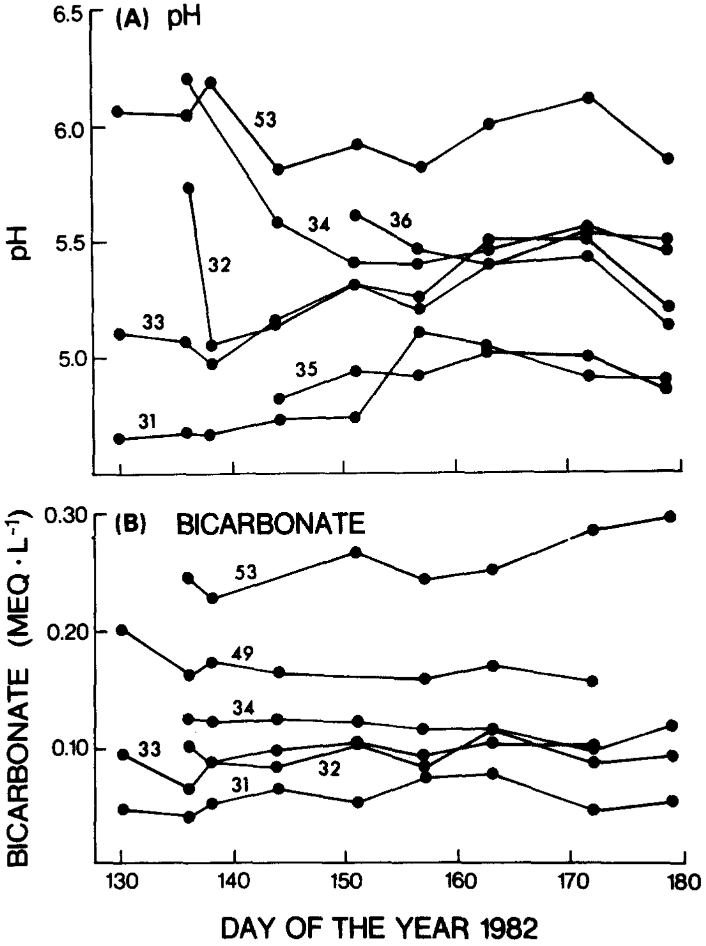

Fig. 1. Seasonal changs in (*A*) pH and (*B*) bicarbonate alkalinity for several soil solution lysimeters (indicated by number) in 1982 at the Nash Fork lodgepole pine ecosystem, southeastern Wyoming.

Carbon, nitrogen and phosphorus

Concentrations of dissolved organic carbon (DOC) in root-zone solutions were much lower than for organic horizon leachates in these forests. A relationship between DOC and soil clay content was obvious, with much lower DOC in the fine soil at French Creek than the coarse soils at Nash Fork and Albany. Much lower equilibrium DOC concentrations were observed for the French Creek than the Nash Fork soils (Table 3) based upon adsorption/desorption isotherms (McDowell & Wood 1984). DOC con-

Table 3. Equilibrium concentrations of dissolved organic carbon (DOC) for air-dry mineral soils (< 2 mm fraction) collected from two soil depths in two lodgepole pine ecosystems, southeastern Wyoming (see text for method).

Site	Incubation time	Equilibrium DOC (mg/L)	
		0–15 cm depth	15–30 cm depth
Nash Fork	0.1–0.3 h	58	37
	1.5–4 h	24	32
French Creek	0.1–0.3 h	14	10
	1.5–4 h	17	16

centration increased in the early stages of snowmelt and declined late in the leaching period.

Most of the soil solution N was in organic forms (85–95%, Table 2), as concentrations of NH_4 and NO_3 were very low at all times. The same was true for phosphorus, although the proportion of organic P was lower, and ortho-P exceeded organic P in the high clay soil at French Creek.

Concentrations of NH_4 were significantly higher early in the snowmelt period in four of the sites in certain years, and differences between sites were insignificant (Table 2). For NO_3, all sites had unweighted mean concentration less than 10 ug/L, except for French Creek which was significantly higher at 20 ug/L.

Aluminum, iron and silicon

Despite the high pH values observed in the root-zone solutions, concentrations of dissolved aluminum were relatively high (grand mean = 0.11 mg/L; Table 2). Most of the Al probably was in the form of organo-Al complexes and the overall correlation between DOC and Al was fairly high ($r = 0.62$, $n = 292$). Non-volatile acidity, a measure of the concentration of undissociated acid-functional groups of DOC, exhibited the highest correlation with Al ($r = 0.65$). Trends in dissolved iron concentrations in root zone solutions were similar to those for Al ($r = 0.78$), and the molar concentrations of these principal soil constituents also were comparable. Levels of dissolved silica were very high (grand mean = 12.4 mg/L) and showed a weak declining trend as snowmelt proceeded.

Major cations and anions

The concentrations of six important ions (Ca, Mg, K, Na, SO_4, Cl) were usually highest at the initiation of snowmelt drainage, declined steadily during the first few weeks of melt, and reached rather constant minimum

Table 4. Between site comparison of (a) initial maximum solute concentration and (b) late season minimum solute concentration for major cations (Ca, Mg, K, Na) and strong-acid anions (SO_4, Cl, NO_3) in soil solutions of six lodgepole pine ecosystems, southeastern Wyoming. In columns, values with the same letter are not significantly different ($p < 0.05$).

Stand	Molar concentration (m mol/L)	
	Initial maximum	Late minimum
	Basic cations	
Nash Fork	0.67^{a}	0.31^{b}
Chimney Park	0.54^{b}	0.36^{a}
Dry park	0.48^{b}	0.29^{b}
French Creek	0.31^{c}	0.15^{c}
Albany	$0.26^{c,d}$	0.14^{c}
Rock Creek	0.21^{d}	0.15^{c}
	Strong-acid anions	
Nash Fork	0.38^{a}	0.15^{a}
Chimney Park	0.28^{b}	0.14^{a}
Dry Park	0.26^{b}	$0.11^{b,c}$
French Creek	0.19^{c}	0.08^{c}
Albany	$0.14^{c,d}$	0.08^{c}
Rock Creek	0.12^{d}	0.06^{cd}

concentrations in the mid and late stages of snowmelt drainage. We analyzed variation in concentrations of these ions by describing this temporal pattern with three parameters:

— the initial maximum concentration (y-intercept; mg/L),
— the slope of concentration decline ($\mathrm{mg\,L^{-1} - day^{-1}}$) and
— the mean minimum concentration (mg/L).

Each parameter was estimated in each year for every lysimeter, and ANOVA was used to judge the significance of the relationships between site, year, and soil solution concentrations.

Concentrations of major cations and anions in the soil solution varied both among stands and years. A three-fold range was observed in unweighted mean concentrations among the six stands, and both early-season maxima and late-season minima differed significantly for most of these solutes (Table 4). There were large differences between years for all except K. Thus, the K concentration in the root-zone solution early in snowmelt differed widely from site to site but not from year to year (Fig. 2).

Close inspection of Fig. 2 reveals that for Ca (also Mg, Na, and SO_4), all stands had high initial concentrations in 1981 and low in 1980 (except French Creek), 1982, and 1983. Two stands had very high concentrations of these ions in the first year of collection (Nash Fork, Chimney Park), perhaps resulting from disturbance associated with installing the lysimeters. Thus, only 1981 can be considered as clear evidence for high annual variation.

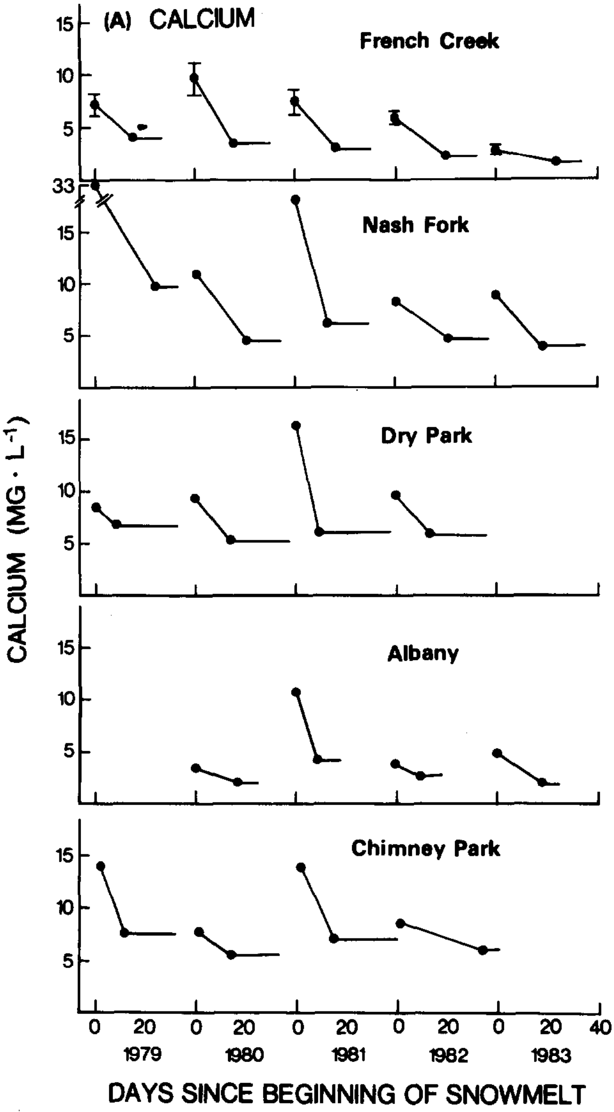

Fig. 2.

Relative slope values (i.e. slope/Ymax) provide an index of the rate of depletion of the various ions from exchangeable or storage pools in the early stages of snowmelt. The relative slope of concentration decline differed significantly among the six major solutes (Fig. 3), with the highest values for Ca (.038), Mg (.036), SO_4 (.038), and Cl (.037); intermediate values for Na (.028); and lowest for K (.019).

As expected, high correlations were observed between the major inorganic solutes. The highest correlation was observed between Ca and Mg (Spearman's rho = 0.86, n = 1,907) and high correlations of these ions with Na

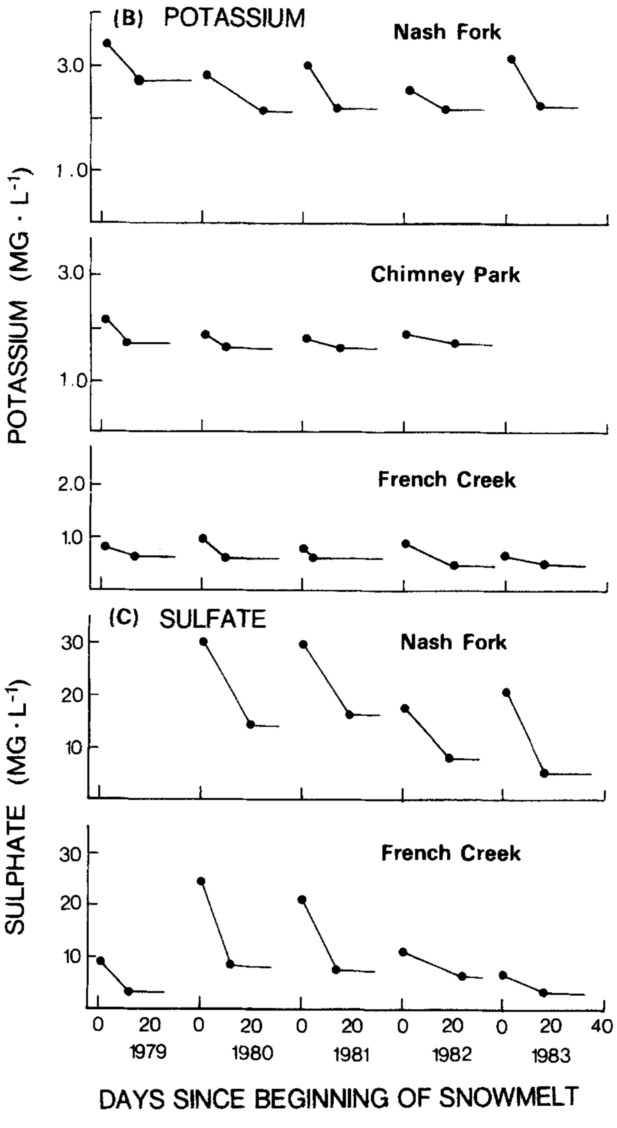

Fig. 2. (*A*) Changes in the concentration of calcium in soil solutions of lodgepole pine ecosystems, southeastern Wyoming, during the snowmelt drainage period for five years and five stands. (*B*) same for potassium in three stands. (*C*) same for sulfate in two stands. The seasonal patterns are based on regression equations developed from 8 to 12 collections from 6 to 10 lysimeters at each site in each year (see text).

also were observed (Ca vs. Na, $r = 0.71$; Mg vs. Na, $r = 0.69$). Much lower correlations were observed between K and the other cations, and between these base cations and the strong-acid anions (SO_4 and Cl).

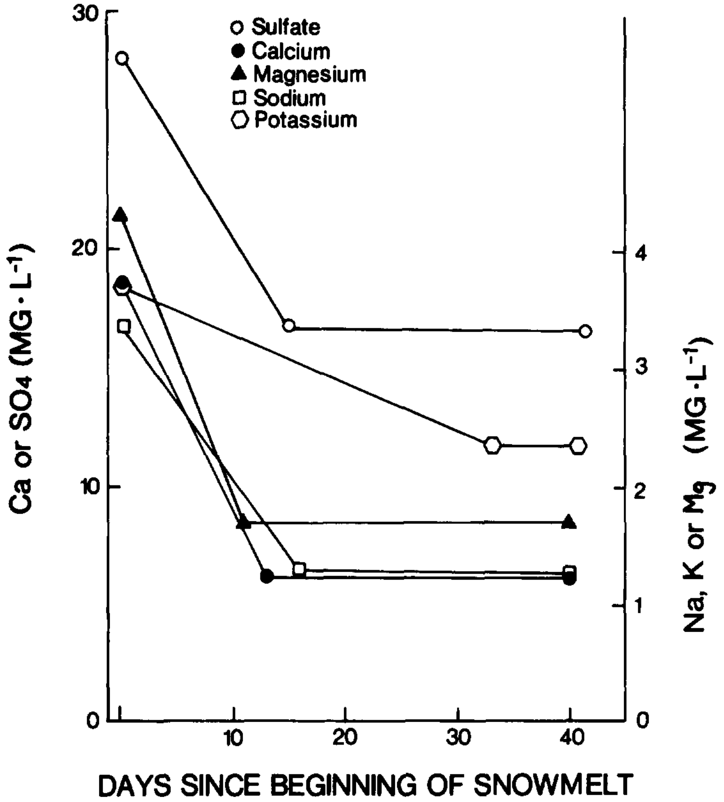

Fig. 3. Changes in the concentration of five major dissolved ions in soil solutions of the Nash Fork lodgepole pine ecosystem during snowmelt period, 1981.

Charge-balance deficit

For most of the soil solution samples a substantial charge-balance deficit (i.e. sum of cation equivalence minus sum of anion equivalence) was observed, indicating that some unmeasured anions contributed to the ionic strength of the solutions. In some of the samples much of this deficit was accounted for as dissociated organic anions as detected by acidimetric titrations (i.e. non-volatile acid-neutralizing capacity [ANC]). In general, non-volatile ANC exhibited time trends and between-site differences which were similar to DOC and, as expected, the correlation between these related solutes was high ($r = 0.60$). Low values of both were observed in the fine-textured soils at French Creek. In many of the soil solution samples a large charge-balance deficit was observed even when non-volatile ANC was included in the calculation, suggesting that some of the functional groups of the DOC behaved as relatively strong acids and apparently remained disso-

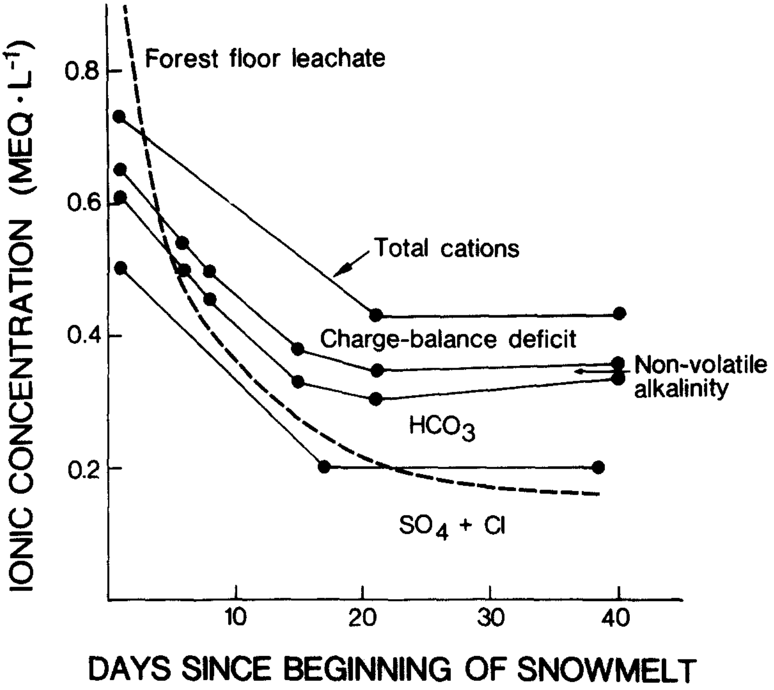

Fig. 4. Changes in concentrations of total cations and various groups of anions in soil solutions during snowmelt 1982 at the Nash Fork lodgepole pine ecosystem, southeastern Wyoming (see text for method of calculation). The dashed line indicates total cation concentrations in forest floor leachate (from Yavitt & Fahey 1986).

ciated at the acidimetric titration end-point. The charge-balance deficit at the Nash Fork stand was much larger than the non-volatile ANC, and increased slightly in the early stages of snowmelt before declining in the middle and late stages (Fig. 4). This component was much lower in solutions from the fine-textured soil at the French Creek stand, as was previously noted for DOC and non-volatile ANC (Table 2).

Post-snowmelt concentrations

Increasing concentrations of several dissolved ions were observed at the end of the snowmelt drainage period for some lysimeters and years. Surprisingly, this phenomenon was noted most frequently for K (44% to 61% of the lysimeters in the various stands), with intermediate values for Na (16% to 48%) and lower for Ca and Mg (16% to 37%). The relative slope of the increase (slope/Ymin) was similar for the various cations within sites but differed substantially among sites.

Because soil solutions could be obtained only when the soil was near field capacity, samples rarely were obtained during mid-summer or fall in this summer-dry environment. However, unusually heavy summer rains resaturated the soil profile later in the season at most sites on two occasions during the study: late August 1979 and early October 1982. During the former event, extremely high concentrations (about 5 times higher than the Ymin concentration) of Ca, Mg, and SO_4 were observed at all the sites and moderately high values (about 2 times Ymin) were noted for the other major solutes (K, Na, Cl). However, during the latter event concentrations of all these solutes were much lower than during the event in 1979 (less than 2 times Ymin).

Discussion

Temporal patterns in solute concentrations

Within-season patterns of leachate chemistry have rarely been reported for forest ecosystems (Feller 1977; Sollins & McCorison 1981). In these lodgepole pine ecosystems a persistent snowpack melts in a continuous spring flush. We observed a rapid decline in the concentrations of strong-base cations (Ca, Mg, K, Na) and strong-acid anions (SO_4, Cl) in the early stages of snowmelt in a regular pattern which has not been reported for other forest ecosystems (Fig. 2). We will briefly discuss four possible contributors to this pattern:

1. A similar temporal pattern in chemistry of infiltrating snowmelt (i.e. forest floor leachate; Yavitt & Fahey 1986);
2. Longer residence times of soil solution because of slow water movement;
3. Mobilization of salts added by small rainstorms during the previous summer and fall; and
4. Mobilization of products of soil weathering reactions.

1. Yavitt & Fahey (1986) observed declining concentrations of total cations in forest floor leachate at three of these sites (Fig. 4), but this decline was associated primarily with depletion of soluble organic anions. In contrast, sulfate, the principal dissolved anion (Fig. 4), accounted for most of the decline in base cations in mineral soil solutions. Thus, infiltrating solutions do not entirely account for the within-season patterns in cation and anion concentrations.

2. Slow rates of snowmelt early in the season (Knight et al. 1985) could lead to longer residence times. Except at French Creek, soil hydraulic conductivities are high enough not to limit snowmelt percolation even under the most rapid melt rates (Nyberg & Fahey, in press).

3. Summer rain events usually are not large enough to leach through the soil, and solutes carried to the soil by these rains could accumulate and be re-mobilized by snowmelt. Yavitt & Fahey (1984) estimated that forest floor leaching in summer transported about 50 mEq $m^{-2} yr^{-1}$ of strong-acid anions to the mineral soil.

4. Soil weathering products also could accumulate in the soil in the 10-month interval between leaching events. For example, proton extrusion by roots, owing to excess of cation over anion uptake by roots (Fahey & Knight 1986) accounts for about 100 mEq $m^{-2} yr^{-1}$ in the Nash Fork site, apparently consumed in weathering and ion exchange reactions.

We tentatively conclude that each of these processes may have contributed to the observed declining ion concentrations during snowmelt. It will be very difficult to quantify the magnitude of each of these individual influences.

Just as the phenomenon of declining solute concentrations cannot be explained in a simple way, so also the relative slope of the concentration decline probably is controlled by complex interactions. The highest relative slopes (i.e. slope/Ymax) were observed for the divalent cations and SO_4, with lower values for the monovalent cations (Fig. 3). The cations are supplied to the soil solution by leaching of the forest floor and by ion exchange and "weathering" in the mineral soil, whereas concurrent root uptake of nutrient ions as well as precipitation of organic complexes provide potentially large sinks for the base cations. Except at the beginning of snowmelt leaching, major ion concentrations were higher in soil solutions than in forest floor leachate (Fig. 4), suggesting that dissolution from the solid and adsorbed phases in the mineral soil was an important source of ions. Based upon the usual cation exchange isotherms (Bolt 1967), preferential desorption of Na and K would be expected, leading to high relative slopes; low levels of adsorbed Na and high biotic demand for K could help to explain this observation. Also, the stability of SO_4 complexes with these monovalent cations probably is lower than for the divalent cations (Snyder & Harter 1984), but only a low proportion of Ca and SO_4 would occur in complexes at these solution concentrations (Drever, pers. comm.).

Surprisingly, bicarbonate alkalinity in root-zone solutions did not change in a systematic manner as snowmelt leaching proceeded (Fig. 1). Initially we hypothesized that accumulation of CO_2 beneath the winter snowpack would depress soil solution pH and stimulate mineral weathering resulting in peak HCO_3 concentrations early during snowmelt; however, high CO_2 accumulation in late winter was not observed. In fact the highest soil atmosphere CO_2 concentrations were measured soon after snowmelt drainage was complete. It is possible that CO_2 generated by respiration during the winter diffused downward through the dry sub-soil horizons (Knight et al. 1985), as CO_2 concentrations were very low at the 1.5 m soil depth (mean = 0.2%; Fahey, unpub. data).

Constant concentrations of most solutes were observed in soil solutions during the mid to late stages of snowmelt, but these probably were not the result of a simple equilibrium between infiltrating water and the soil solid phase because cation exchange and water and nutrient uptake by the trees occur simultaneously. Notably, the composition of the root-zone solution at this time was considerably different from forest floor leachate (Yavitt & Fahey 1986), which also reached rather constant composition (Fig. 4).

Site variation in solute concentrations

Because of the contrasting forest and soil characteristics at the various sites (Table 1), it was not surprising that significant differences in root-zone solution chemistry were observed between these lodgepole pine stands (Table 4). Knight et al. (1985) reported no significant differences in snowpack chemistry at these sites, and Fahey et al. (in press) detected no significant differences in bulk rainfall and throughfall chemistry in five lodgepole pine ecosystems. For the latter, differences may exist but they could not be detected without very large sample sizes. Although a direct relationship between forest floor mass and leachate chemistry might be expected, Yavitt & Fahey (1986) detected no such relationship, probably in part because of complexities of hydrology and chemistry of forest floor materials and spatial and temporal variation in microbial activity. Thus, although some of the between-site variation in root-zone solution chemistry probably was caused by variation in infiltrating solutions, we have no clear evidence to support this contention. Consequently, variation in the soil solution composition among stands probably was induced mostly within the mineral soils.

The available evidence strongly suggests that soil clay content has a profound effect on soil solution chemistry in these forests. Three effects of clay content could be important:

1. Increased soil water-holding capacity, with consequent direct effects on site productivity and water flow through soils;
2. Increased cation exchange capacity; and
3. Precipitation or adsorption of sulfate and organic anions.

1. The effect of clay content on the hydrology and productivity of these sites has been demonstrated (Knight et al. 1985). A direct effect of low clay content is lowered productivity due to both water (Fahey & Young 1984) and possibly nutrient limitation. Based upon proton budget assumptions

(e.g. Binkley & Richter 1987), the amount of nutrients circulating in forests with low clay content would be lower and soil solution concentrations very low. However, high total soil water flux would partly compensate. The Albany site fits this scenario very well.

In clayey soils (French Creek, Rock Creek) snowmelt leaching is minimized by high water retention. In these sites snowmelt rates occasionally exceeded saturated hydraulic conductivity resulting in overland flow (Fahey, pers. observation). Slow soil water movement also would allow closer approach to equilibrium in soil chemical reactions.

2. Higher clay content usually leads to higher cation exchange capacity (Brady 1974) and our sites fit this generalization (Table 1). Low cation concentrations were observed in the soil solutions on the clayey soils despite high productivity at these sites (at least in the case of Rock Creek).

3. Sulfate adsorption varies with clay content in some soils (Johnson & Cole 1980). In the lodgepole pine ecosystem, high soil pH values apparently prohibited significant SO_4 adsorption (Weaver et al. 1985), as only small amounts were observed for Nash Fork and French Creek soils in laboratory SO_4 adsorption/desorption surveys (Fahey & Yavitt, pers. observation). In contrast, adsorption or precipitation of dissolved organic solutes was strongly dependent upon clay content in these soils, probably explaining the significant differences in dissolved organic C and N in the contrasting soils (Table 2). It is well known that mineral colloids favor the formation of insoluble organomineral complexes from soil solution DOC (Dawson et al. 1978; Nys et al. 1981). The importance of this process cannot be overstated: it limits the movement of organic anions and associated nutrient cations, as well as N and P, from the soil rooting zone.

The general lack of large differences among stands in concentrations of NH_4, NO_3 and ortho-P in root-zone solutions probably can be attributed to the high biological demand for N and P in these forests. In fact, the most productive stand (Rock Creek) had lower concentrations of NH_4 than the others, and the old, low productivity stand at French Creek had the highest NO_3 concentrations. As detailed by Fahey et al. (1985), low N availability in these lodgepole pine ecosystems results from low N inputs, strong immobilization in detritus, and periodic losses by volatilization in fires.

Although concentrations of organic P in forest floor leachate may be relatively high, particularly in the early stages of snowmelt (100–250 ug/L; Yavitt & Fahey 1986), organic P concentration in soil solutions always were low in all the stands, rarely exceeding 25 ug/L. As pointed out by McGill & Cole (1981), the nature of organic P probably favors its rapid mineralization, particularly when the element is in high demand by heterotrophs.

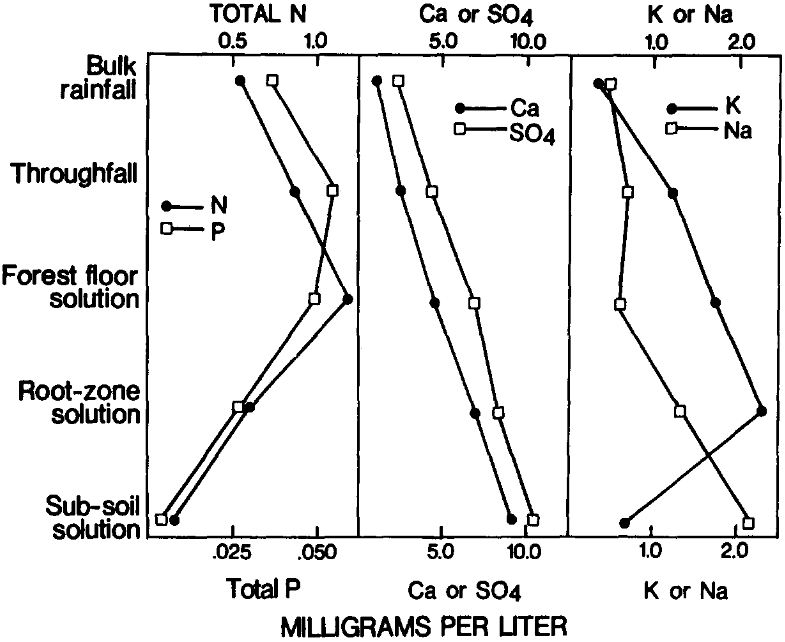

Fig. 5. Changes in flux-weighted mean concentrations in solutions during passage through a lodgepole pine ecosystem (Nash Fork site), southeastern Wyoming (see text for methods of calculation).

Therefore, low organic P concentrations in root-zone solutions may result largely from mineralization (and subsequent immobilization) rather than from precipitation of dissolved organic compounds containing P. This hypothesis is supported by the observation that organic C:P ratios were about twice as high in root-zone solutions (Table 2) as in forest-floor leachate (Yavitt & Fahey 1986).

Concentrations of the major mineral-forming elements, Al, Fe and Si, differed among the three sites for which measurements were available (Table 2). Because the solubility of Al and Fe in mineral soils is enhanced by organic anions (Huang & Keller 1971), the greater mobility of organic solutes in the coarse soils (Nash Fork and Albany) than the clay soil (French Creek) probably partly explains the differences in Al and Fe concentrations between these sites. Furthermore, the fact that Si concentrations were similar at these sites (Table 2) supports the contention that solubility of this element is less affected by organic solutes (Razzaghe-Karimi 1976). Chesworth & Macias-Vasquez (1985) suggested that vertical separation of Si from Al and Fe can occur in near-neutral pH soils only when mobile organic solutes are present. In the absence of high concentrations of soluble organics such as at French Creek, inorganic equilibrium reactions would control ion solubilities (Lindsay 1979), and in this case solubility of Si would exceed that of Fe and Al at the pH values of these soils.

Annual variation in solute concentrations

Long-term observations of soil solution chemistry in forests have revealed some unexplained annual variations (Feller 1977; Sollins & McCorison 1981). Concentrations of most of the major solutes varied significantly among years (Table 3), in the lodgepole pine ecosystems, the only exception being K. This observation probably is explained by the strong biotic control and possibly limited amounts of K in these lodgepole pine ecosystems, as evidenced by strongly declining concentrations during passage through soils (Fig. 5). In effect, the trees may reduce the soil K levels to the same degree in every growing season. In contrast, it appears that the other major ions are supplied to the soil solution in quantities far exceeding the demand of the biota, because concentrations increase with depth. Thus, variation between years in supply to the soluble pool in the soil may be reflected in differing concentrations, particularly during the early stages of snowmelt (Fig. 2).

No clear evidence was obtained to explain the significant annual variations in ion concentrations in root-zone solutions. In particular, there was no simple explanation for the high ion concentrations observed in root-zone solutions in four of the stands in 1981, as compared with 1980, 1982, and 1983 (Fig. 2). The summer and autumn of 1980 were not unusual in terms of bulk rain chemistry or quantity, and the soil was dry at the time when snow began to accumulate. The influence of the major eruption of Mount St. Helens in May 1980 could be involved; however, our bulk precipitation and forest floor leaching studies (Fahey & Yavitt, pers. observation) showed no evidence for an effect of ash fall from the volcano during summer 1980, concurring with observations of Lewis & Grant (1981) in Colorado. Although the initial eruption plume contained high levels of particulate SO_4, subsequent eruptions had low concentrations (Gandrud & Lazrus 1981).

Root-zone leaching

To calculate root-zone leaching and flux-weighted mean concentrations, we required estimates of daily soil water flux. Because hydraulic conductivity of these soils was much higher than the maximum snowmelt rate (except for the high-clay soils: Nyberg & Fahey, in press) after the root-zone is saturated with water, daily soil water flux is equal to daily snowmelt minus root uptake. We estimated daily soil water flux with a stand-level hydrologic model (H20TRANS; Running 1984) applied using detailed site- and year-specific data. Root-zone leaching was estimated as the product of daily soil water flux and daily root-zone solute concentrations (Fig. 2). Also, volume-weighted mean concentrations were estimated from total solute flux and total water flux. We emphasize that these values are tentative because the complex hydraulic characteristics may make it difficult to obtain soil water representative of leachate. However, we have observed only small differences between chemistry of saturated flow (zero-tension lysimeters) and suction extracts in these sites (Nyberg & Fahey, in press).

We present root-zone leaching estimates for three contrasting sites: Nash Fork, Albany, French Creek (Table 5). The calculations were made by applying soil solution chemistry equations (means of 4 to 5 years) for each site to the soil water flux data for 1981. This year was used because climatic conditions were typical for the study area and because we had complete parameter data (particularly detailed snowmelt data).

Root-zone leaching was higher in the sandy loam soil at Nash Fork than at the other two sites (Table 5). This relatively high production site (Pearson et al. 1987) had higher nutrient recycling rates than the xeric Albany site (gravelly, loamy sand) or the old-growth French Creek (clay loam). Soil infertility and low biotic activity probably explain the low leaching at Albany, whereas the low mobility of organic anions and high soil water retention contribute to the low leaching at French Creek.

Volume-weighted mean concentrations of major ions peaked in the root-zone solution (K) or in the sub-soil (Ca, SO_4, Na; Fig. 5). In contrast, peak concentrations of N and P, mostly in organic complexes, were observed in

Table 5. Gross element fluxes via root-zone leaching during the snowmelt period in an average year for three lodgepole pine ecosystems, southeastern Wyoming. For comparison, estimates of fluxes via summer rainfall (wetfall), throughfall, litterfall, forest floor leaching and sub-soil (1.5 m depth) leaching are provided for one of the sites.

Flux pathway	Site	$g\,m^{-2}yr^{-1}$						
		Ca	Mg	K	Na	N	P	S
Root-zone leaching	Nash Fork	1.48	0.34	0.48	0.28	0.11	0.006	0.86
Root-zone leaching	Albany	0.92	0.17	0.20	0.22	0.09	0.005	0.59
Root-zone leaching	French Creek	1.02	0.23	0.17	0.24	0.05	0.003	0.66
Wetfall[1]	Nash Fork	0.11	0.02	0.06	0.06	0.10	0.004	0.13
Throughfall[1]	Composite	0.41	0.09	0.22	0.12	0.15	0.010	0.25
Litterfall[2]	Nash Fork	0.73	0.12	0.16	0.03	0.62	0.055	0.10
Forest floor leaching[3]	Nash Fork	1.83	0.42	0.97	0.32	0.66	0.030	1.20
Sub-soil leaching[4]	Nash Fork	1.09	0.45	0.09	0.28	0.01	0.001	0.45

[1] from Fahey (per. observ.); [2]from Fahey (1983) and Fahey & Yavitt (pers. observ.); [3]from Yavitt & Fahey (1986) and Yavitt & Fahey (pers. observ.); [4]from Knight et al. (1985) and Fahey & Knight (pers. observ.).

forest floor leachate. Although solution fluxes of all the major nutrients were highest for the forest floor (Table 5), the higher water fluxes at this level diluted the ionic concentrations. In effect, evapotranspiration from the root-zone soil concentrated the abundant ions at that level in the ecosystem, whereas precipitation of the organic complexes lowered the concentrations of N and P in the mineral soil.

Surprisingly, all three classes of major soil solution anions (organic, bicarbonate, strong-acid) were important in these forests, departing from the usual situation where one or two major classes predominates (Johnson et al. 1977). Organic-acid anions were important in transport of nutrient cations through the rooting zone and in forming soluble complexes with Fe and Al. The interaction between mineral colloids and DOC, evident in the limited mobility of DOC in the clay-rich soils, certainly plays a critical role in controlling the flux of base cations as well as N and P through the soil root zone, but the possible importance of rapid biological oxidation of the DOC requires further study. Also, the predominance of relatively strong acid-functional groups of the DOC brings into question the generalization of Krug & Frink (1983) that lowering soil solution pH leads to rapid declines in both solubility and dissociation of organic acids under conditions of high deposition of strong acids in precipitation, thereby limiting acid rain effects on cation leaching.

Because soil and solution pH in these ecosystems is near neutral, the potential for carbonic acid leaching of cations (e.g., McColl & Cole 1968) was anticipated. However, low respiration rates, perhaps combined with the ease of diffusion of CO_2 through the dry soils, limited its accumulation beneath the winter snowpack. More detailed studies of the rate and fate of respiratory CO_2 produced beneath the snowpack are needed to confirm this hypothesis.

The unexpected importance of SO_4 as a mobile anion in the soil solution suggests that further study of S sources and transformations is needed. The importance of volcanic activity in the upwind areas of western North America as a long-term S source needs to be further evaluated as does dry deposition from regional anthropogenic sources. The high SO_4 leaching apparently enhanced the dissolution of Ca and Mg as compared with the monovalent cations.

Strong biotic control of the often-limiting nutrients, N, P and K, was apparent in these lodgepole pine ecosystem. Despite high biotic uptake and recycling (e.g. litterfall flux, Table 5) root-zone and sub-soil leaching of these nutrients was low. Marked changes in the N:P ratio as snowmelt passed through the forest floor and soil (Fig. 5) appears to support the paradigm of McGill & Cole (1981) who postulated that P is readily mineralized from organic forms independent from the oxidation of organic matter, whereas N is mineralized coincidentally with the utilization of organic matter as an energy source by soil heterotrophs.

In summary, root-zone soil solution chemistry exhibited a regular seasonal pattern in these lodgepole pine ecosystems, with peak concentrations at the beginning of the spring snowmelt period probably resulting mostly from atmospheric and weathering inputs the previous summer and fall. Soil solution concentrations varied significantly across this montane landscape largely in response to differences in soil clay content; soil texture apparently influenced forest production and biomass through effects on water (Knight et al. 1985) and nutrient availability, with concomitant effects of biological activity on element cycling rates and the solubility and leaching of nutrients. Also, clay content directly affected root-zone leaching by inducing the precipitation of organic complexes. Although all three classes of dissolved anions (mineral, organic, bicarbonate) were important in the root-zone solution, soil leaching was minimized by:

— low mobility of organic anions,
— low bicarbonate concentrations owing to low soil atmosphere CO_2 concentrations, and
— limited soil water flux.

Finally, the high year-to-year variation, observed for many solutes, could not be easily explained. Together with similar unexplained annual variations observed by Feller (1977) & Sollins (pers. commun.) in the Pacific Northwest, these results indicate that short-term studies of soil solution chemistry should be interpreted and extrapolated with caution.

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