

PROCESSES CONTROLLING THE COMPOSITION OF
INFILTRATING WATER IN
FORESTED MOUNTAIN WATERSHEDS

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ABSTRACT

Chemical weathering in a high-elevation pine forest was studied by analysis of percolating soil solutions and associated solid phases. In the shallow soil (above 40 cm), soil-water chemistry is controlled by biological processes -- uptake by plants and decay in the litter layer. Below 40 cm mineral weathering becomes more important as a control, but solution compositions are so variable in space and time that it is impossible to define a simple weathering stoichiometry. Kaolinite is forming in the upper part of the soil profile and smectite in the lower part, although solution compositions indicate that kaolinite should be the more stable phase at all depths.

Dissolved organic carbon (DOC) values are high (average 38 mgC/l) in the forest floor litter, and decrease with depth in the mineral soil. In clay-rich, low-permeability soil the DOC loss and acquisition of cations take place close to the surface, whereas in more permeable soils DOC transport and chemical weathering extend to greater depths. There is some enhanced transport of Al and Fe as a result of complexing by organic acids. The mechanisms by which DOC is removed from solution are not clear.

INTRODUCTION

Weathering of rocks in the soil zone is the major source of solutes for ground and surface waters, and of clay minerals which are ultimately transported to form sediments and shales. Chemical processes in soils are very difficult to study. Chemical conditions such as temperature and moisture content vary rapidly, secondary phases are often poorly crystallized and hard to characterize, and the activities of the biota, which cannot be described in simple chemical terms, play an essential role. Many studies (for a summary, see Drever, 1982) have inferred the nature of weathering reactions from stream and spring water compositions, but there have been relatively few geochemically-oriented studies of water percolating through soils (for example Graustein, 1975, 1976, 1981; Best and Monk, 1975; Dawson et al., 1978; Antweiler and Drever, 1983). The general conclusion of these studies is that biological processes are at least as important as inorganic processes in controlling the chemistry of solutions in the weathering environment.

An experimental ecology group in the Botany Department at the University of Wyoming has been studying nutrient cycling in eight lodgepole pine (Pinus contorta) stands in the Medicine Bow Mountains of Wyoming (Fahey, 1979, 1983; Knight et al., in press). Three of these sites were selected for this study of chemical weathering; the work reported here relies heavily on the

earlier work of the ecology group.

The purpose of this study was to investigate the mechanisms controlling cation acquisition in the soil zone, with the long-term objective of predicting the effect of possible future acid deposition. This report discusses cation acquisition in the undisturbed system, which will form the basis of future studies on the impact of acid deposition.

STUDY AREA

Some characteristics of the three sites chosen for this study are presented in Table 1. The geology of the area is described by Houston et al. (1968).

Soils at the Albany site are developed directly on Sherman granite (Precambrian) for which McCallum (1964) reported a generalized composition of 30-40% microcline, 20-35% plagioclase (An 12-33, usually zoned), 20-40% quartz, 1-5% hornblende, and 1-5% biotite. The soil consists of an organic layer of variable thickness (1-3 cm) and a fairly uniform 25-30 cm thick A horizon lying directly on deeply weathered granitic bedrock. The transition zone between the soil and the underlying regolith is only about 5 cm thick. Regular joint patterns in the Sherman granite are still evident in the regolith below 30 cm.

The Nash Fork site is located on Pleistocene till.

TABLE 1. Study site characteristics.

	<u>Albany</u>	<u>Nash Fork</u>	<u>French Creek</u>
Elevation (m)	2760	2845	3005
Stand age (y) ¹	uneven	110	240
Tree density (no/ha) ¹	1920	1850	420
Tree biomass (t/ha) ¹	76.1	174.8	174.7
Thickness of organic horizon	0-3 cm	8 cm	6 cm
Soil type ²	Inceptisol Lithic cryocrept (loamy skeletal)	Alfisol Typic cryoboralf (fine loamy)	Alfisol Typic cryoboralf (loamy skeletal)
Number of 40 cm lysimeters	8	11	5
Number of 140 cm lysimeters	1	5	5
1982 snowmelt period:			
Date of first lysimeter collection	April 25	May 10	May 17
Date of last lysimeter collection	June 14	July 9	July 22
Location	NW¼ Sec 16 T14N R78W	NW¼ Sec 20 T16N R78W	SE¼ Sec 29 T16N R80W

¹from Knight, Fahey and Running (in press).

²from Yavitt (1984)

The pebble to boulder fraction of the till is primarily migmatite and quartzo-feldspathic gneiss with 10% each of biotite gneiss and amphibolite, and 2% dolomite. Although some phyllite and slate would be expected on the basis of the source area, none was observed in the coarse fraction, probably due to their low physical competency during transport.

The French Creek site is located on Pleistocene till, which had its source in the Medicine Bow quartzite (Precambrian) and flowed westward. The pebble to boulder fraction of the till is almost exclusively Medicine Bow quartzite, with only 1-2% amphibolite.

The soil profiles at both Nash Fork and French Creek are very poorly developed with the transition between the A and B horizons extremely gradational and not immediately evident in the field. At both sites the soil contains interspersed boulders and is quite heterogeneous. The soil profiles at all three sites have developed over a maximum period of about 10,000 years, the age of the end of the last Pleistocene glaciation, and have only very weakly developed zones of leaching and deposition.

Long-term climatic data are available for the Nash Fork site (Wyoming Water Resources Research Institute, 1967-1976). The other sites should be similar. Mean annual precipitation is about 60 cm with about two thirds in the form of snow from October to May. However, large variations in annual precipitation (over two-fold) are characteristic of the Medicine

Bow Mountains. Winter snow accumulations may be several meters, and the spring snowmelt is the only time of significant soil water movement. Sporadic summer storms wet only the soil surface, although after one exceptionally heavy October rainstorm, most lysimeters at 40 cm depth and several at 140 cm did collect a small volume. In July the mean daily maximum temperature is about 20 C and the minimum temperature about 4 C, with occasional subfreezing temperatures at night. January mean daily maximum temperatures are about -5 C and the minimum temperatures about -13 C.

METHODS

One soil profile at each site was sampled from excavated trenches at 10 \pm 2 cm intervals from 0 to 40 cm and at 20 \pm 2 cm intervals to the bottom of the trench at 140 to 180 cm. Pebbles larger than 1 cm were removed from soil samples by hand, the <1 mm and <75 micrometer fractions were separated by sieving, and the <2 micrometer fraction by repeated ultrasonic dispersion and centrifugation. The clay mineralogy of the <2 micrometer fraction was determined by X-ray diffraction. Total carbon content of the <75 micrometer fraction was determined by ignition to CO₂ (estimated precision: \pm 10%; detection limit: 0.1%); inorganic carbon was determined by acidification and titration of evolved CO₂ (estimated precision: \pm 10%; detection limit: 0.1% C),

and organic carbon by difference. Three selective dissolutions were used to estimate amorphous and sesquioxide aluminum, iron and silica phases in the <1 mm and <2 micrometer fractions; 1) extraction of "organically" bound aluminum and iron by 0.1 M sodium pyrophosphate (McKeague, 1967), 2) extraction of "amorphous" phases by 0.2 M ammonium oxalate acidified to pH 3.0 (McKeague and Day, 1966), and 3) dissolution of "crystalline" iron sesquioxides by the citrate-dithionate-bicarbonate method of Mehra and Jackson (1960). Fey and Le Roux (1977) give a comparison of the relative selectivity and effectiveness of these extractions. Iron, aluminum, and silica in the selective dissolution extracts were determined by induced plasma atomic absorption on a Perkin Elmer CIP/5500.

Soil solution samples were collected by suction tube lysimeters (Parizek and Lane, 1970) at a vacuum of 0.12 bars from depths of 40 cm and 140 cm. Samples of solution from the base of the organic layer were collected with tension aluminum plate lysimeters (Cole, 1958) from the interface of the O₂ layer and the mineral soil. Collections were made at intervals of 2 - 4 days in the early snow melt, and then about every week in the later spring. Contamination and adsorption by the ceramic cups was found not to be a problem in an earlier study (Antweiler, 1981). The lysimeters had been in place and sampled for three years, so transient disturbance or contamination caused by their emplacement or alteration of organics by the ceramic plate or cup should have disappeared (Dawson and Hrutfiord, 1976).

Throughfall and bulk precipitation were collected by funnel rain gauges, throughfall by a network of 10 collectors under the forest canopy in the stand proper, and precipitation in nearby unobstructed areas.

All water samples were returned to the laboratory and analyzed for pH by glass electrode (estimated precision ± 0.02 pH units) within six hours of collection. Sample bottles were sealed immediately after collection (completely filled if there was sufficient sample), and not opened until the pH measurement was made. Despite these precautions there was probably some carbon dioxide loss while the samples were under vacuum in the lysimeters before collection. This would result in the measured pH being higher than the in-situ soil solution pH. The measured soil atmosphere was consistently about 0.30% carbon dioxide by volume (Fahey and Yavitt, unpublished data), an order of magnitude higher than atmospheric carbon dioxide. If the soil solutions totally reequilibrated with atmospheric carbon dioxide, the measured pH would be a maximum of one pH unit higher than the in situ pH. The soil solutions, however, are probably not totally equilibrated with atmospheric carbon dioxide, and are buffered by organic acids, so the actual error in the pH is probably much smaller than 1 pH unit. Following filtration of the samples through 0.45 μ m glass fiber filters, the following quantities were determined within 24 hours after collection: total alkalinity by titration to pH 4.5; dissociated weak organic acids by purging with N₂ for 15 minutes at pH 4.5 and back

titrating to the original pH; total acidity by titration to pH 8.3; and undissociated organic acids by purging with N₂ for 30 minutes at the natural pH and titrating to pH 8.3. Samples were stored in polyethylene bottles and refrigerated at 4 C at all times between analyses.

Calcium, magnesium, potassium, and sodium were determined by atomic adsorption spectrophotometry (estimated precision $\pm 5\%$). Aqueous silica was determined colorimetrically by the molybdate blue method (estimated precision: $\pm 2\%$; detection limit: 0.05 mg/l). Chloride, sulfate and phosphate were analyzed using standard colorimetric methods for a Scientific Instruments continuous flow autoanalyzer, chloride by the mercuric thiocyanate method, sulfate by the methylthymol blue method preceded by a peroxide digestion and ultraviolet irradiation to minimize organic interferences (Cronan, 1979), and phosphate by a molybdate blue method. Dissolved organic carbon (DOC) was determined by persulfate digestion in sealed ampules, with detection of evolved CO₂ by coulometric titration (estimated precision: $\pm 5\%$; detection limit: 0.1 mg/l).

Following filtration through a 0.1 m membrane filter, dissolved aluminum was determined by the pyrocatechol violet method of Dougan and Wilson (1974) (estimated precision: $\pm 5\%$; detection limit: 0.010 mg/l) and dissolved iron by the ferrozine method of Stookey (1970) (estimated precision: $\pm 5\%$; detection limit: 0.025 mg/l). There are some uncertainties in the

analytical values for aluminum and iron due to flocculation of dissolved organic matter between the time of collection and the time of analysis causing removal of some dissolved aluminum and iron from solution. This may cause the aluminum and iron values in samples with high DOC values (primarily samples from Nash Fork) to be low, but it should not affect the samples from Albany or French Creek, where DOC values are lower.

RESULTS AND DISCUSSION

Solid Phases

Grain Size Distribution The soil was separated by sieving at 1 mm and by centrifugation (Fig. 1). With the French Creek soil, there was a problem of clay aggregates which did not pass through the 1 mm sieve. As a result, a larger proportion of the soil at French Creek is <1 mm than indicated in Fig. 1, and the French Creek soil is considerably finer than that at Nash Fork. Note that the Albany soil is rather coarse even near the surface, the regolith below 30 cm is essentially gravel. The Nash Fork and French Creek soils have a fairly fine, clay-rich matrix with interspersed pebbles, cobbles and boulders and a heterogeneous character typical of glacial tills. All three sites have the highest concentration of clay at the surface; below 20 cm there is very little variation in size distribution with depth.

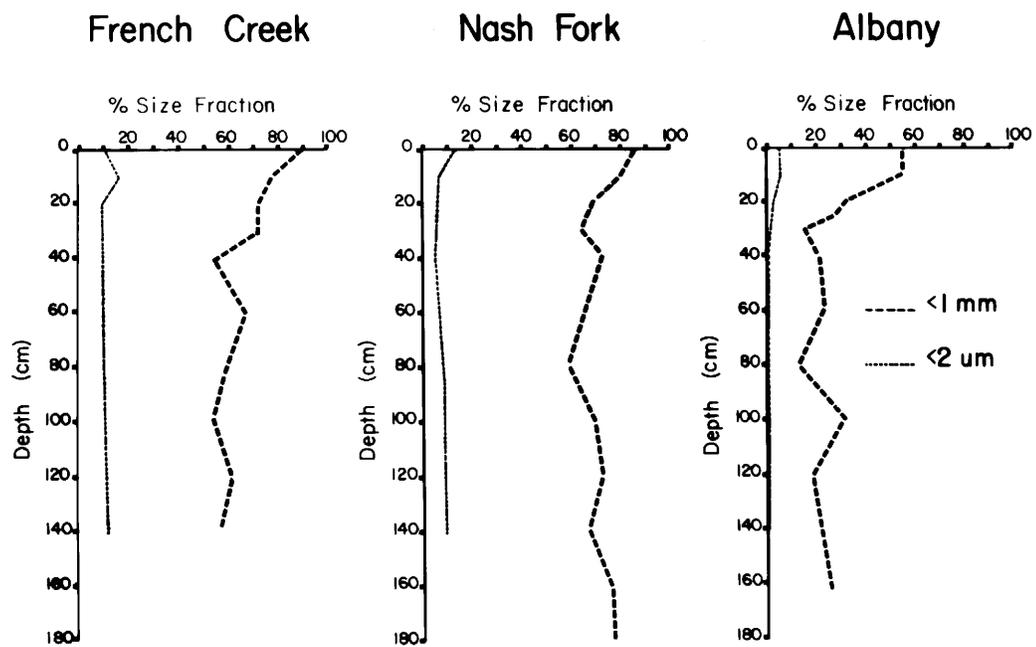


Figure 1. Grain-size distribution in soil profiles from the three study sites.

Organic Carbon

The distribution of solid organic carbon is presented in Fig. 2. Carbon content was determined on the <75 micrometer fraction in order to get a rough measure of the highly decomposed, "mineralized", and/or transported carbon, rather than undecomposed needles and roots. All the sites have very low organic carbon contents below 20 cm. The values at Albany decrease less rapidly with depth, probably because the <75 micrometer fraction at Albany is so much smaller a proportion of the total soil than is the case at Nash Fork or French Creek. Thus the organic carbon content expressed as percent of total soil may be quite similar at the three sites. There is no evidence for the accumulation of organic matter at depth in the soil profile of any of the three sites.

Clay Mineralogy

Albany Site- The clay minerals identified by X-ray diffraction in the <2 micrometer fraction of the soil and underlying regolith at the Albany site were kaolinite, vermiculite, smectite, and mica. Kaolinite was present throughout the profile, but the X-ray peaks broaden with depth below 30 cm, the approximate soil-regolith contact, suggesting decreasing crystallinity and/or increasing organic and oxide coatings. Vermiculite X-ray intensity increases from the surface to 20 cm, decreases from 20 cm to 60 cm, and vermiculite peaks are not present below 60 cm. The vermiculite is probably formed from the alteration of biotite

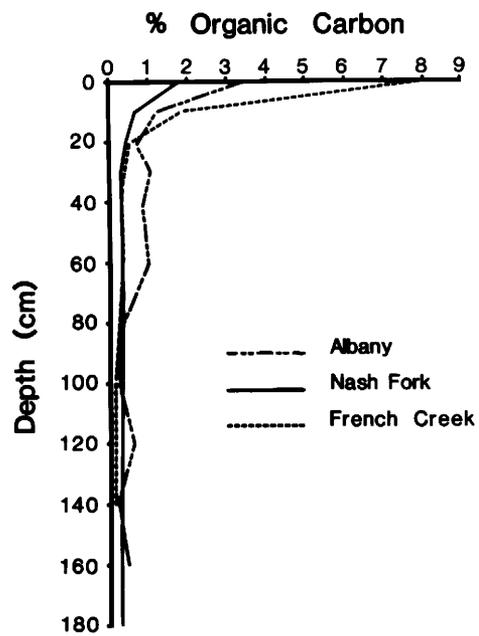


Figure 2. Organic carbon (wt %) in the <75 μm size fraction of soil profiles from the three sites.

in the Sherman granite . Smectite X-ray peaks are barely discernible above 60 cm, but below 60 cm they increase in intensity with depth becoming the dominant peak below 120 cm. A mica peak of uniform low intensity is present throughout the profile, and is presumably mica derived directly from the Sherman granite.

Nash Fork and French Creek Sites- The clay minerals identified in the <2 micrometer fraction of the soil at Nash Fork and French Creek are chlorite, illite, kaolinite and smectite. Chlorite and illite are present throughout the profile, and are probably derived from the metasediments in the glacial source area. At Nash Fork kaolinite is a major clay mineral from the surface to 30 cm, and kaolinite is undetectable below 60 cm. At French Creek the kaolinite is present throughout the profile, but becomes much weaker, broader and poorly defined below 60 cm. At both sites the smectite peak is of very low intensity from the surface to about 60 cm, but by 80 cm the smectite peak has become a relatively sharp, dominant peak.

Selective Extractions

Three selective extractions, pyrophosphate, oxalate, and citrate-dithionite-bicarbonate (CDB) were performed in order to determine the distribution of sesquioxides of aluminum and iron, and the distribution of amorphous aluminosilicate material. All

of these methods are largely empirical, and the quantities of iron and aluminum extracted cannot be strictly equated with specific phases (Schwertmann, 1973; Fey and Le Roux, 1977). In general, the selective extraction results show a great deal of scatter reflecting the heterogeneity of these soils. The silica values from all the extractions are quite low ($< 0.4\%$), and show no significant trends.

At all three sites, oxalate and CDB extractable aluminum shows a poorly-defined maximum value at 10 cm, and then decreases with depth. This suggests a small amount of aluminum has been mobilized and has accumulated at shallow depths in the soil as amorphous aluminum hydroxides. However, at none of the sites is there a well defined aluminum and/or iron sesquioxide-rich horizon.

Solution Chemistry

Composition

Precipitation- Bulk precipitation in the Medicine Bow Mountains is rather dilute with calcium as the major cation and bicarbonate and sulfate as the major anions (Table 2). The bulk precipitation has a moderately high average pH of 5.21 (atmospherically equilibrated pure water is about 5.6). The high sulfate values are balanced by calcium and other cations, not mineral acidity. It is not clear whether the sulfate is

TABLE 2: Average concentrations ($\mu\text{moles}/\ell$) of solutes in rainfall, throughfall, and soil solutions from the organic layer from lodgepole stands in the Medicine Bow Mountains, 1979-81 (Knight, Fahey and Yavitt, unpublished data)

	<u>Bulk Rainfall</u>	<u>Throughfall</u>	<u>Organic layer solutions</u>
No of samples	200	830	103
Ca	42.7	74.4	153.2
Mg	8.2	23.5	57.2
K	14.8	42.5	79.0
Na	18.7	42.2	51.8
Mn	0.9	3.8	4.7
SO ₄	32.8	51.1	78.6
Cl	14.1	29.3	28.2
NH ₄	15.7	10.9	
NO ₃	6.3	8.4	
pH (pH units)	5.21	4.65	5.75
HCO ₃			172
DOC (mg/l)			27.9 ¹

¹Average of 43 samples.

anthropogenic pollution from several large coal-fired plants to the southwest which has been neutralized by particulate calcium carbonate, or is naturally derived particulate calcium sulfate from the arid areas to the west.

Throughfall- The composition of throughfall is extremely variable, both spatially and temporally, and on average shows a decrease in pH and an increase in the concentration of most ions, particularly potassium, over bulk precipitation (Table 2). The proportion of the increase in the solute concentration of throughfall from a) leaching of the foliage, b) dissolution of impacted particulates on the foilage, and c) evaporative concentration, is presently unknown. Fahey (1979) suggested that impaction and evaporation are major sources of increased cation concentrations in throughfall. Graustein and Armstrong (1983), using Sr87/Sr86 ratios in a New Mexico Engelmann spruce and subalpine fir stand, found that 66% of the strontium in throughfall was atmospherically derived, emphasizing the probable importance of impacted particulates to the composition of throughfall in a coniferous forest.

Organic Layer Solutions- Solutions were not collected from the organic layer at the three sites used in this study, but were collected at several of the other lodgepole pine stands in the Medicine Bow Mountains used in the ecology study (Yavitt, 1984). The solute concentrations in the solutions from the organic layer are so spatially variable that solutions from the various stands

are statistically indistinguishable. We can use the data on solutions from the organic layer during snowmelt from these sites (Table 2) to discern at least the general nature of the solution entering the mineral soil.

Soil Solutions- The unweighted average solute concentrations from 40 cm and 140 cm tube lysimeters at each site are presented in Table 3. Volume-weighted averages and fluxes could not be computed because variations in permeability and the poorly defined geometry of the region sampled by the tube lysimeters mean that the volume of solution collected by the tube lysimeters is not necessarily representative of solution flux through the soil.

DISCUSSION

Initially we had hoped to find the soil and soil solutions spatially homogenous, with variations only in depth and time. Unfortunately, all three stands are extremely heterogeneous. Some factors which could lead to this spatial heterogeneity are variations in: 1) vegetative canopy cover which significantly modifies the volume, organic and inorganic composition of precipitation actually reaching the forest floor; 2) spatial variations in the litter layer; 3) drifting of the snowpack, which could result in large spatial differences in water flux from snowmelt; 4) variations in the soil composition, particularly in the tills; and probably most importantly,

TABLE 3: Unweighted average concentrations ($\mu\text{moles}/\ell$) of major solutes in soil solutions sampled by suction tube lysimeters during 1982 snowmelt period.

	Albany		Nash Fork		French Creek	
	40 cm	140 cm	40 cm	140 cm	40 cm	140 cm
Ca	74.4	107.3	149.3	225.5	66.3	68.5
Mg	26.3	36.0	73.4	164.5	28.1	31.2
K	22.6	14.5	60.2	35.1	14.5	9.8
Na	32.7	94.0	44.2	108.9	30.4	35.1
SO ₄	58.0	53.4	119.2	92.2	81.8	193.4
Cl	22.3	9.2	65.7	29.7	18.7	18.8
HCO ₃	78	73	104	725	73	110
pH (pH units)	5.95	5.68	5.99	6.67	5.73	5.89
Al	2.37	1.33	5.31	0.20	0.38	0.35
Fe	1.33	0.67	5.79	0.14	0.37	0.39
Si	231	482	349	498	253	267
DOC ¹	8.8	9.3	17.3	6.9	4.4	4.3
Dissoc. organic acids ²	22	17	40	24	7	11
Undissoc. organic acids ²	30	38	72	23	27	28
¹ mg/l				² meq/l		

5) variations in permeability within the soil. A large portion of soil solution transport may take place along high permeability channels, infiltrating quickly, and contacting only these narrow channels. A smaller volume of solution may reside in more isolated pore spaces within the soil for much longer periods. The heterogeneous nature of the soil has been documented by measurements of infiltration rates at all three sites (Fahey and Nyberg, unpublished data) These heterogeneities would result in large variations in soil solution compositions over short distances. In addition, the collection of 0.5 to 1.0 liters of soil solution within a 24 hour period affects the residence time of soil solutions in the immediate vicinity of the lysimeter cup, and thus could affect their compositions.

Clay Mineral Formation- At all three sites the predominant clay phase formed by weathering is kaolinite in the near surface and smectite at depth. As the soil solutions percolate through the soil and weathering reactions proceed, soil solutions should accumulate cations and dissolved silica and the pH should increase. This should tend to favor the formation of smectite rather than kaolinite (Fig. 3). However, calculations using WATEQF (Plummer et al., 1976) indicate that the sampled soil solutions, even those from 140 cm, are more supersaturated with respect to kaolinite than with respect to smectite. Several of the early 140 cm samples from Nash Fork are very close to the

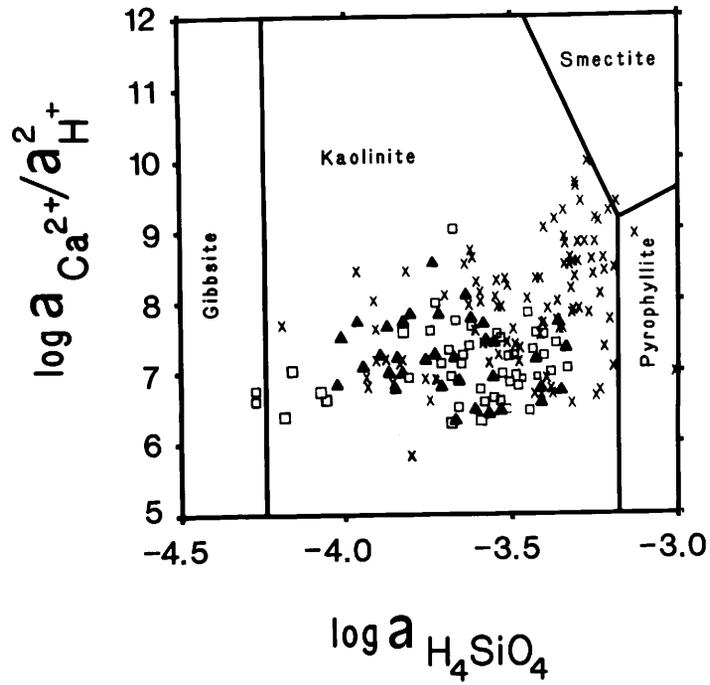


Figure 3. Soil solution compositions plotted on a stability diagram for selected minerals in the system CaO-Al₂O₃-SiO₂-H₂O at 25°C (after Drever, 1982). Activities were calculated using WATEQF. X = Nash Fork, ▲ = Albany, □ = French Creek.

kaolinite-smectite stability boundary, but the vast majority of the Nash Fork and all of the Albany and French Creek samples are firmly in the kaolinite stability field. There is uncertainty associated with the position of the smectite-kaolinite stability boundary, but the boundary was largely established by observation of solution chemistry in natural weathering environments, so the behavior observed here represents a departure from the "normal" relationships between clay mineral formation and solution chemistry.

One explanation of the apparent contradiction between the clay phase predicted from soil solution compositions and the clay phase actually observed, may be that a large proportion of the water flux is through high permeability channels, and it is therefore primarily channel flow that the lysimeters collect. The majority of the soil particles, however, may actually be in contact with pore waters with much lower percolation rates. The longer residence time of pore water in the soil allows the accumulation of higher concentrations of dissolved cations and silica from weathering reactions, probably pushing the solution composition into the smectite stability field. These more concentrated pore waters may account for a very small proportion of the total water flux, and yet because they are in contact with a large proportion of the particle surface area subject to weathering, they may dominate the formation of secondary weathering products. This could account for the dominance of smectite over kaolinite at depth, even at Albany and French Creek

where the soil solutions sampled by the lysimeters are dilute and should favor kaolinite formation.

Another possible explanation for the smectite formation is that soil solutions move through the soils at these sites for only about three months during the year. During the remainder of the year soil solutions may reside in the soil for a long period, accumulating high solute concentrations, and forming smectite as a weathering product. However, the soils are all quite dry during the late summer and winter, and the extent to which hydrolysis -type weathering reactions could take place during this period appears quite limited.

Trends with Time and Depth

Major Ions- Concentrations of the major cations (Na, K, Ca, and Mg), silica, DOC, and organic acids have high values in the first spring melt water to percolate through the organic layer in the forest floor (Fig. 4). However, a single plot of all the soil solution (40 and 140 cm) solute concentrations versus time displays no obvious trends. The calcium versus date plot (Fig. 5) is rather typical of the apparent incoherency of soil solution compositions with time. This is presumably a result of the heterogeneity of the soil and the differences in the date enough snow had melted that soil solution could be collected at the various lysimeters. However, when individual lysimeters are plotted (Fig. 6), several trends become evident. Solute

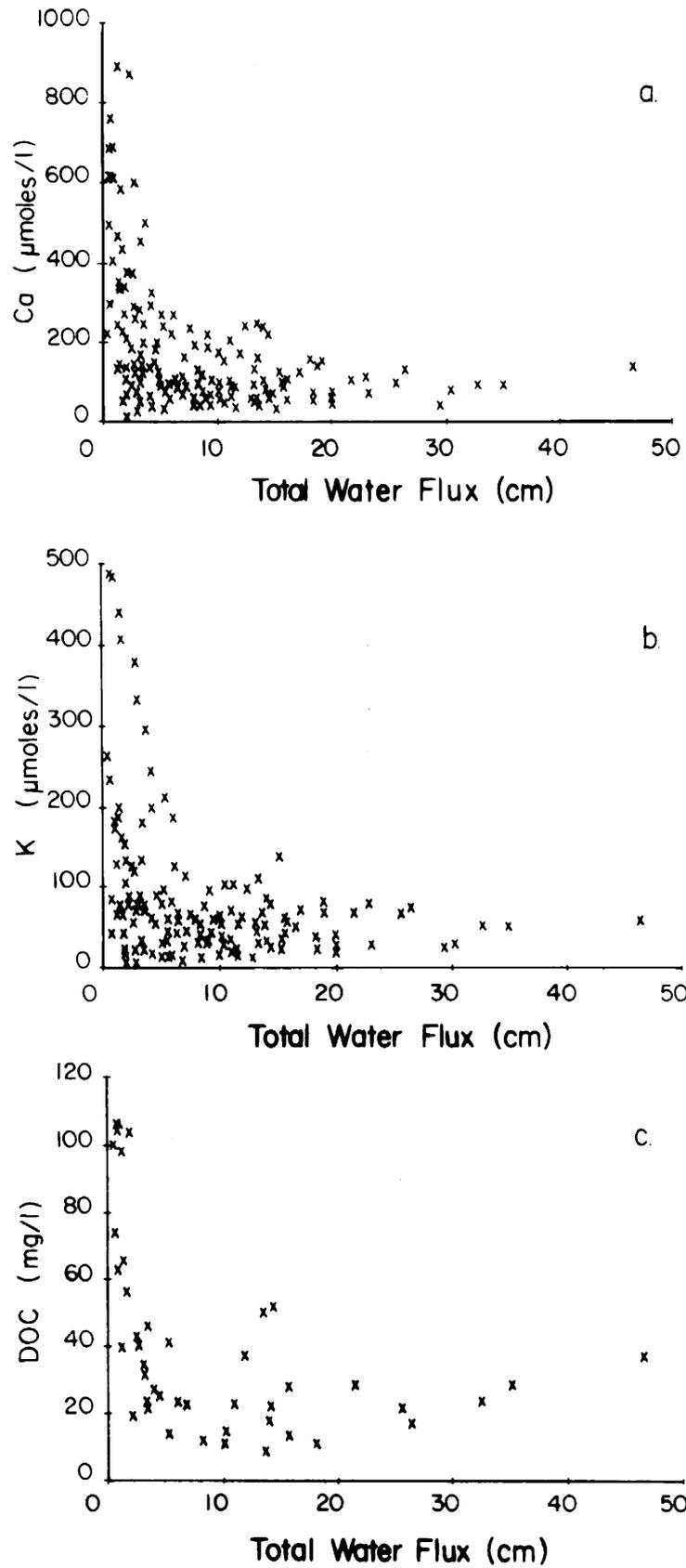


Figure 4. Calcium, potassium and DOC concentrations vs. total water flux for all organic layer solutions. Water flux is determined by the total volume of solution collected at the individual plate lysimeters, which approximates the total water flux through the soil since the start of snowmelt.

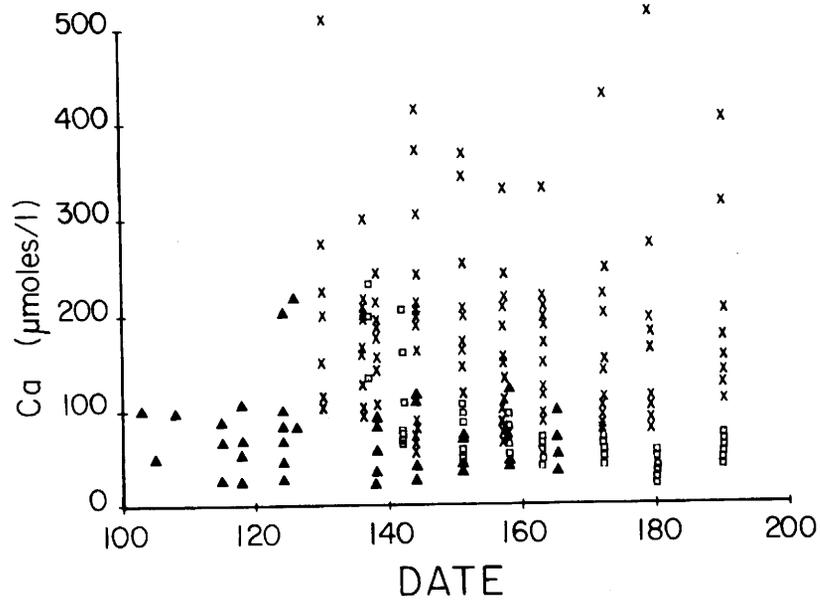


Figure 5. Calcium concentration vs. Julian date for all 40 cm and 140 cm soil solutions. ▲ = Albany, X = Nash Fork, □ = French Creek.

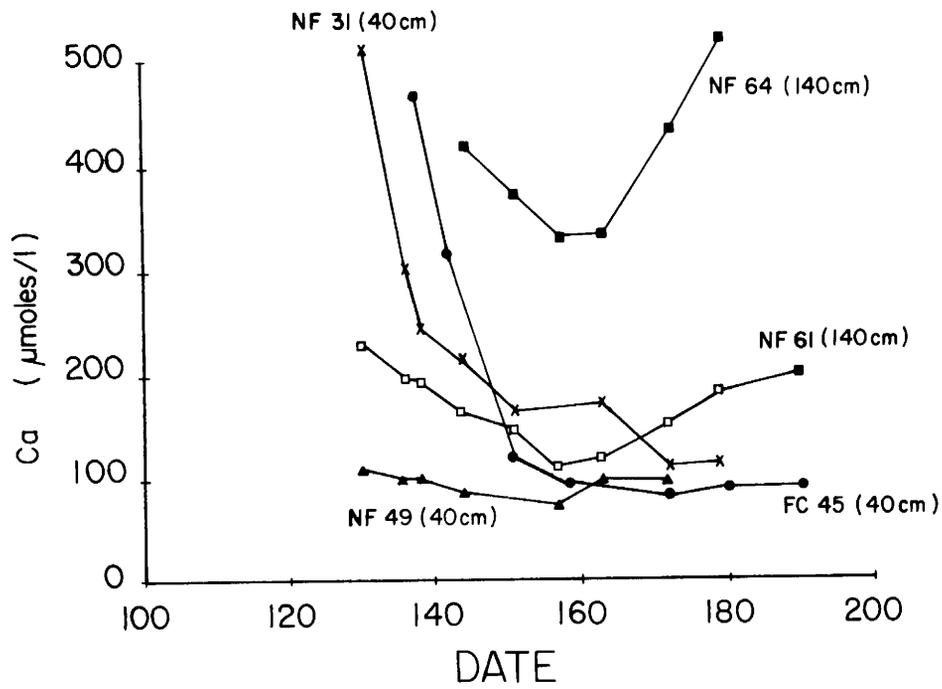


Figure 6. Calcium concentration vs. Julian date for selected lysimeters. NF = Nash Fork, FC = French Creek.

concentrations generally decrease with time through the main snowmelt period, with a slight rise (probably due to evapotranspiration) at the end of the snowmelt.

The high initial concentrations can be explained as a combination of 1) the flushing of accumulated weathering and decay products from the fall and winter, and of solute inputs from small rainstorms during the previous summer, 2) residence time of the soil solution (the initial meltwater percolates slowly), and 3) the concentration of organic solutes in the soil solution and their influence over weathering rates in the mineral soil.

Winter decomposition is the major factor controlling the high initial solute concentrations in the solutions from the organic layer; it is not clear whether the high initial soil solution concentrations at 40 cm and 140 cm represent winter weathering within the mineral soil proper, simply reflect the higher input of solutes from the forest floor litter, or are a function of longer solution residence time. The higher initial DOC concentrations suggest the litter must have a major influence, even at 140 cm.

Plots of average compositions of rainfall, throughfall, and soil solutions are shown in Fig. 7. These plots must be interpreted with caution as they use unweighted average concentrations and not elemental fluxes. There are two competing factors controlling the concentrations of the major ions in soil

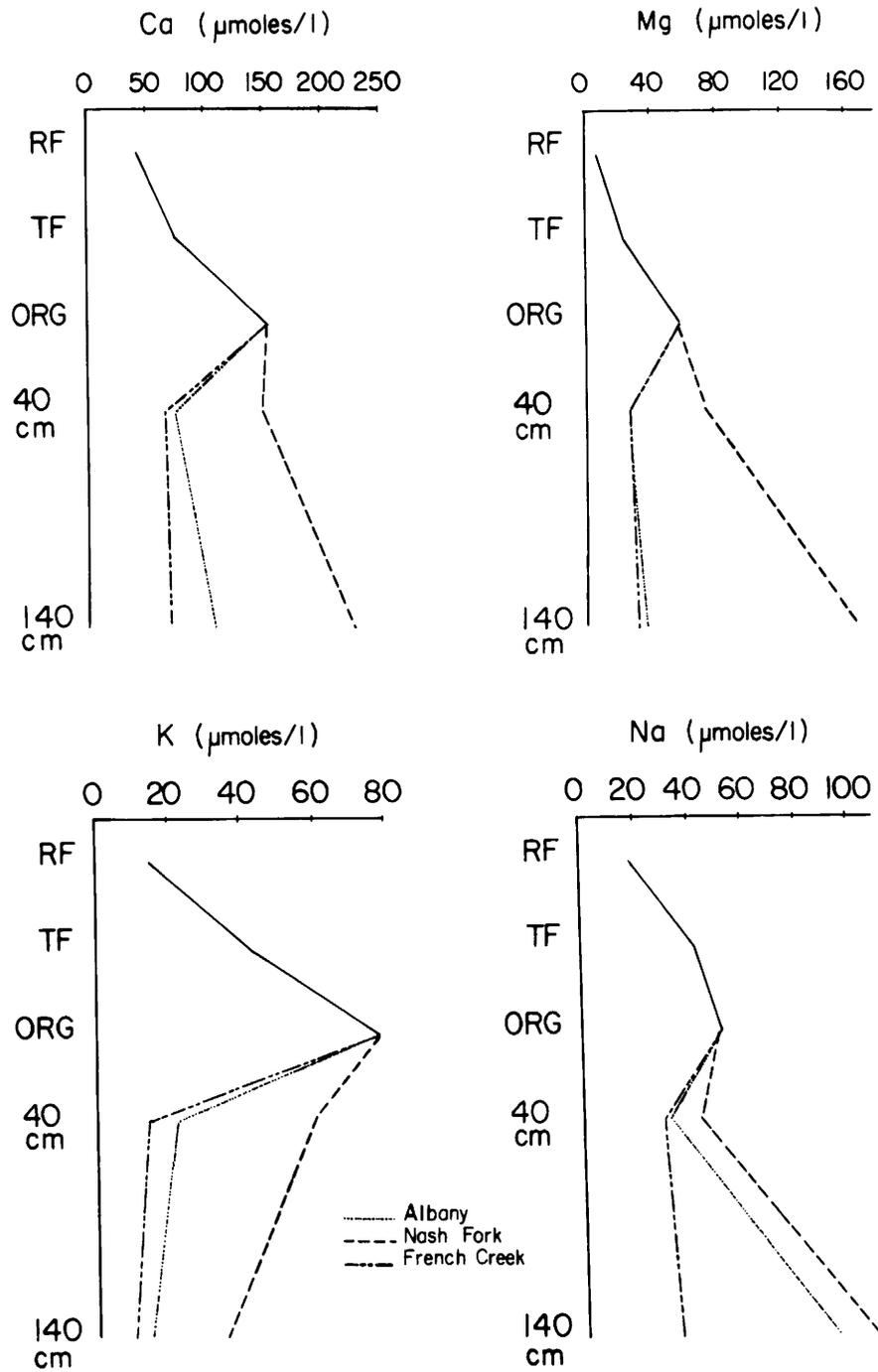


Figure 7. Changes in major ion concentrations (averages) as solution progresses through the vegetative canopy and soil. RF = rainfall, TF = throughfall, ORG = organic layer of soil, 40 cm and 140 cm = depths in soil.

solutions, 1) vegetative uptake and recycling, primarily of potassium, calcium, and magnesium, and 2) release of ions by weathering reactions (i.e. dissolution and precipitation of solid phases). The decrease in concentration of calcium, magnesium and potassium between the organic layer and 40 cm is a result of vegetative uptake in the densely rooted zone above 40 cm being much greater than the contribution of these elements from weathering. Below 40 cm, the average concentrations of calcium and magnesium as well as of sodium, silica, and bicarbonate increase markedly with depth as weathering begins to predominate over vegetative uptake. Potassium, however, is scavenged so vigorously by vegetation that it continues to decrease in concentration, even below 40 cm.

The importance of vegetative recycling in controlling soil solution composition is demonstrated in Table 4. The rate of vegetative recycling of elements is approximated by the elemental flux to the forest floor in vegetative litterfall. The contribution of elements from weathering above 140 cm is calculated as the difference between element loss in solution from the stand at 140 cm, below any significant vegetative uptake, and the elemental input in bulk precipitation. The water flux at 140 cm is based on the hydrologic model of Running (1983). It should be emphasized that the resulting ratio of vegetative recycling to weathering is a minimum value, since vegetative recycling of elements leached from foliage by throughfall is not included in recycled elements, and dissolved

TABLE 4: Fluxes of major cations in vegetative recycling and weathering at the Nash Fork site. Units are g/m²/y.

	Ca	Mg	K
Flux to the forest floor in litter ¹	0.73	0.123	0.155
Outflow in solution at 140 cm ²	1.09	0.282	0.093
Input in precipitation ²	0.27	0.044	0.095
Contribution from weathering (outflow-input)	0.82	0.238	0.00
Ratio of vegetative cycling flux to weathering flux	0.89	0.52	very large

¹from Fahey (1983) ²from Knight et al (in press)

impacted particulates are not included in atmospheric input.

At Nash Fork essentially all the potassium is recycled by vegetation, atmospheric input approximately equalling outflow, and 89% as much calcium and 52% as much magnesium is recycled as is contributed by weathering. Considering that most vegetative uptake takes place above 40 cm, whereas much of the weathering takes place between 40 cm and 140 cm, the importance of vegetation in controlling the composition of soil solutions in the near surface is quite dramatic. Unfortunately, sodium and silica concentrations were not available for leaf-fall, and so similar balances could not be computed for these elements. Graustein (1981) reports silica concentrations of 0.45% by dry weight in spruce foilage and Rodin and Bazilevich (1967) report silica concentrations of 0.12% by dry weight in Pinus silvestris litter fall. Thus, silica is probably also recycled substantially in these lodgepole pine stands. Although sodium comprises a much lower percentage of the biomass, the amount recycled by vegetation could still be large enough to mask any weathering stoichiometry in the near-surface solutions.

A further important aspect of the cycling of elements through the biomass is the effect of increases in the biomass on the net export of elements in solution. The compositions of solutions leaving the base of the soil zone reflect both supply by weathering of minerals and loss by net uptake by the biomass (compare Likens et al., 1977). In the pine forests of the

Medicine Bow Mountains the biomass generally accumulates until there is a major destruction/ release by fire, which occurs at intervals of typically 100 to 200 years. On time-scales shorter than this, the export of cations in solution does not correspond exactly to the release of cations by weathering.

Dissolved Organic Compounds

The litter layer is the major source of DOC in the soil solution, and concentrations of DOC, weak dissociated organic acids, and undissociated organic acids all decrease rapidly with depth in the mineral soil (Fig. 8). The fate of these dissolved organic compounds is uncertain. They may be: 1) taken up by vegetation; 2) metabolized by soil microorganisms; 3) flocculate or polymerize to form persistent "mineralized" organic matter in the soil; or 4) be adsorbed on clay or sesquioxide surfaces. The absolute amount of carbon lost from soil solutions between 40 cm and 140 cm is so small, however, that the accumulation of organic carbon would be difficult to detect.

Dissolved organic carbon shows a pronounced trend of high spring concentrations in the organic layer similar to that of the cations. However, the trend is progressively less pronounced at 40 cm and 140 cm, which tend to have their highest DOC values slightly later in the snowmelt period. This may be due to retardation of dissolved organic compounds from the forest floor litter by adsorption on clay and oxide surfaces, slowing their passage through the soil.

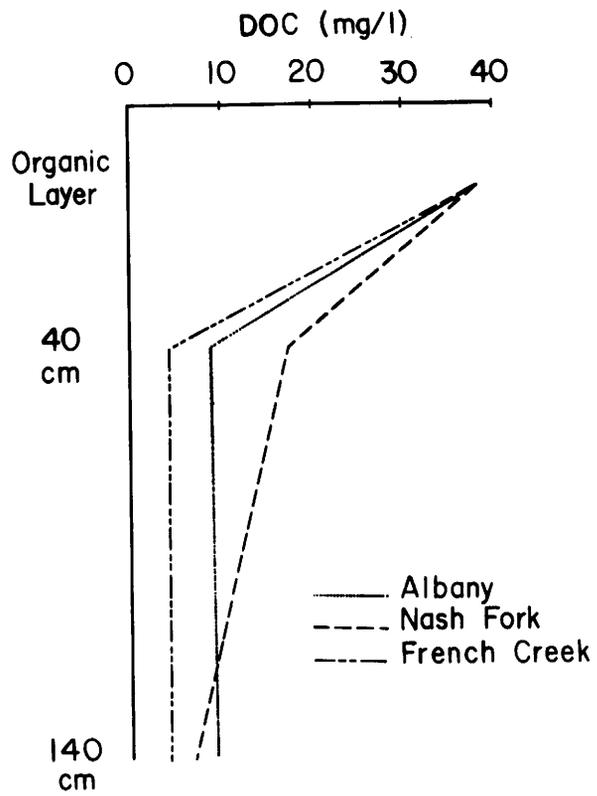


Figure 8. Variation of average DOC concentration with depth in the soil.

Aluminum and Iron- The solubilities of aluminum and iron as free ions and inorganic complexes are quite low at pH values between about 4 and 10 (Drever, 1982). Equilibrium calculations using WATEQF indicate that the samples with higher aluminum values should be oversaturated with respect to gibbsite. This is despite the probable decrease in aluminum concentrations during storage discussed earlier. WATEQF does not include organic complexes in its calculations, and it is organic complexation that is presumably responsible for the high aluminum values.

The correlations between aluminum, iron and DOC in the soil solutions of this study (Fig. 9) are not as good as those found in other studies (Antweiler and Drever, 1983; Graustein, 1981; Beck et al., 1974), perhaps because the DOC values here are much lower than the general levels in these other studies. The samples with high aluminum concentrations also have high DOC values, but some samples with high DOC values have low aluminum concentrations. This could partially be an artifact of aluminum and iron removal by organic flocculation before analysis, particularly at Nash Fork. However, at Albany the correlations between DOC, aluminum and iron are poor, yet there are good correlations between iron and aluminum and both dissociated and undissociated organic acids (Fig. 10). This suggests that it is carboxylic acids rather than total DOC that controls aluminum and iron concentrations, and that the proportion of DOC in soil solutions which is capable of complexing aluminum and iron is variable.

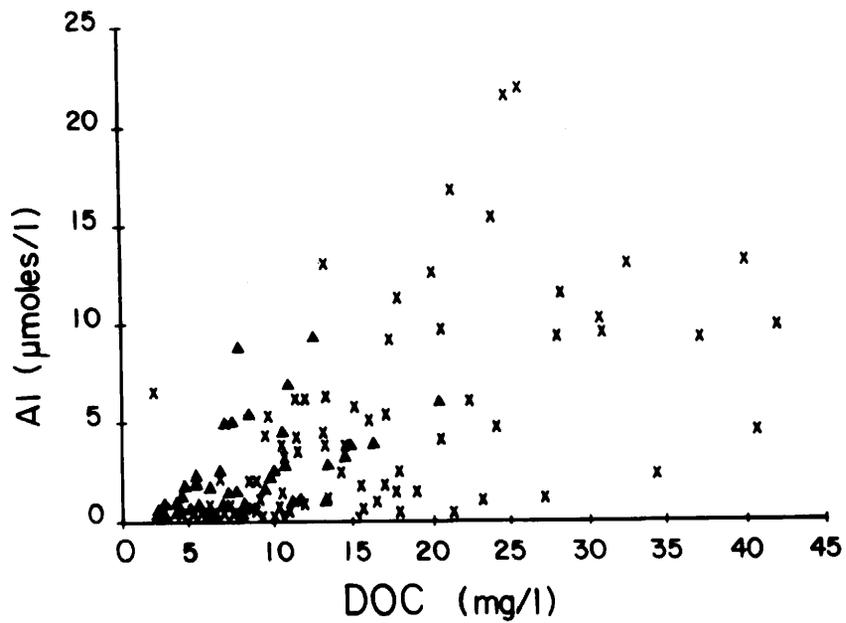


Figure 9. Aluminum and DOC concentrations in soil solutions from 40 and 140 cm. ▲ = Albany, X = Nash Fork.

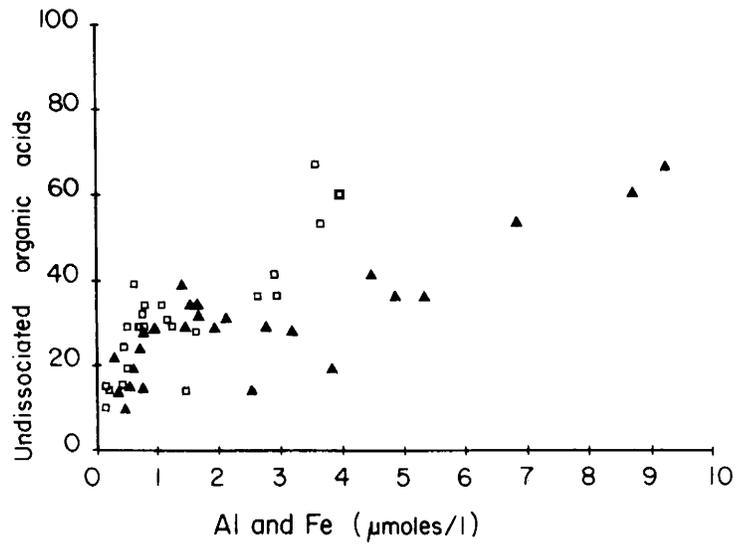
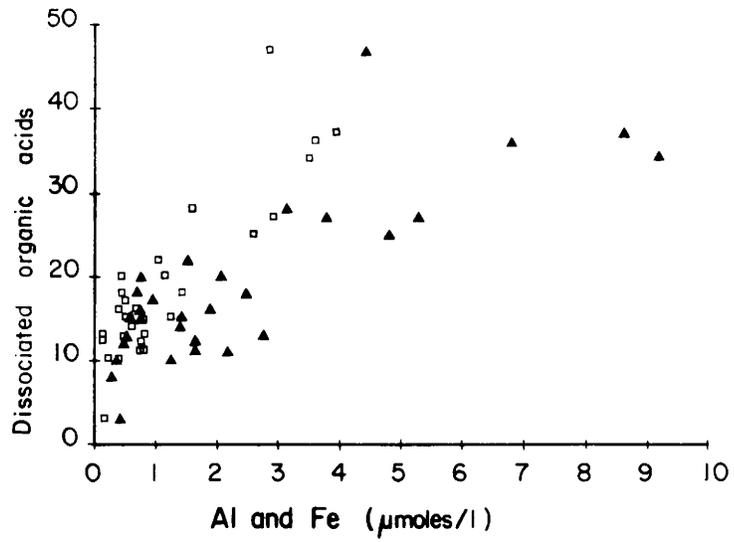


Figure 10. Dissolved Al (\blacktriangle) and Fe (\square) concentrations vs.
 a. dissociated and b. undissociated weak organic acids
 ($\mu\text{eq/l}$) in Albany soil solutions.

Elemental Ratios

The matrix of linear correlation coefficients of major species in the soil solutions is presented in Table 5. There are two groups of variables which tend to have mutually high correlation coefficients: 1) calcium, magnesium, sodium, silica and pH -- the species whose concentrations at 40 cm and below are predominately controlled by weathering reactions; and 2) potassium, iron, aluminum, dissociated and undissociated organic acids, and DOC -- the species dominated by biological processes. Aluminum and iron are biologically controlled because their solubilities are dependent upon organic complexing.

Although the correlations within the groups of weathering and biologically controlled species are highly significant, there is still considerable variability in the composition of soil solutions. Even element pairs such as silica-sodium and calcium-sodium, which have relatively high correlation coefficients and are controlled predominantly by weathering reactions display considerable scatter and no definitive stoichiometry (Figs. 11 and 12).

By far the strongest correlation is between calcium and magnesium which display a linear relationship in the solutions from the organic layer and the mineral soil of all three sites (Fig. 13). This is somewhat surprising, as they have different mineral sources and behave very differently in the biotic system (Fahey, 1983). The close correlation may be a result of buffering

TABLE 5: Linear correlation coefficients of solutes from 40 cm and 140 cm lysimeters, computed using all 1982 data from all three sites.

	<u>Mg</u>	<u>Na</u>	<u>K</u>	<u>SO₄</u>	<u>Cl</u>	<u>HCO₃</u>	<u>pH</u>	<u>Si</u>	<u>Al</u>	<u>Fe</u>	<u>DOC</u>
Ca	.86	.60	.57	.58	.62	.38	.44	.62	.19	.15	.28
Mg		.74	.43	.32	.40	.50	.54	.52	.02	.12	.11
Na			.20	.39	.25	.39	.53	.65	-.16	-.10	-.06
K				.54	.68	.00	.13	.36	.47	.47	.68
SO ₄					.65	.13	-.08	.53	.24	.19	.31
Cl						-.10	-.06	.28	.29	.25	.58
HCO ₃							.45	.21	-.22	-.16	-.19
pH								.29	-.40	-.40	-.16
Si									.19	.14	.13
Al										.78	.67
Fe											.61

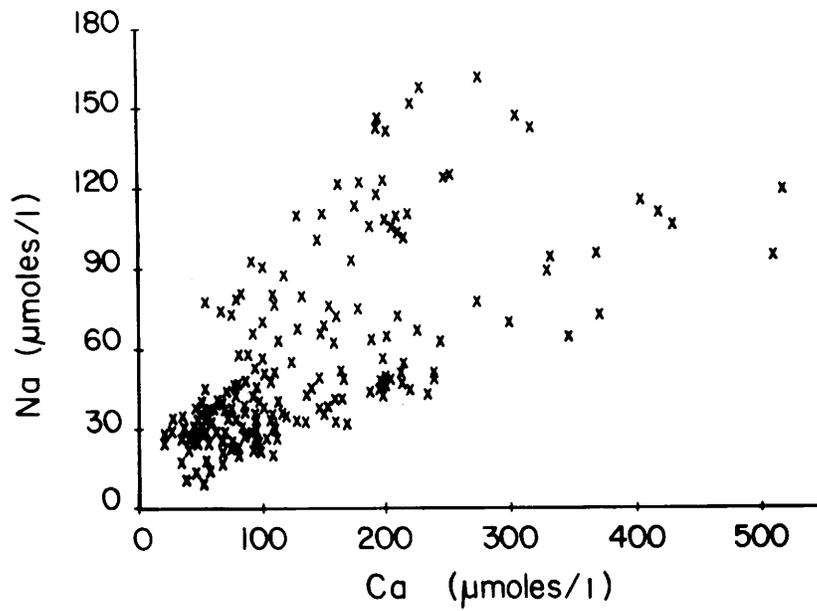


Figure 11. Ca and Na concentrations for all 40 and 140 cm soil solutions.

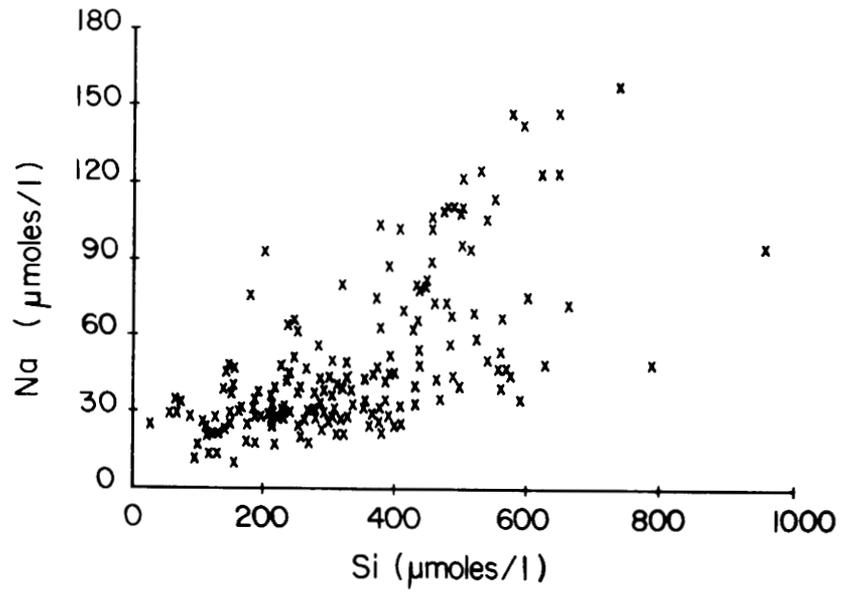


Figure 12. Dissolved silica vs. Na concentrations for all 40 and 140 cm soil solutions.

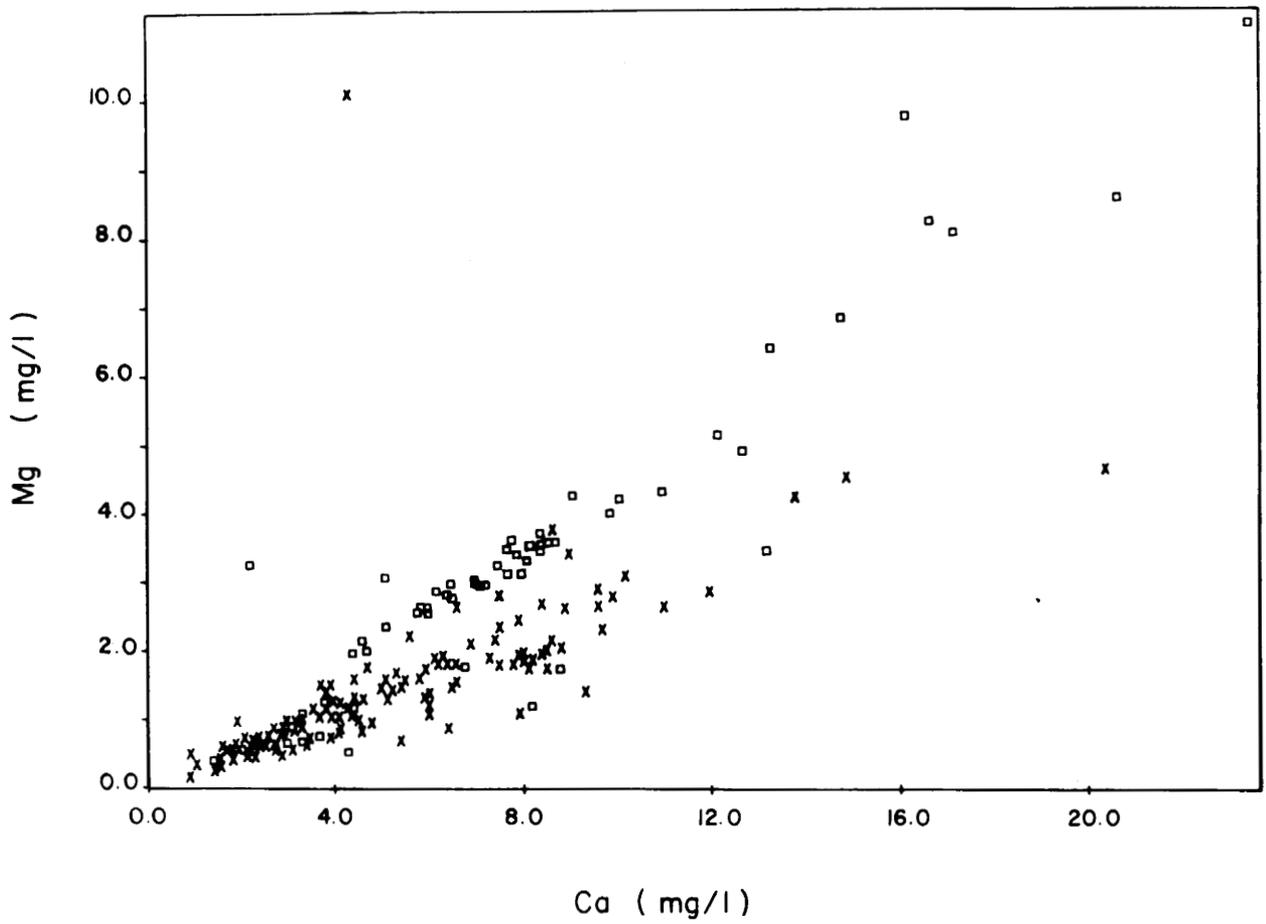


Figure 13. Ca vs. Mg concentrations for 40 (X) and 140 (□) cm soil solutions from all sites.

by cation exchange.

Between-Site Variations

The three study sites have similar climatic and vegetative conditions, and yet have very different soil solution compositions. The mineralogy of the soil should affect the composition of the soil solution both through differences in adsorption properties and through different susceptibilities of the minerals to weathering. The soil structure is important in controlling the residence time of soil solutions, and as discussed earlier, channeling probably has a profound influence on the overall soil permeability. Of course, soil mineralogy and permeability are related; high clay soils tend to have low permeabilities. Although three sites is a rather small sample from which to draw conclusions on the cause of between-site variations, we can make several observations.

Of the sites studied, French Creek has by far the lowest inorganic and organic solute concentrations in soil solutions. It also has a very fine soil with high clay content which results in a very low permeability. The high clay content means the soil should have a high adsorption capacity. The low permeability means a longer residence time for weathering reactions to proceed and release cations to solution, but also for vegetative uptake of cations and metabolism and flocculation of organic solutes.

The organic layer at French Creek is fairly thick (6 cm), yet the 40 cm soil solutions at French Creek have very low DOC and dissociated and undissociated organic acid concentrations. This probably results from some combination of adsorption on clay surfaces and a long residence time for flocculation and metabolism. The very slow infiltration rate has been documented by Fahey and Nyberg (unpublished). The long residence time of the soil solutions should favor acquisition of cations and silica from weathering. However, cation and silica concentrations in the soil solutions at French Creek are very low. This could be a function of two factors; 1) the efficient removal of organic acids at a shallow depth means they are not available for complexing during weathering in the mineral soil, decreasing the kinetics of the weathering reactions, and 2) the soil at French Creek is predominately clays and quartz grains, both of which are extremely resistant to weathering.

The soil at the Albany site is quite porous and permeable (Fahey and Nyberg, unpublished), and has a very low clay content. As a result, both the residence time of the soil solution and the adsorption capability of the soil should be much lower than at French Creek, and, as would be expected, DOC and organic acid concentrations decrease much more slowly with depth. The average DOC values at Albany actually increase slightly with depth (although the increase is statistically insignificant), and are twice as high as DOC values at French Creek. This is despite French Creek having a much thicker organic layer. Cation

concentrations at Albany increase dramatically between 40 cm and 140 cm. This is probably a result of; 1) the high availability of minerals susceptible to weathering, particularly amphibole, biotite, and plagioclase; and 2) the persistence of organic acids in the soil solution to greater depths to act as a complexing agent and pH buffer. The zone of weathering extends quite deep into the granitic bedrock at Albany; a backhoe was able to dig to two meters very easily, with no indication of a significant decrease in the extent of weathering. The depth of weathering is probably a result of the high permeability and low clay content which allows solutions with high concentrations of organic solutes to penetrate to depth.

The Nash Fork site has a permeability and clay content intermediate between those of French Creek and Albany. While at French Creek most DOC loss and cation acquisition take place above 40 cm, and at Albany weathering and DOC loss continue on well below 140 cm, at Nash Fork the lower boundary of the zone of active weathering seems to lie between 40 cm and 140 cm; the Nash Fork soil solutions show a dramatic decrease in DOC and increase in cation concentrations between 40 cm and 140 cm.

SUMMARY AND CONCLUSIONS

1. In the shallow soil (40 cm and above), soil water chemistry is dominated by biological processes -- uptake by roots and

- release from decay in the litter layer. Below 40 cm, weathering of minerals becomes more significant.
2. Soil water compositions at these sites are highly variable, both spatially and temporally. The variability makes it impossible to define any simple weathering stoichiometry. Soil solutions are most concentrated in early spring, as the accumulated products of weathering and biological decay are flushed out.
 3. Uptake by the biomass cannot be ignored in mass balance calculations for weathering in these forests. Elements (particularly potassium) accumulate in the biomass until they are released by fire, which occurs every 100 to 200 years. The biomass can be regarded as being in a steady state only for time-scales of several centuries or longer.
 4. Kaolinite is forming near the surface and smectite at depth in the soils, even though thermodynamic calculations indicate that kaolinite should be favored at all depths. The inconsistency may be because the lysimeters tend to sample preferentially water from high-permeability channels.
 5. Complexing by dissolved organic matter is important in the transport of aluminum and iron. Dissolved aluminum and iron correlate much more closely with dissolved organic acids than with DOC, suggesting that organic acids, rather than DOC in general, are responsible for complexing these elements. The

depth at which dissolved organic compounds, and therefore aluminum and iron, are removed from soil solutions appears strongly dependent on soil permeability and infiltration rates. Adsorption on sesquioxides does not appear to be a major factor in the immobilization of dissolved organic compounds.

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