

TRANSPORT OF METAL CATIONS THROUGH A NUTRIENT-POOR FOREST ECOSYSTEM

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ABSTRACT. Metal cations were analyzed in bulk precipitation, soil water, and stream flow in a southeastern U.S. lower Coastal Plain pine flatwoods for 6 yr. Extractable ions in mineral soil and total amounts in herbaceous vegetation were also determined. Concentrations for all ions were higher in soil water than in bulk precipitation, but especially Na^+ and Mg^{++} . There were smaller concentration differences between soil water and stream flow, except for three-fold higher Ca^{++} in stream flow. Base saturation in the mineral soil was less than 10%, with Al dominating cation exchange sites. Of all cations, only K showed a significant relationship between exchangeable amounts in the soil and total amounts in herb layer vegetation. Soils in the watershed-ecosystem are experiencing minimal mineral weathering, although this can be spatially quite variable. We conclude that the chemistry of such soils is susceptible to change over several forest harvest rotations and continued acid deposition.

1. Introduction

Nutrient cycling studies in forest ecosystems have focussed most commonly on factors affecting the dynamics of N and P. This is understandable, especially for N, considering that these nutrients are often growth-limiting in both natural and managed forests. Less emphasis has been placed on the cycling of nutrient cations in forest systems. Studies of such cycling may be particularly important in highly-weathered systems.

The soils throughout much of the Coastal Plain of the southeastern United States provide classic examples of highly-weathered systems. These soils, which are typically older (and usually highly-weathered) in the upper Coastal Plain than in the lower Coastal Plain, are often derived from sediments eroded from the Piedmont plateau, the Appalachian Mountains, or from weathered marine sediments. Such highly-weathered conditions are especially common in forested areas of the region. Indeed, given some projected patterns of continued weathering, nutrient cations eventually may limit productivity of these forests (Binkley *et al.* 1989; Richter, 1990). An additional concern is the potential long-term effects of acidic deposition on cation loss from Coastal Plain forests and concomitant increases in exchangeable Al in the soil, both of which may potentially affect forest productivity.

We describe the movement of metal cations through a lower Coastal Plain pine flatwoods ecosystem, focussing on factors that influence metal cations in several components of the

system: bulk precipitation, mineral soil, soil water, and stream flow. Long-term changes in metal cations in mineral soil and soil water are simulated with computer models.

2. Materials and Methods

2.1. STUDY SITE

The study site for this research was Watershed 77 (WS77) of the Santee Experimental Forest, located in the Francis Marion National Forest in the lower Coastal Plain of South Carolina (33°N, 80°W). WS77 is approximately 165 ha in total area, with topographic relief ranging less than 5.5 m.

Soils of WS77 are clayey, mixed, thermic, Vertic Aquults of the Bayboro, Bethera, Craven, and Wahee series. The soils are derived from parent materials composed of highly-weathered sedimentary sediments of an alluvial origin, as well as montmorillonitic deposits of a marine origin. As a result, these soils are typically acidic, infertile, and low in weatherable minerals.

WS77 has typical pine flatwoods vegetation. The overstory is dominated by pine species, particularly loblolly pine (*Pinus taeda* L.) and longleaf pine (*P. palustris* Miller). Dominant shrubs were lowbush blueberry (*Vaccinium tenellum* Aiton.) and wax myrtle (*Myrica cerifera* L.). The herbaceous layer was dominated by broom sedge grass (*Andropogon virginicus* L.).

The region experiences a climate of mild winters and warm, moist summers, classified as humid mesothermal (Trewartha, 1954). Lowest temperatures occur in January; highest temperatures occur in July. Precipitation averages around 1350 mm annually, while stream flow averages around 350 mm annually.

2.2. SAMPLING AND ANALYSIS

2.2.1. Bulk Precipitation. Bulk precipitation was sampled using a network of nine pairs of funnel-bottle collectors. Samples were collected on a weekly basis, and volume of precipitation to the watershed was estimated using the polygon method of Thiessen (1911). Following each weekly collection, 1 mL of phenyl mercuric acetate was added to one of the collectors of each pair as a biocide. A sub-sample was taken from the untreated sample and was analyzed within several hours for pH and specific conductance at the field site. The other (treated) sample was frozen and later shipped to Duke University for chemical analysis.

In the chemical analysis laboratory, metal cations (Na^+ , K^+ , Ca^{++} , Mg^{++}) were determined with an atomic absorption spectrophotometric method described in Isaac and Kerber (1971). Cation fluxes were calculated by multiplying weekly volume estimates with weekly cation concentrations. The bulk precipitation sampling was continuous for the 6-yr (1977-1982) period of the study.

2.2.2. Groundwater. Groundwater in these Aquults is at or above groundlevel for several months each year, and surficial groundwater solutions were sampled in the winter of 1978-1979. These collections were conducted to test effects of prescribed fire on groundwater chemistry, but since fire did not significantly alter groundwater chemistry (Richter *et al.*, 1982), pre- and post-burn data are composited in this paper.

Groundwater wells were constructed from polyvinyl chloride (PVC) pipe to sample soil water from A and B soil horizons using different well designs. Surface soil water (A horizon) was collected from PVC pipes which were installed so that perforations were just above the B horizon. The bases of these "type A" wells were sealed with acrylic resin. Soil water from the illuvial B horizons was collected from piezometers of PVC pipe ("type B" wells) placed in the B horizon and open only to water flow from the open bottom of the pipe. The depths from which solutions were collected were from either 100 to 150 mm or from 300 to 350 mm from the soil surface.

There was a total of 32 wells, 16 wells of each type. Sampling was carried out on a weekly basis and samples were analyzed chemically using procedures described previously for precipitation.

2.2.3. Stream Flow. Weekly stream flow volume was calculated from continuous monitoring of stage heights at the calibrated weir at WS77. Daily flow volume was estimated from these continuous readings by U.S.D.A. Forest Service computer programs.

Weekly stream flow grab samples were taken behind the weir. These samples were also analyzed chemically using procedures described for bulk precipitation. Cation output was estimated by multiplying weekly flow volume with the average cation concentrations at the beginning and end of that week.

2.2.4. Mineral Soil. WS77 was divided into 20 sampling compartments of about 8 ha each. Mineral soil was sampled throughout the watershed from 10- x 10-m plots; 10 plots located in each sampling compartment. Samples were taken with a 2.0-cm soil diameter corer, as described in Gilliam and Richter (1988).

Mineral soil samples were air-dried and mill-ground to pass a 2-mm screen. Soil pH was determined with a glass electrode and a 1:1 (v:v) extractant:soil ratio, using water and 1N KCl soil suspensions. Sub-samples of 10-g each were extracted with a dilute double-acid solution according to Mehlich (1953). Extracts were analyzed for base cations using atomic absorption spectrophotometry. Soil samples were taken additionally in one compartment were extracted with 1N KCl and analyzed for Al^{+++} , also using atomic absorption spectrophotometry (McLean, 1965).

2.3. MODEL SIMULATIONS

Long-term (~200 yr) changes in exchangeable soil base cations and soil solution chemistry (including pH, HCO_3^- , Al, and total base cations) were simulated using the MAGIC model. This is a lumped-parameter, process-oriented model, emphasizing processes that are important in controlling stream flow chemistry over long time periods (Cosby *et al.*, 1985). Details of the model, including input-output parameters, are provided in Binkley *et al.* (1989) and Richter (1990).

3. Results

In general, soils of WS77 were extremely acidic and low in base cations (Table I). Soil pH was lowest at the 0 to 5 cm depth and increased significantly in subsoil depths. Extractable cations showed no consistent patterns, neither decreasing nor increasing with depth. Exchangeable Al was extremely high at both depths sampled. Concentrations of KCl-

extractable Al were approximately four times the sum of the other metal cations at both 0 to 5 and 5 to 10 cm soil depths.

Table I. Soil pH and extractable cations at three sampling depths for WS77. Extraction methods are described in text.

Depth (cm)	pH (H ₂ O)	pH (KCl)	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	Al ⁺⁺⁺
			-----meq·kg ⁻¹ -----				
0-5	4.26c*	3.40b	0.63a	0.92a	7.74a	3.64a	45.95a
5-10	4.43b	3.62a	0.39a	0.41b	4.47a	2.74a	30.93a
10-20	4.55a	3.62a	0.45a	0.33b	4.03a	3.22a	--

*Mean differences between soil depths by Duncan's Multiple Range Test, $p < 0.05$.

Bulk precipitation at WS77 was also extremely acidic, with H⁺ being the predominant cation, representing >44% of total cations (Table II). Na⁺ was the second most abundant cation in bulk precipitation solutions, accounting for about 22% of the total dissolved cations. Concentrations of all ions, except H⁺, were higher in soil solution than in precipitation. This was especially the case for Na⁺ and Mg⁺⁺, both of which have important dry deposition inputs from sea salt aerosols that were not measured in this sampling. There were much smaller differences between cation concentrations in soil water and stream flow. The exception to this was Ca⁺⁺, which was three times higher in stream flow (Table II).

Table II. Volume-weighted cation chemistry for bulk precipitation, groundwater, and stream flow for WS77.

Solution	pH	H ⁺	Na ⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺
			-----μeq·L ⁻¹ -----			
Bulk Precipitation	4.38	41.7	20.4	2.1	19.5	9.1
Groundwater:						
A	4.69	16.7	200.0	6.8	39.5	73.8
	*	*	*			*
B	4.62	24.0	185.0	4.4	35.0	65.5
Stream Flow	4.80	15.8	148.8	7.9	106.8	65.8

*Significant difference between A and B means at $p < 0.01$.

Precipitation input and stream flow output data for the 6-yr study period generally showed net outputs of metal cations from the watershed (Table III). The exception to this was K^+ , which showed a net input-output balance. Stream flow output of H^+ was minimal relative to bulk precipitation input (Table III), suggesting a major consumption of H^+ by the watershed. These data are carefully interpreted in the Discussion section, and a case will be made that mineral weathering approaches zero in this watershed ecosystem.

Table III. Watershed budget calculations for cations in bulk precipitation (I) and stream flow (O) for WS77.

Flux	H^+	Na^+	K^+	Ca^{++}	Mg^{++}
	-----keq/ha/yr-----				
Precipitation	0.54	0.27	0.03	0.26	0.13
Stream Flow	0.05	0.49	0.03	0.37	0.22
Net (I-O)	+4.9	-.22	0	-.11	-.09

Computer simulations, spanning the years 1844 to 2024, using the MAGIC model, indicated long-term decreases in exchangeable base cations in the mineral soil, given current acid deposition inputs and current management practices of harvest removals (Figure 1a). A similar decreasing pattern was found for pH and HCO_3^- concentrations in soil water (Figure 1b). Total base cation concentrations increased in soil water over the first 160-yr period. In contrast, soil water Al exhibited little change through the same 160-yr period, although Al gradually increased as soils slowly acidified (Figure 1c). The increased cation leaching is due to increased sulfate deposition and leaching during this period.

4. Discussion and Conclusions

Data from this study strongly suggest that mineral weathering reactions represent a very small, but spatially variable source of cation input to the watershed ecosystem. The extremely acidic and infertile conditions of these soils has arisen from the interactions of several factors. First, soils are derived from weathered secondary parent materials which have experienced several weathering and erosion cycles and consequently are low in weatherable minerals (Gilliam, 1988). Second, long-term climatic conditions wherein precipitation consistently exceeds evapotranspiration on an annual basis at this site have resulted in continued leaching of soil exchangeable ions, especially from upland soils.

Traditional watershed budgetary calculations using bulk precipitation and streamflow data suggest for the 6-yr study net outputs of metal cations from the watershed. Interpretations of these data lead to several significant hypotheses and tentative conclusions that are cation-dependent.

For Na^+ and Mg^{++} , these difference calculations do not include dry deposition inputs from sea salt aerosols, especially aerosols that depend on free canopies for deposition

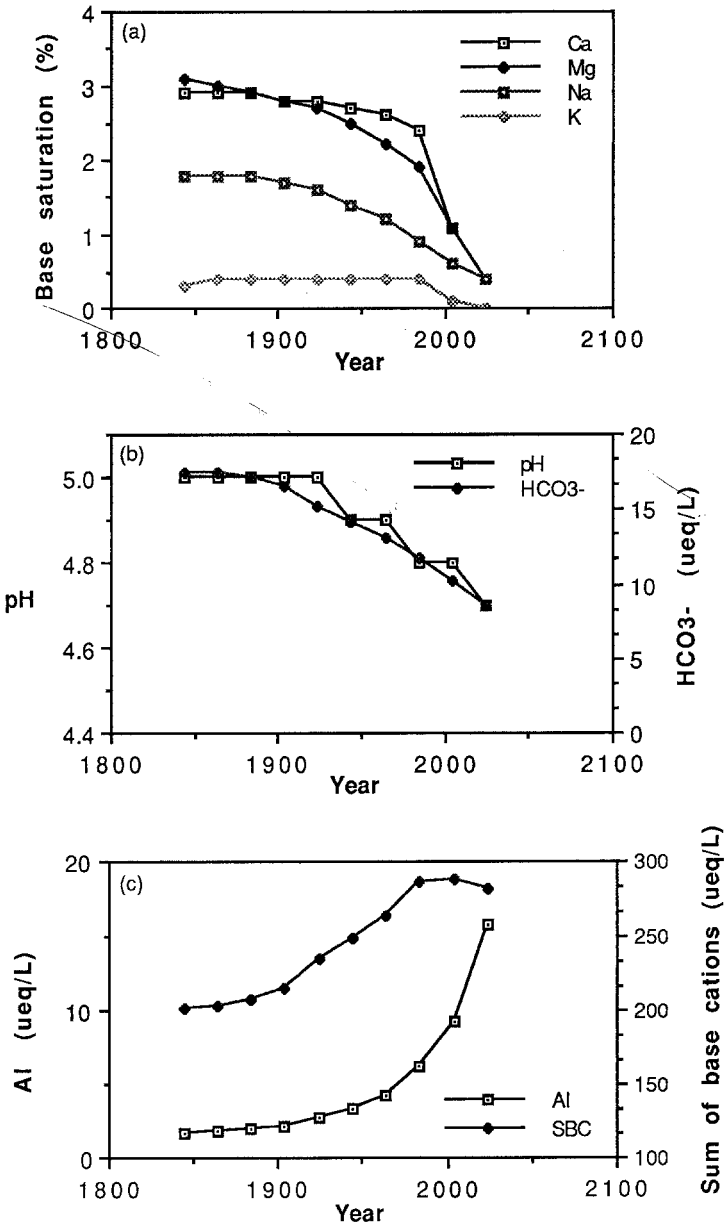


Fig. 1. MAGIC simulations for soil (a) and soil water (b) and (c).

surfaces. The upland groundwater collections suggest that these unmeasured inputs represent important additions of Na^+ and Mg^{++} to the watersheds. Chloride data collected by this study (Richter, 1980; Gilliam, 1983), but not reported here, strongly support the contention that bulk precipitation underestimates atmospheric inputs of Na^+ and Mg^{++} . Mineral weathering input of these cations to the whole watershed are thus less than the difference of 0.22 (Na^+) and 0.09 (Mg^{++}) $\text{keq ha}^{-1} \text{ yr}^{-1}$. Mineral weathering appears to approach zero for Na^+ and Mg^{++} .

Calcium flux though the watershed ecosystem contrasted with that of the other cations. We suggest that Ca^{++} concentrations were higher in stream water than in upland groundwater (Table II) due to the spatial distribution of Ca^{++} in soils and secondary substrata of the watershed. Along stream drains in this part of the lower Coastal Plain, locally high concentrations of Ca-rich sediments are common. Our spatial collections of soil chemistry demonstrate this point well (Gilliam and Richter, 1985). Upland soils are more acidic and Ca-poor than soils in lower lying drainages of the watershed. Streamwater Ca^{++} exceeds that of groundwater due to mineral weathering reactions that occur in these riparian zones.

Watershed budgets for Ca^{++} are similar to those of Na^+ and Mg^{++} (Table III), with relatively small net losses. In contrast to these other cations, however, bulk precipitation may provide accurate approximations of total atmospheric deposition of Ca^{++} (Lindberg *et al.*, 1986). The net watershed loss of Ca^{++} of 0.11 keq ha^{-1} is perhaps a good estimate of mineral weathering. As discussed, mineral weathering of Ca-bearing minerals is spatially concentrated in drainage channels. Since the net loss on a whole-watershed basis (0.11 keq ha^{-1} , or 2.2 kg ha^{-1}) is low compared to potential Ca^{++} uptake rates of forests or soil leaching rates, mineral weathering in the majority of upland soils appears to approach zero.

For K^+ , watershed budgets (Table III) suggest that inputs approximate outputs. Because atmospheric inputs of K^+ do not likely exceed bulk precipitation estimates (Lindberg *et al.*, 1986) and fluxes of K^+ in both bulk precipitation and streamflow are low (0.03 $\text{keq ha}^{-1} \text{ yr}^{-1}$) mineral weathering contributions of K^+ are meagre.

The data presented here also support the idea that this system and other pine flatwoods are, to some degree, potentially cation-limited (Shoulders and Tiarks, 1980). For example, Gilliam (1988) described how extractable K^+ in WS77 soils was significantly correlated with total amounts of K in herb layer vegetation, supporting the observation that K deficiencies can be typical of soils derived from marine sediments (Tisdale and Nelson, 1975).

Turner *et al.* (1986) estimated that about 21.7 million ha of the southeastern US east of the Mississippi River have soils of relatively low buffering capacity (low cation exchange capacity). Most of these soils are highly weathered and may have little ability to resupply exchangeable nutrient cations that are used by plant uptake or are lost to leaching. There appear to be soils over extensive areas of the southeast that are somewhat susceptible to changes in their chemistry over time

In interpreting results of the model simulations it is important to consider the data inputs and assumptions that were included in the simulations. Rates of cycling processes were set at values measured at this site (Richter, 1980; Gilliam, 1983) or were set conservatively, to avoid greatly overestimating soil acidification. The exception was the constraint of no mineral weathering. The model simulations thus specifically evaluate the hypothesis that mineral

weathering rates approach zero in these soils. Atmospheric deposition was set at measured values at the site, although for Ca^{++} regional NADP wet deposition data were used to minimize errors encountered at the site from some carbonate road dust contamination (Richter, 1980). Forest stand accumulation of cations was estimated from pine plantation data from Switzer and Nelson (1972) and a 25-yr harvest rotation. Sulfate was allowed to be absorbed to soils at moderate rates.

Results of the model simulations suggest that the system is substantially and rapidly changing in soil exchangeable cations (Figure 1a) and in soil solution chemistry (Figure 1b and c). From a broad perspective, the simulations demonstrate the importance of deep rooting by pine forests. To moderate the changes illustrated in Figure 1, tree roots must tap significant amounts of nutrient cations from deep B and C horizons or from the weathering front in C horizons. If short-rotation pine trees are to be grown sustainably without fertilizer amendments, accelerated sulfate leaching losses must be matched by uptake of cations from deep in the profile. These results also support the conclusions of Binkley *et al.* (1989) and Richter (1990) that soils with characteristics such as those found on WS77 are potentially sensitive to changes imposed by acid deposition and to harvest removals. These characteristics are: 1) cation exchange capacity $<100 \text{ meq kg}^{-1}$, 2) base saturation $<10\%$, and soil solution pH <5.00 . All three criteria apply to WS77 soils and thus suggest that over time current rates of acid deposition and harvest removals will cause important changes in base saturation, acid neutralizing capacity, and Al in soil solution (Binkley *et al.*, 1989).

In conclusion, cation transport through this lower Coastal Plain flatwoods ecosystem is controlled by several factors. Considering the highly-weathered nature of these soils and the relatively small increases in cation concentrations during transport through soils into drainage channels, weathering appears to approach zero in much of the upland areas of the watershed. As indicated by much higher Ca^{++} concentrations in stream flow compared to ground water, weathering on WS77 is spatially confined largely to Ca-rich materials in soils along stream channels.

Although the results of model simulations are by nature speculative, they support conclusions of Binkley *et al.* (1989) and Richter (1990) that soils typical of WS77 are sensitive to long-term effects of acid deposition. For many Coastal Plain regions depletion of nutrient cations from the soil and increased mobility of Al caused by harvest removals and acid deposition represents a potential problem for both natural and managed forests in the future.

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