

Effects of Liming on Soils and Streamwaters in a Deciduous Forest: Comparison of Field Results and Simulations

Dale W. Johnson,* Wayne T. Swank, and James M. Vpse

ABSTRACT

Soil and stream chemical responses to liming in a deciduous forest watershed at Coweeta, NC, are compared with simulation results using the Nutrient Cycling Model (NuCM). Field comparisons of limed and unlimed soils after 23 yr indicated substantial net retention of applied Ca^{2+} and Mg^{2+} in upper soil horizons, even in black locust (*Robinia pseudoacacia* L.) sites where NO_3^- leaching was elevated. We hypothesized that NuCM simulations would also show that (i) retention of most applied Ca^{2+} and Mg^{2+} in the upper horizons and (ii) increased Ca^{2+} and Mg^{2+} retention with increased cation exchange capacity (CEC) and exchangeable H^+ (simulating pH-dependent CEC). Both hypotheses were supported by simulation results for Ca^{2+} , but not for Mg^{2+} . Most applied Mg^{2+} in the simulations was retained in the BC horizon, where the largest pool of exchangeable Mg^{2+} was initially located. Increasing CEC and exchangeable H^+ did result in increased retention of applied Ca^{2+} and Mg^{2+} in surface horizons. However, increasing CEC caused lower Mg^{2+} retention in the BC horizon, which offset the surface horizon increases and resulted in lower total retention of applied Mg^{2+} . Simulated BC horizon soil solution concentrations mimicked the general patterns in streamwater NO_3^- , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , and K^+ between 1971 (12 yr after liming) and 1979. NuCM simulations did not, nor was it possible to simulate the observed effects of an insect outbreak on streamwater NO_3^- .

LIMING IN AGRICULTURAL SOILS is frequently necessary because most crops are intolerant of low pH and because N fertilizers are acidifying (Barber, 1967). Liming is known to not only increase pH, base saturation, exchangeable Ca^{2+} , and (in the case of dolomitic lime) Mg^{2+} , but also to increase microbial activity (including N fixation), improve soil organic matter status, and increase the availability of several nutrients (Jackson, 1967; Oades, 1988; Persson et al., 1990). Many studies of liming have been made in agricultural soils, including those on the effects listed above as well as more practical considerations such as the rate of lime dissolution as a function of particle size, type of carbonate material used, and methods of application. An excellent summary of this research is presented in the book *Soil Acidity and Liming* (Pearson and Adams, 1967).

The longest study of liming effects on forest soils is found at Rothamsted Experiment Station in England, where limed agricultural lands were allowed to revert to forest in 1881. Soil samples taken in 1881, 1904, and

1964 showed no perceptible change in pH or carbonate content, but did show large increases in organic C and N (Jenkinson, 1970). Similarly, Andersson and Lundqvist (1989) noted that base saturation, exchangeable Ca^{2+} , and Mg^{2+} were still elevated 73 yr after liming a forest soil in Sweden. They also noted that liming stimulated soil biological activity, often creating a temporary N deficiency as microbes competed for available N. They concluded that liming has very long-lasting effects on both soil chemistry and biology. Derome (1990) reported that liming in Finnish forests in the 1950s caused increases in base saturation in humus and surface mineral soils, which persisted at least until the 1970s. He also reported that liming causes an increase in organic matter in the humus layer but not in the mineral soil. Matzner et al. (1983) found that nearly all applied Ca^{2+} and Mg^{2+} was retained within the humus layer following liming plus N-K fertilization beech (*Fagus sylvatica* L.) and spruce [*Picea abies* (L.) Karst.] soils at Soling, Germany. Liming caused increased NO_3^- leaching in both stands, but resulted in reduced leaching of Al, Mn, and SO_4^{2-} leaching in the spruce stand. In a later paper, Matzner and Meiwes (1990) concluded that liming had very little effect on NO_3^- leaching in the beech site, but caused temporary (1-3 yr) increases in the spruce site. They also observed that liming had moderate effects on soil pH and base saturation in the surface horizons, whereas the soil solution Ca/Al and Mg/Al ratios were improved. They attributed the relatively moderate effects of liming on soils in these sites to the slow dissolution of the limestone.

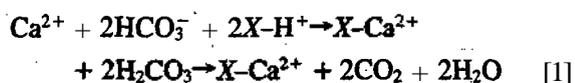
Mohamed et al. (1993) assessed the effects of a mixture of limestone, quicklime, and magnesium oxide (CaMg) and a mixture of these plus ammonium nitrate, potassium sulfate, and superphosphate (NPKCaMg) on an acid forest soil in France. Five years after liming, they found the expected very large ($\approx 10\times$) increases in exchangeable Ca^{2+} and Mg^{2+} in upper soil horizons (0-7 cm), with less effect in deeper horizons. Increases in exchangeable Ca^{2+} and Mg^{2+} were less in the NPKCaMg than in the CaMg treatment, as would be expected due to the competition with NH_4^+ and K^+ for exchange sites. Mean annual budgets for a 1-yr period 4 yr after liming showed very, little leaching loss of applied Ca^{2+} (<1% of that

D.W. Johnson, Biological Sciences Center, Desert Res. Inst., P.O. Box 60220, Reno, NV and Environmental and Resource Sciences, Univ. of Nevada, Reno, NV 89512; and W.T. Swank and J.M. Vose, Coweeta Hydrologic Lab., U.S. Forest Service, 999 Soweeta Lab Road, Otto, NC 28763. Received 27 Jan. 1994. *Corresponding author (dwj@maxey.dri.edu)

Abbreviations: ANC, acid-neutralizing capacity; CEC, cation exchange capacity; D_0 , initial diameter of lime particles; IFS, Integrated Forest Study; LIME, simulation scenario with lime mineral; LIMING, simulated application of lime; M^{a+} , cation of valence a; M^{b+} , cation of valence b; NO LIME, simulation scenario without lime mineral; NuCM, nutrient cycling model; WS6, Watershed 6, which was limed; X, exchange phases equivalent fraction.

applied) and somewhat greater leaching of Mg^{2+} (5-10% of that applied). The greater leaching of Mg^{2+} may have been due to mass action (1347 kg ha^{-1} of Ca^{2+} was applied as opposed to 241 kg ha^{-1} of Mg^{2+}) and perhaps also the greater selectivity of Ca^{2+} for exchange sites. The CaMg treatment caused reduced NO_3^- leaching but had no effect on SO_4^{2-} leaching.

The literature cited above shows that there is generally little movement of added Ca^{2+} and Mg^{2+} from surface to subsurface horizons following liming. There are at least three possible reasons for this. One is the slow dissolution of limestone, as noted by Matzner and Meiwes (1990). Another is the lack of a mobile anion to transport Ca^{2+} and Mg^{2+} to deeper horizons. Carbonate and HCO_3^- from dissolving limestone will become rapidly protonated in acid soils forming carbonic acid, CO_2 , and water, removing mobile anions for transport of associated Ca^{2+} or Mg^{2+} to deeper horizons. The reaction can be summarized as follows for calcium bicarbonate:



where X denotes a soil cation exchange site.

The activation of pH-dependent cation in exchange (CEC) sites by liming in organic-rich surface horizons may enhance the retention of applied Ca^{2+} and Mg^{2+} . On the other hand, such increases might be offset by the formation of nonexchangeable metal hydroxides on inorganic exchange sites as pH is raised above the point where all monomeric Al precipitates (5.5) (Coleman and Thomas, 1967). The net result is sometimes a decrease in CEC to pH 5.5 and an increase thereafter (Coleman and Thomas, 1967).

At Coweeta Hydrologic Laboratory, in North Carolina, the effects of liming followed by site occupation by N-fixers (black locust; *Robinia pseudoacacia* L.) on soil and soil solution chemistry have been investigated (Montagnini et al., 1986, 1991). Comparisons of soils from the limed watershed with those from an unlimited watershed suggested that most applied Ca^{2+} and Mg^{2+} was retained within the upper (0-30 cm) soil horizons over two decades later, despite the fact that NO_3^- leaching was considerably increased by the presence of N-fixers on the limed watershed (Montagnini et al., 1986, 1991). In this paper, we complement these previous investigations with an evaluation of long-term trends in stream chemistry and simulation of liming at the site with the nutrient cycling model (NuCM). We hypothesized that (i) NuCM simulations, like the field data, would predict that most of the applied Ca^{2+} and Mg^{2+} would be retained in the upper soil profile, and (ii) simulated soil Ca^{2+} and Mg^{2+} retention would be greater with increased CEC and exchangeable H^+ (simulating pH-dependent CEC).

MATERIALS AND METHODS

Site

The history of Watershed 6 (WS6) has been described in detail by Hibbert (1969) and Johnson and Swank (1973). Only a brief summary will be presented here. As is often the case in watershed studies, there were, unfortunately, no replications

of the treatments imposed on WS6. The 9-ha watershed was harvested for all merchantable timber in 1958, slash piled, burned, grubbed, and harrowed, and planted to grass (Kentucky 31 fescue, *Festuca arundinacea* Schreb.) as part of a study on the difference in water yield between grass and mixed hardwood. In March 1959, the site was fertilized with 6700 kg ha^{-1} of dolomitic limestone (56% $CaCO_3$, 32% $MgCO_3$) and 2200 kg ha^{-1} of 2-12-12 (N-P-K) fertilizer. In May 1960, 3 ha were fertilized with NH_4NO_3 (33.5% N) at 224 kg ha^{-1} . In March 1965, 672 kg ha^{-1} of 30-10-10 (N-P-K) fertilizer and 170 kg ha^{-1} of potash containing 60% K were applied. In May 1966, herbicide control of grass cover was initiated for a 2-yr period, and thereafter the site was allowed to reforest. The total applications of fertilizer are calculated to be as follows: Ca^{2+} , 1500 kg ha^{-1} ; Mg^{2+} , 600 kg ha^{-1} ; K^+ , 331 kg ha^{-1} ; N, 242 kg ha^{-1} to most of the watershed, 317 kg ha^{-1} to 3 ha; and P, 331 kg ha^{-1} . These were significant additions to soil-exchangeable Ca^{2+} (940 kg ha^{-1}), K^+ (510 kg ha^{-1}), and available P (30-50 kg ha^{-1}) levels in the soil (90-cm depth), using other Coweeta data as a rough guideline (Henderson et al., 1978; Johnson and Lindberg, 1991). The additions to exchangeable Mg^{2+} (600-1200 kg ha^{-1}) were smaller, and additions to total N (6800 kg ha^{-1}) trivial. Additions to available N were larger, but temporary.

Vegetation on WS6 in 1969 was dominated by a dense cover of a variety of herbaceous species, and by 1970 woody shrubs were established over the watershed. By 1969, the watershed was dominated by black locust, blackberries (*Rubus* spp.), and numerous vines (*Vitis* spp., *Climatis* spp., and *Smilax* spp.). Dense black locust stands occupied 73% of the watershed, 12% was occupied by pine-mixed hardwood, and 15% was occupied by mesic mixed hardwood (Montagnini et al., 1986). A heavy infestation of the locust stem borer (*Megacyllene robiniae*) began in 1979, and by 1982, 21% of the black locust trees were standing dead and 18% had more than 50% crown dieback due to stem borer damage. This infestation produced an abrupt increase in flow-weighted mean annual NO_3^- concentrations from 50 to 75 $\mu mol \cdot L^{-1}$ (Swank and Waide, 1988).

The dominant soil series on lower slopes and in coves is the Brevard-Saunooke, a member of the fine-loamy, mixed, mesic family of Humic Hapludults. Soils on the slopes and ridges belong to the Evard-Cowee series, a member of the loamy, mixed, mesic family of Typic Hapludults.

METHODS

Existing data on streamwater chemistry, soil chemistry, and vegetation growth were analyzed to determine time trends and to parameterize the NuCM model. These data, along with other data necessary for parameterization, were input to the NuCM model and simulations run for 30 yr. A brief description of the NuCM model containing only the details relevant to this application is provided below; see Liu et al. (1991) for more detail.

The NuCM model was developed as part of the Electric Power Research Institute's Integrated Forest Study (Liu et al., 1991; Johnson and Lindberg, 1991). The NuCM model links the soil-solution chemical components of the ILWAS model (Goldstein et al., 1984) with traditional conceptual models of forest nutrient cycling on a stand level. The forested ecosystem is represented as a series of vegetation (foliage, bole, roots; overstory and understory), litter, and soil components. The soil includes multiple layers (up to 10), and each layer can have different physical and chemical characteristics. Tree growth potential is defined by the user and is subject to reduction in the event that nutrients or moisture become limiting.

Using mass balance and transport formulations, the model

tracks 16 solution-phase components including the major cations and **anions** (analytical totals), acid-neutralizing capacity (**ANC**), an organic acid analog, and total **monomeric** aluminum (Liu et al., 1991). The concentrations of hydrogen ion, aluminum and carbonate species, and organic acid **ligands** and complexes are then calculated based on the 16 components. The model routes precipitation through the canopy and soil layers, and simulates **evapotranspiration**, deep **seepage**, and lateral flow. The movement of water through the system is simulated using the continuity equation, **Darcy's** equation for permeable media flow, and Manning's equation for free surface flow.

The processes that govern interactions among nutrient pools include decay, nitrification, **anion adsorption**, cation **exchange**, and mineral weathering. The model simulates the **noncompetitive** adsorption of **sulfate**, phosphate, and organic acid. Sulfate adsorption is simulated in NuCM using both linear and **Langmuir** (saturation), **pH-dependent adsorption** isotherms. Because sulfate is adsorbed **noncompetitively**, there is no direct mechanism by which additions of large amounts of phosphate **will** cause sulfate **desorption**. Phosphate adsorption in the model is represented by a linear isotherm.

Cation exchange is represented by the **Gapon** equation:

$$\frac{XM^{a+} (M^{b+})^{1/b}}{XM^{b+} (M^{a+})^{1/a}} = Q \quad [2]$$

where X = exchange phase equivalent fraction,

() = soil solution activity,

M^{a+} = cation of valence a,

M^{b+} = cation of valence b, and

Q — selectivity coefficient (constant).

The NuCM model does **not** deal explicitly with pH-dependent cation exchange (CEC) **sites**, but does include exchangeable H^+ as well as Al^{3+} and base cations. Because we felt that the inclusion of **pH-dependent** CEC would be important for the response to liming, we ran two scenarios: one with CEC and exchangeable cations measured with unbuffered NH_4Cl (as **analyzed** for the Integrated Forest Study [**IFS**] and used **in** previous simulations for Coweeta **ecosystems**; Johnson et al., 1993), and one where CEC **in** the A horizon was doubled, with the additional exchange sites filled with exchangeable H^+ . This gave exchangeable H^+ percentages close to those measured directly by **Montagnini** et al. (1986) using the method of Adams and Evans (1962) (measurement of pH **in** a buffered solution of **p-nitrophenol**, **borate**, **KCl**, and **KOH**).

Mineral weathering reactions are described **in** the model using rate expressions with dependencies **on** the mass of mineral present and solution-phase H^+ concentration taken to a fractional power. In these simulations, mineral weathering rates were set to low values appropriate for the Coweeta basin (Johnson et al., 1993), except **in** the case of the LIME mineral (see **below**).

The NuCM model was parameterized for Watershed 6 using data from the **IFS** and from long-term **records** according to the procedures outlined in the **user's manual** (Munson et al., 1992). Watershed 6 has been studied intensively at intermittent periods since 1970 at the initiation of the international Biological Program. Hydrologic research began **in** 1934 and has continued to the present time. Data files input from previous site-specific research included physiographic, meteorological, and atmospheric chemistry data; soil physical data (horizon depths, bulk, density, hydraulic conductivities, water retention characteristics, root distribution and uptake properties, and temperature); organic matter decay rates, and nitrification

rates. Nitrogen inputs via fixation were simulated by increasing ammonium deposition by **24-fold** (to approximately 50 kg N $ha^{-1} yr^{-1}$). Data files taken from the **IFS** and/or other historical research included soil chemical data (primary minerals, mineral dissolution rates and **stoichiometries**, and sulfate adsorption parameters.) Other model parameters (such as organic acid adsorption, phosphate adsorption, snowmelt characteristics, fractions of **leachable** nutrients in litter, etc.) were left as in the original model formulation (Liu et al., 1991). It is noteworthy that the first soil layer includes litter, and thus the properties of this layer were the average of the **litter** and A horizon of the mineral soil. Requirements for soil chemical data precluded the option of making Layer 1 simply a litter layer.

During the process of calibration, soil hydraulic conductivity, the *evapotranspiration coefficient* and saturated hydraulic conductivities were used to obtain the correct **evapotranspiration**, soil water flux, and lateral flow values. Hydraulic calibration was greatly enhanced by stream gauging data, which served as a point of constraint in determining calibration parameters. The stream routing routine was not used, since the first-order stream draining WS6 is very small (<270 m in length). **Thus**, drainage from the deepest soil layer (specified at 600 cm) was equated to discharge for chemistry and trend comparisons.

Liming was simulated by adding a mineral, LIME, with the correct **stoichiometry** for the Ca, Mg, P, and K additions at the correct concentrations **in** Layer 1 so as to approximate the inputs by liming and fertilization. It was not possible to simulate the additions of K and P fertilizers at the actual times that these were applied (6 yr after the initial **liming**), so these were included **in** the original mineral and were released beginning in the first year of the simulation. The weathering rate for the LIME mineral was initially set such that it dissolved over the first 10 yr of the simulation. This was based on the nomograph and equation given by Pearson and Adams (1967) for limestone dissolution. They give the **equation**:

$$(1 - u)^{1/3} = 1 - ct \quad [3]$$

where u = fractional mass dissolved, $c = 2k/pD_0$ (where k = a constant, p = particle density, and D_0 = **initial** diameter), and t = time. Pearson and Adams (1967) present a nomograph that plots $(1 - u)^{1/3}$ vs. t (wk) for limestone and note that the slope should equal c . Using this nomograph for a 10 to 20-mesh (1-2 mm) limestone and setting $c = 0.01$ (99% **dissolution**), the solution of Eq. [2] for t gives a value of 212 wk (approximately 4 yr). The value of 10 yr was set **in** the model because of the presumption that dolomite mesh size was somewhat greater than 1 to 2 mm and because of the observation that dolomite dissolves at about half the rate of pure limestone (Pearson and Adams, 1967).

RESULTS AND DISCUSSION

Field Data

Streamwater Concentrations

Streamwater NO_3^- on WS6 was **elevated** relative to other watersheds at Coweeta, reflecting the presence of black locust (Fig. 1A). Streamwater NO_3^- concentrations also reflected the outbreak of the locust borer in 1979. To more clearly show this effect, the regressions of concentration against time (**i.e.**, month number beginning in October 1971) were broken into two components, pre- and post-1979. Before the locust borer outbreak in

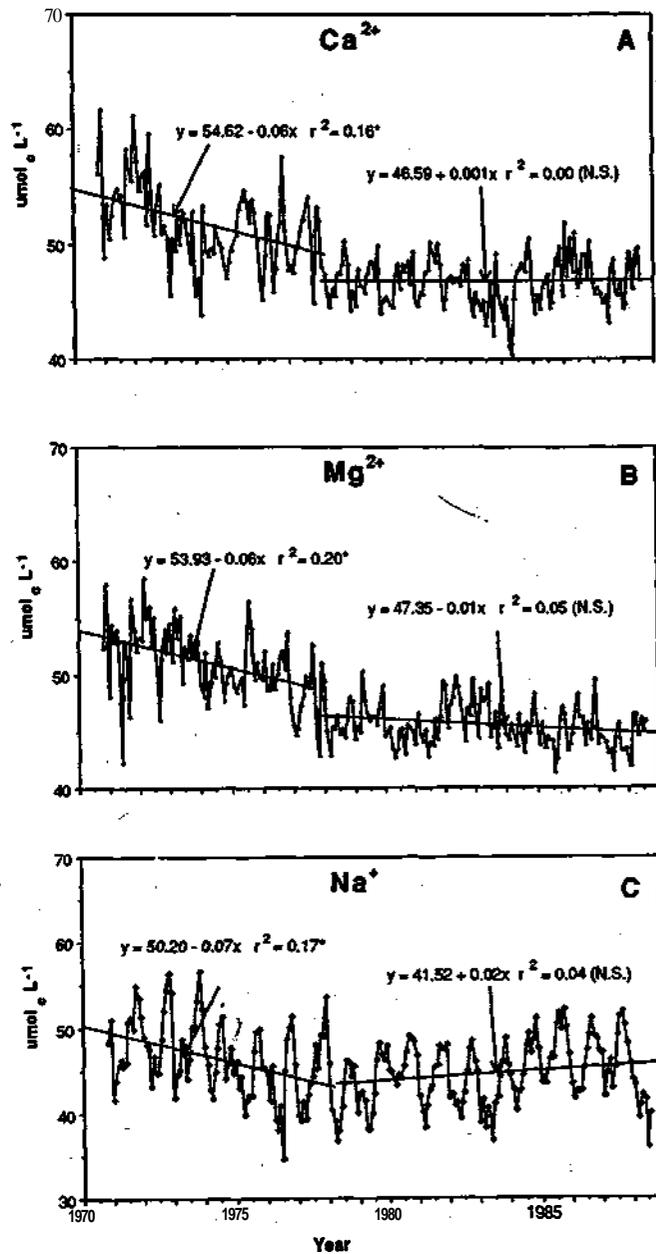
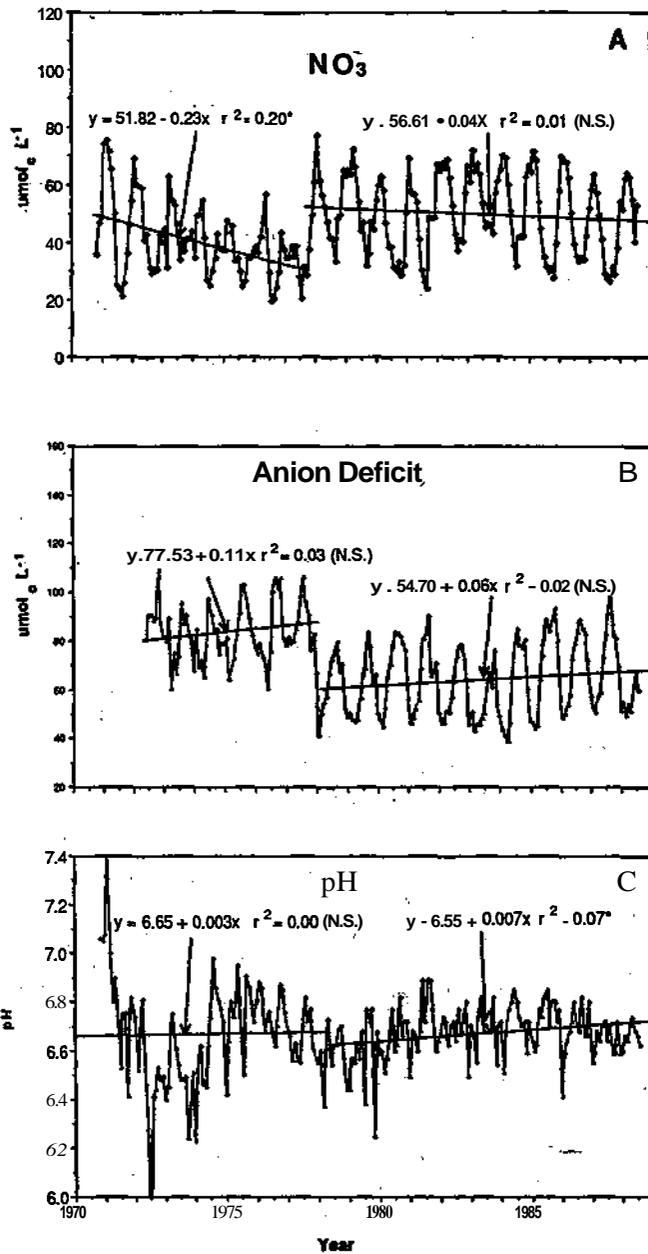


Fig. 1. Streamwater concentrations of (A) NO₃⁻, (B) anion deficit (total cations — total anions, not including alkalinity), and (C) pH in Watershed 6 (* = statistically significant regression, N.S. = not significant).

Fig. 2. Streamwater concentrations of (A) Ca²⁺, (B) Mg²⁺, and (C) Na⁺ and in Watershed 6 (* = statistically significant regression, N.S. = not significant).

1979, there was a weak but statistically significant decline in Streamwater NO₃⁻. After 1979, there was a sharp

increase in NO₃⁻ but no statistically significant trend. Unfortunately, the alkalinity data are insufficient to analyze time trends, but an estimate of alkalinity can be

Table 1. Correlation matrix (r² values) for Streamwater chemical concentrations.^t

	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	An. def.‡	pH
NO ₃ ⁻	X	X	X	X	X	X	X	X	X
Cl ⁻	0.20-	X	X	X	X	X	X	X	X
SO ₄ ²⁻	NS	0.29-	X	X	X	X	X	X	X
K ⁺	0.20+	0.47+	0.28+	X	X	X	X	X	X
Ca ²⁺	0.25-	0.65+	0.26-	0.22+	X	X	X	X	X
Mg ²⁺	NS	0.70+	0.46-	0.23+	0.73+	X	X	X	X
Na ⁺	0.54-	0.46+	NS	NS	0.39+	0.22+	X	X	X
An. def.‡	0.93-	0.40+	0.17-	NS	0.60+	0.42+	0.65+	X	X
pH	NS	0.14-	0.26-	NS	NS	NS	NS	NS	X

^t + next to a number indicates positive correlation, — indicates negative correlation, NS indicates not significant, 95% level.
[‡] Anion deficit (cations - anions), including alkalinity.

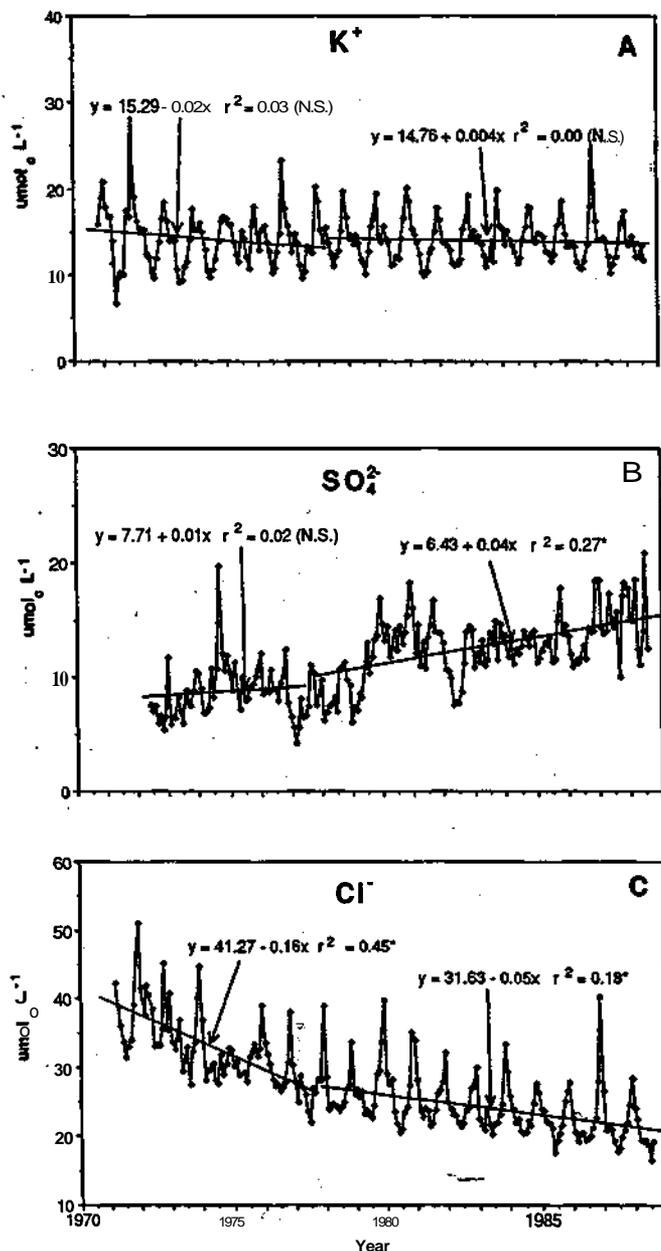


Fig. 3. Streamwater concentrations of (A) K^+ , (B) SO_4^{2-} , (C) Cl^- and in Watershed 6 (* = statistically significant regression, N.S. = not significant).

obtained from the anion deficit (i.e., $\Sigma cations - \Sigma anions$). This method would include both organic and inorganic (OH^- and HCO_3^-) sources of alkalinity; however, inorganic sources (probably HCO_3^-) are probably dominant in this case. There was a weak but significant ($r^2 = 0.12$) overall decline in anion deficit from 1973 to 1989, but this was due to a sharp decline after 1979. The trends both before and after 1979 were not statistically significant (Fig 1B). The sharp decline in anion deficit in 1979 was not associated with a detectable decrease in pH, and there was no significant overall trend in pH with time (Fig. 1C). The variation in anion deficit was driven primarily by variations in NO_3^- , as shown by the positive correlation between the two (Table 1). The

Table 2. Simulated exchangeable Ca^{2+} and Mg^{2+} pools in the soil.

Horizon and depth (cm)	After 30 yr				
	Initial	Low CEC		High CEC	
		No lime	Lime	No lime	Lime
	$kmol\ ha^{-1}$				
	Calcium				
A (0-13)	34.6	26.3	42.4	18.9	50.9
BA (13-22)	0.5	0.2	0.4	0.6	1.4
BC (22-67)	2.4	1.1	9.2	5.4	8.6
Total	37.5	27.6	52.0	24.9	60.9
	Magnesium				
A (0-13)	5.0	3.5	3.2	1.2	2.7
BA (13-22)	1.3	0.4	0.4	0.4	0.9
BC (22-67)	25.4	16.5	27.3	19.2	25.9
Total	31.7	20.4	30.9	20.8	29.5

correlations between pH and NO_3^- or HCO_3^- were not significant.

Streamwater Ca^{2+} , Mg^{2+} , and Na^+ concentrations followed the same basic patterns as NO_3^- : weak but statistically significant declines from 1971 to 1979 and no trend thereafter (Fig. 2). In the case of K^+ , there was no significant trend either before or after 1979, or overall (Fig. 3A). Streamwater SO_4^{2-} concentrations increased steadily over the monitoring period (Fig. 3B), suggesting a saturation of SO_4^{2-} adsorption sites in the soil, as noted in other watersheds at Coweeta (Swank and Waide, 1988; Johnson et al., 1993). However, the trend was not statistically significant until after 1979. Surprisingly, Cl^- concentrations decreased throughout the 1971 to 1989 period (Fig. 3C). This was not correlated to changes in streamflow or evapotranspiration, and may have been due to desorption of Cl^- previously absorbed from dissolving potash. Although Cl^- is normally thought of as an inert tracer ion for hydrologic purposes, it can adsorb onto Fe and Al hydrous oxide surfaces at high concentrations (Johnson and Cole, 1980).

Streamwater Ca^{2+} , Mg^{2+} , and Na^+ concentrations were most positively correlated with Cl^- , reflecting the similarity in long-term temporal patterns among these ions (Table 2). Streamwater K^+ was also most positively correlated with Cl^- because of similar seasonal patterns, even though the long-term temporal patterns among these two ions differed. Correlation coefficients among anion deficit and Ca^{2+} , Mg^{2+} , and Na^+ were positive and significant, indicating that seasonal variations in these cations influenced anion deficit, even though long-term trends differed. The correlation between anion deficit and K^+ was not significant, however.

The abrupt increase in Streamwater NO₃⁻ without concurrent increases in cation concentrations in 1979 suggests that an anion shift (from HCO₃⁻ and organic anions to NO₃⁻) occurred. Although there is insufficient alkalinity data to directly test this hypothesis, the conclusion is nearly inescapable, given the requirement for charge balance. Normally, such an anion shift would require a reduction in pH (causing a reduction in HCO₃⁻); however, no change in Streamwater pH was noted. It is possible that there was a reduction in soil solution pH that was not detectable in streamwaters because of pH rise with

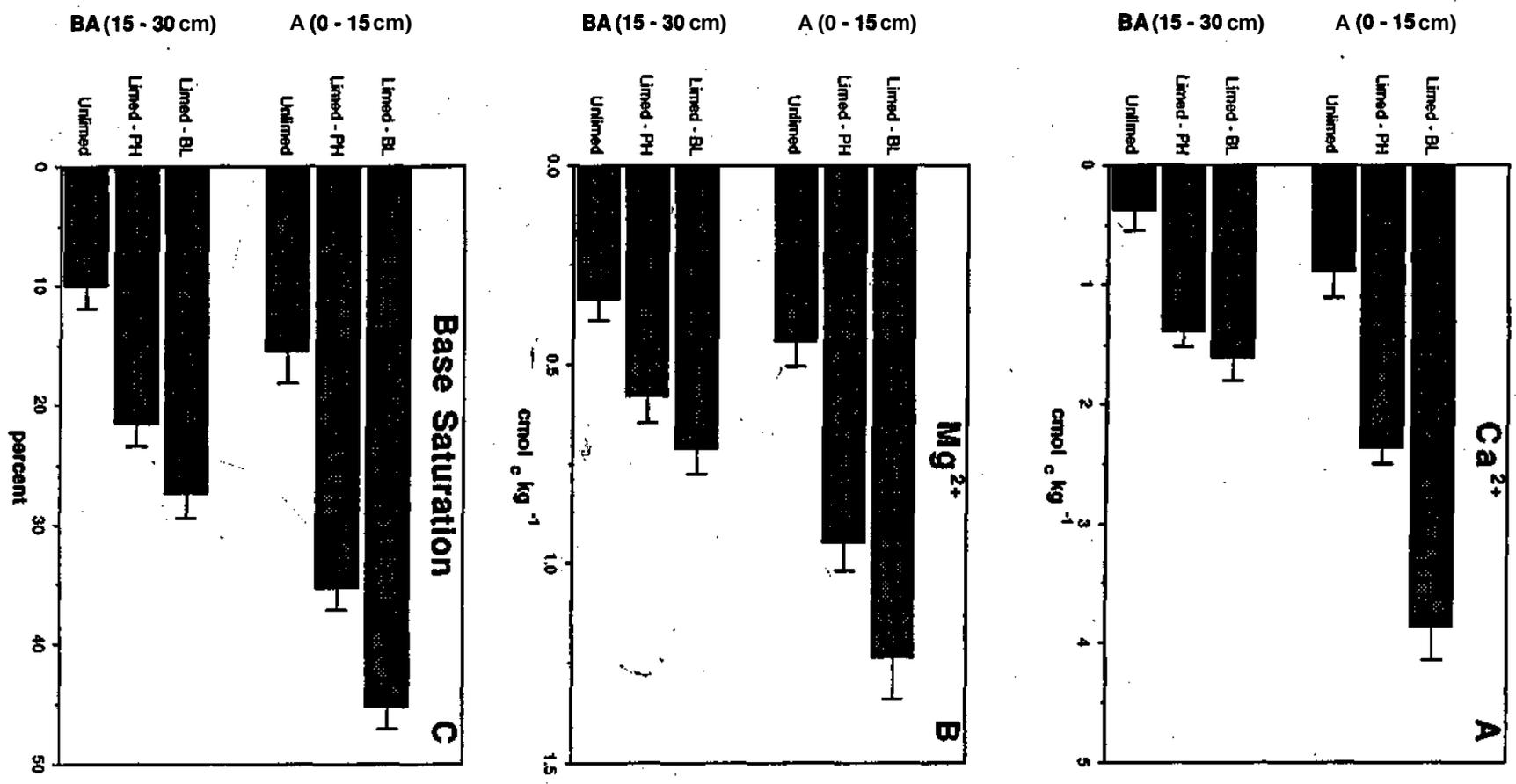


Fig. 4. Exchangeable (A) Ca²⁺, (B) Mg²⁺, and (C) base saturation in soils beneath black locust on watershed 6 (Limed-BL) pine-hardwood on Watershed 6 (Limed-PH), and in a nearby oak-hickory watershed (Unlimed) in July 1982 at Coweeta (data from Montagnini et al., 1986, 1991).

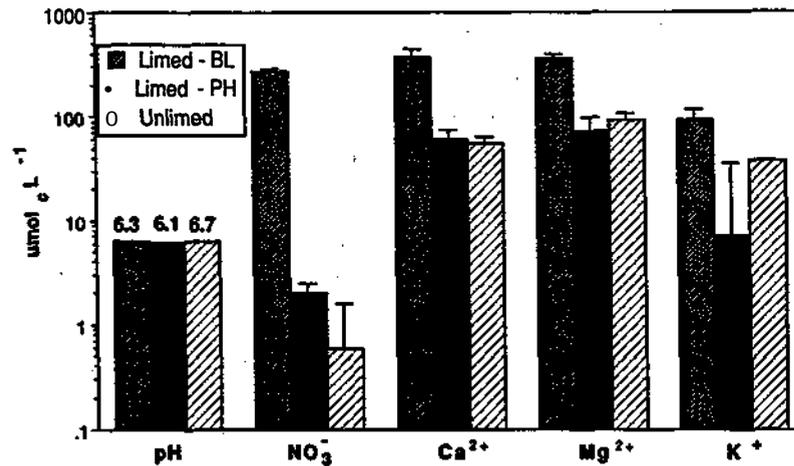


Fig. 5. Soil solution concentrations under black locust vegetation (Limed-BL) and pine-hardwood vegetation (Limed-PH) on Watershed 6 (limed) in a nearby oak-hickory watershed (Unlimed) in 1984 (data from Montagnini et al., 1986, 1991).

CO₂ degassing (Reuss and Johnson, 1985). Alternatively, a change in streamwater or soil pCO₂ would have to be invoked to produce a change in alkalinity without a change in pH.

Soil and Soil Solution Concentrations

Montagnini et al. (1986, 1991) have previously published soil and soil solution data for WS6; their results are briefly reviewed here for the sake of comparison with stream data and model simulations. They sampled soils by depth in March and July of 1982 and soil solutions from September 1983 to December 1984. In both the March and July sampling, 0- to 30-cm soils from both WS6 vegetation types (black locust and pine-hardwood) had significantly higher exchangeable Ca²⁺, Mg²⁺, and base saturation than soils from the unlimed watershed. Figure 4 illustrates the results of the July sampling, when the pine-hardwood soils on WS6 had lower exchangeable Ca²⁺, Mg²⁺, and base saturation than black locust soils on WS6 in the 0- to 15-cm depth. There were no significant differences in these two vegetation types in the March sampling, and the reason for the apparent change in the pine-hardwood soils is not known. In any event, there was no evidence of soil acidification by black locust vegetation, despite the fact that soil solution NO₃⁻ and base cation concentrations were elevated (see below). When expressed on a weight basis, the differences between limed and unlimed soils amounted to approximately 1000 kg ha⁻¹ of Ca²⁺ and 200 kg ha⁻¹ of Mg²⁺, or about 75 and 33% (respectively) of what was added with liming. Unfortunately, there are no pretreatment soil data from WS6, so the actual retention of lime can only be approximated through this comparison.

Patterns in soil solution differed substantially from those in the soils. Montagnini et al. (1991) reported elevated soil solution NO₃⁻, Ca²⁺, Mg²⁺, and K⁺ concentrations under black locust vegetation on WS6 compared with pine-hardwood vegetation on WS6 and the nearby unlimed watershed (Fig. 5). Differences between the pine-hardwood and unlimed soil solutions were not statistically significant. Streamwater NO₃⁻ concentrations

from WS6 at this time were nearly an order of magnitude lower than in black locust soil solutions, but an order of magnitude greater than in the pine-hardwood soil solutions (Fig. 1A). Streamwater Ca²⁺, Mg²⁺, and K⁺ concentrations at this time were lower than in black locust soil solutions but in the same range as soil pine-hardwood and unlimed soil solutions (Fig. 2 and 3A).

Collectively, the soil and soil solution data collected by Montagnini et al. (1986, 1991) suggests that the Ca²⁺ and Mg²⁺ applied in the lime were tightly retained in the surface soils, and that increased cation leaching 25 yr after liming occurred only as a result of excess NO₃⁻ production under black locust vegetation rather than as a result of the liming treatments.

NuCM Simulations

Simulation outputs showed many interesting interactions among vegetation, soils, and nutrients as a result of the treatments imposed. In most cases, the applicability of these results to the field situation are unknown because comparable field data are lacking. Thus, only a limited selection of output is described below, representing parameters for which some comparisons with field data can be made.

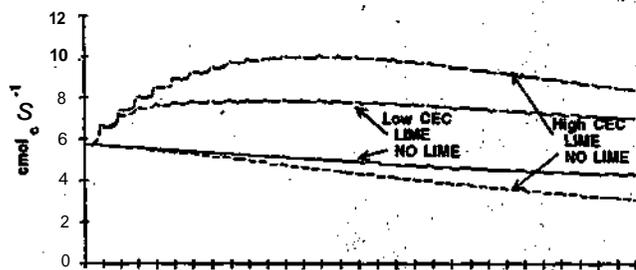
Simulated Soil Concentrations and Contents

Simulated exchangeable Ca²⁺, Mg²⁺, and base saturation changed continuously over the 30-yr simulation, with or without LIME (Fig. 6-8). Thus, the effects of the LIME treatments must be assessed against continuously changing baselines (NO LIME treatments). Increasing CEC caused significant changes in the baseline: high CEC caused greater Ca²⁺ translocation from the A to the BA and BC horizons than Low CEC did (Fig. 6-8). In several cases, the effect of high CEC on baseline shift was as great or greater than its effect on the LIME scenarios (e.g., BC horizon Ca²⁺, A horizon Mg²⁺, A horizon base saturation; Fig. 6-8).

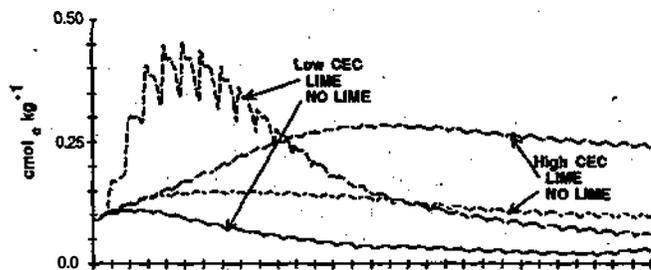
LIME caused prolonged increases in exchangeable Ca²⁺ compared with NO LIME in all horizons at both low and high CEC (Fig. 6). High CEC caused greater

Exchangeable Ca^{2+}

A Horizon



BA Horizon



BC Horizon

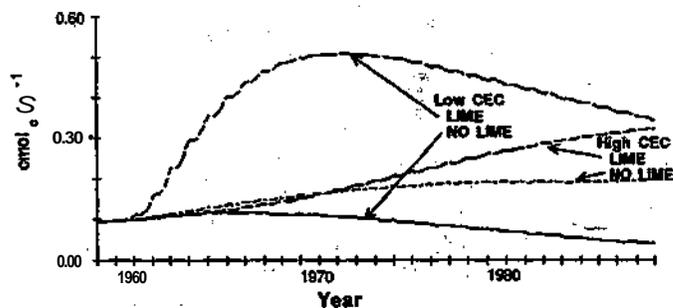


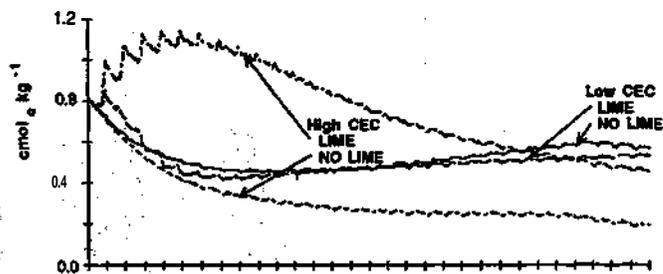
Fig. 6. Simulated exchangeable Ca^{2+} for the NO LIME, low and high CEC and LIME, low and high CEC scenarios.

Ca^{2+} retention in surface (A and BA) horizons and lower Ca^{2+} retention in the BC horizon (as indicated by the differences between LIME and NO LIME scenarios; Fig. 6). In the BA horizon, LIME with low CEC caused a distinct pulse in exchangeable Ca^{2+} which peaked in 3 to 5 yr after liming and declined until the end of the simulation (Fig. 6). LIME with high CEC caused a more delayed and prolonged increase in BA horizon exchangeable Ca^{2+} , which declined only slightly toward the end of the simulation.

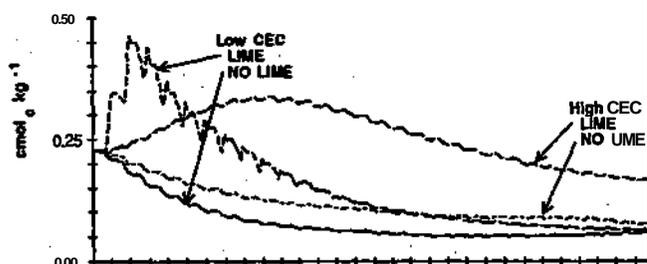
Increasing CEC also had a large effect on Mg^{2+} retention in the surface (A and BA) horizons (Fig. 7). In the A horizon, the patterns for exchangeable Mg^{2+} in the LIME and NO LIME, low CEC scenarios were nearly identical, indicating very little retention of applied Mg^{2+} ,

Exchangeable Mg^{2+}

A Horizon



BA Horizon



BC Horizon

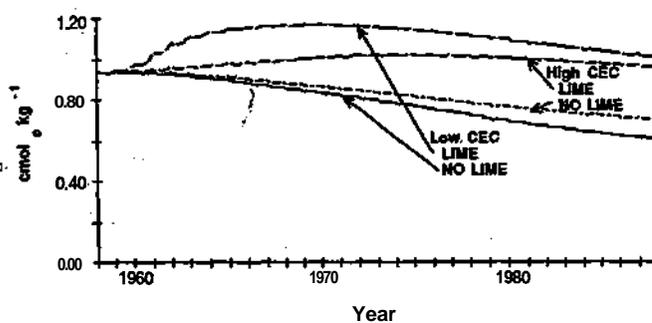


Fig. 7. Simulated exchangeable Mg^{2+} for the NO LIME, low and high CEC and LIME, low and high CEC scenarios.

whereas there were large and prolonged differences in exchangeable Mg^{2+} in the LIME and NO LIME, high CEC scenarios (Fig. 7). In the BA horizon, there were initially large differences in exchangeable Mg^{2+} in the LIME and NO LIME, low CEC scenarios, but the lines converged by the end of the 30-yr simulation (Fig. 7). In the high CEC scenario, the differences in BA horizon exchangeable Mg^{2+} due to liming were initially less pronounced but persisted through the end of the simulation. In the BC horizon, liming caused prolonged increases in exchangeable Mg^{2+} with both low and high CEC scenarios, but the differences were greater with low CEC.

The primary reason for the lower Ca^{2+} and Mg^{2+} retention in the LIME, low CEC scenario appears to be

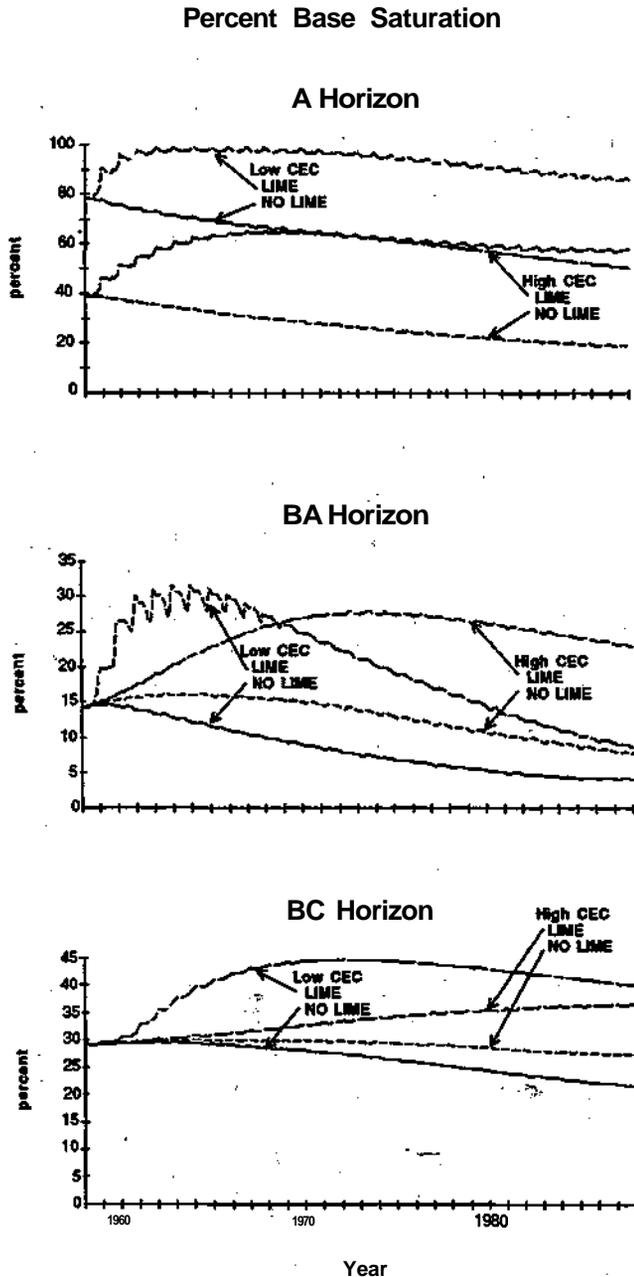


Fig. 8. Simulated base saturation for the NO LIME, low and high CEC and LIME, low and high CEC scenarios.

that the CEC sites were saturated: base saturation reached nearly 100% after liming and exchangeable Ca^{2+} and Mg^{2+} occupied 88% of the exchanger. Thus, the potential for further Ca^{2+} and Mg^{2+} retention was minimal. In contrast, base saturation remained below 65% in the LIME, high CEC scenario (Fig. 8). The comparative lack of long-term Ca^{2+} and Mg^{2+} retention from LIME in the BA horizon was not due to saturation of the exchanger, however; BA horizon base saturation remained below 40% throughout each scenario (Fig. 8). In the BC horizon, base saturation followed the general patterns of exchangeable Mg^{2+} , which was the major exchangeable cation in this horizon.

The ratios of Ca^{2+} to Mg^{2+} on the exchanger varied considerably with depth (7.0, 0.4, and 0.1 in the A,

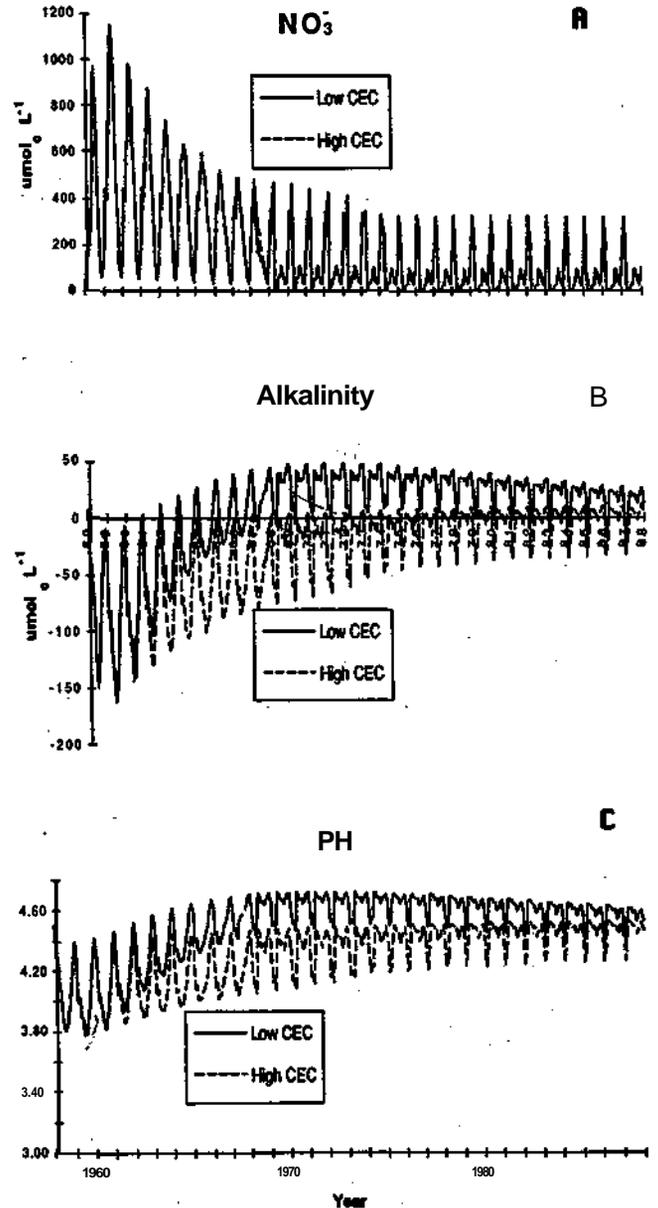


Fig. 9. Simulated (A) NO_3^- , (B) alkalinity, and (C) pH for BC horizon soil solutions in the LIME, low CEC and high CEC scenarios.

BA, and BC horizons, respectively), causing concurrent variation in the Gapon selectivity coefficients ($Q = 0.08$, 0.96, and 3.63 for the A, BA and BC horizons, where $M^{a+} = \text{Mg}^{2+}$ and $M^{b+} = \text{Ca}^{2+}$ in Eq. [1]). This interhorizon variation in selectivity coefficients (which are set initially from exchangeable and soil solution cation concentrations) had a major effect on the potential for Ca^{2+} vs. Mg^{2+} accumulation within the various horizons. Thus, most of the exchangeable Ca^{2+} was in the A horizon initially, and this is the horizon within which most of the Ca^{2+} from the LIME mineral accumulated (Table 2). In contrast, most of the exchangeable Mg^{2+} was in the BC horizon, and this is the horizon within which most of the Mg^{2+} from the LIME mineral accumulated (Table 2). Because of the quantitative importance of the BC horizon for exchangeable Mg^{2+} , there was actually less total retention of applied Mg^{2+} with high

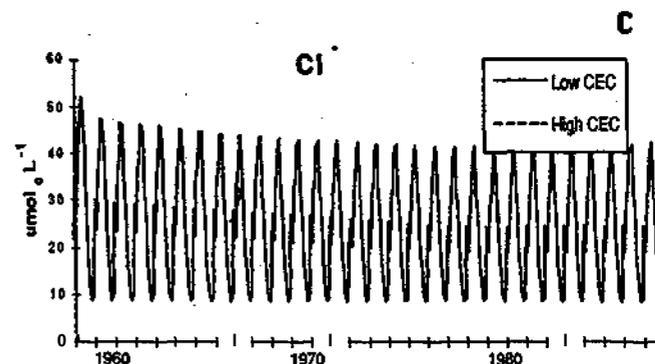
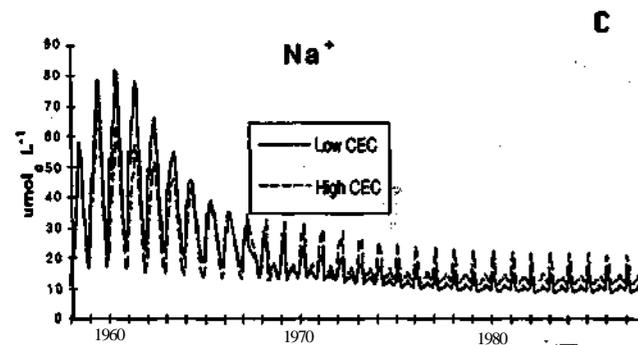
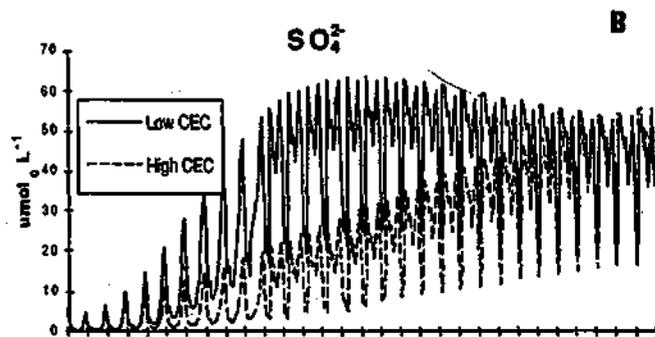
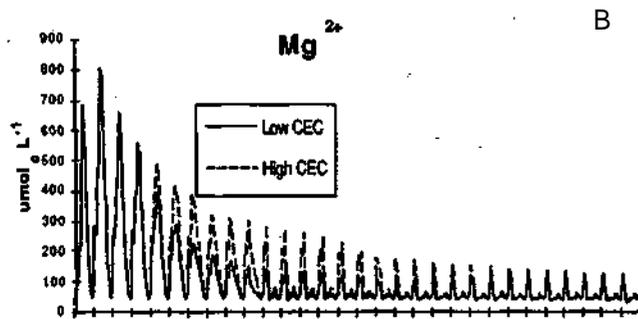
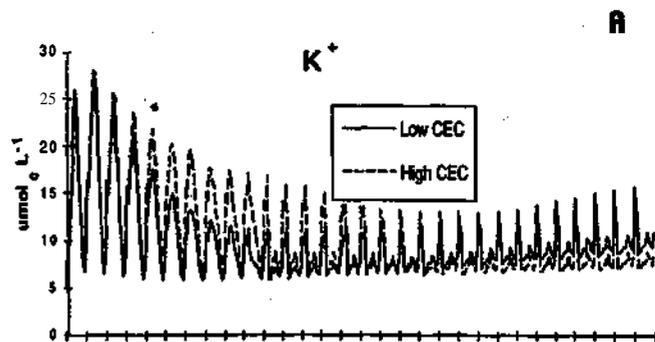
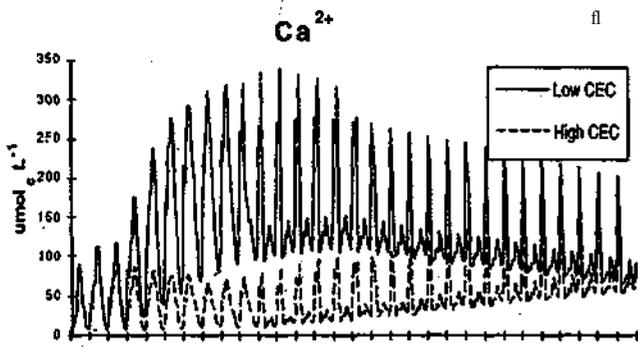


Fig. 10. Simulated (A) Ca^{2+} , (B) Mg^{2+} , and (C) Na^+ for BC horizon soil solutions in the LIME, low CEC and high CEC scenarios.

Fig. 11. Simulated (A) K^+ , (B) SO_4^{2-} , (C) Cl^- for BC horizon soil solutions in the LIME, low CEC and high CEC scenarios.

CEC than with low CEC, even though retention in surface horizons was increased with high CEC.

Simulated Soil Solutions

Simulated soil solution concentrations exhibited large seasonal variations due to variations in water flux and temperature-dependent processes such as nitrification (Fig. 9–11). The range of simulated soil solution concentrations generally bracketed the values observed in the field, with the notable exception of pH. Simulated BC horizon pH was considerably lower than that measured either in soil solutions or streamwaters (Fig. 1B, 1C, 9B, and 9C). One possible factor in the disparity between field and simulated pH in cases of positive alkalinity is CO_2 degassing and associated pH rise as soil solutions are exposed to atmospheric CO_2 pressures. Soil CO_2

pressures are typically 100 to 1000 times atmospheric, and soil solutions in situ can have lower pH's with positive alkalinity than is possible under atmospheric conditions (Reuss and Johnson, 1985). Upon exposure to the atmosphere, CO_2 degassing causes no change in alkalinity but a substantial rise in pH. Consistently positive alkalinities developed only in the low CEC scenario (Fig. 9B).

Simulated BC horizon soil solution mimicked the temporal patterns in streamwater concentrations of most ions (Fig. 9–11). A notable exception was Ca^{2+} : there was a prolonged pulse in simulated BC horizon Ca^{2+} with low CEC, and a steady increase with high CEC (Fig. 10A). These patterns contrast with the steady decrease observed in streamwater Ca^{2+} (Fig. 2A). The initial decline in streamwater NO_3^- concentrations was mimicked by NuCM: simulated BC horizon NO_3^- concentra-

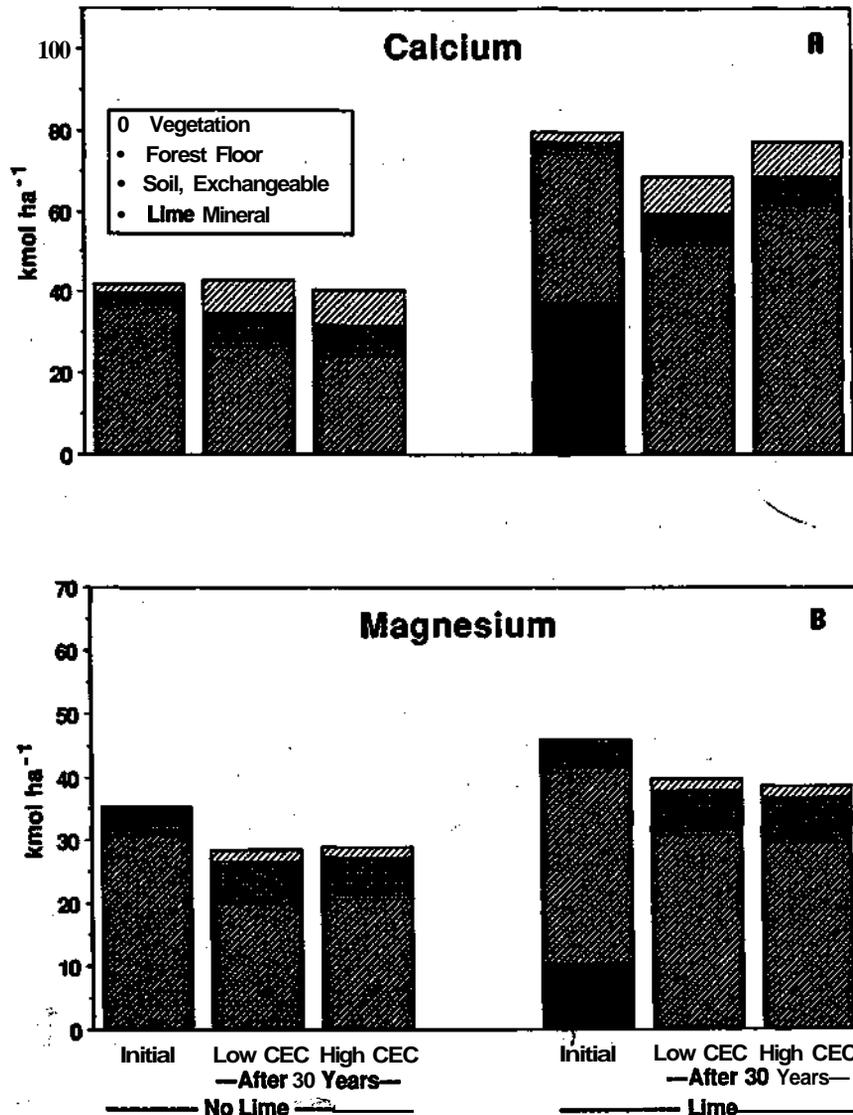


Fig. 12. Simulated (A) Ca and (B) Mg distributions at the beginning and end of the simulations.

tions declined from 1959 to 1975, and remained in a stable, seasonally oscillating pattern thereafter (Fig. 1A and 9A). It was not possible to simulate the locust borer outbreak, and thus the sudden increase in streamwater NO_3^- after 1979 was not mimicked by NuCM. Low vs. high CEC had little effect on simulated NO_3^- . Simulated BC horizon Mg^{2+} concentrations decreased substantially during the early part of the simulation, and matched the general pattern of decline observed in streamwaters between 1971 and 1979 (Fig. 2B and 10B). Interestingly, the seasonal low values for BC horizon Mg^{2+} concentrations did not vary much over the 30-yr simulation. The CEC had only a minor effect on simulated BC horizon Mg^{2+} concentrations, and only during the period 1962 to 1970. The NuCM model mimicked the general patterns in streamwater Na^+ after 1971, and, as was the case with Mg^{2+} , predicted much higher concentrations before that date (Fig. 2C and 10C). As was observed in streamwaters, NuCM predicted no particular trend in BC horizon solution K^+ after 1971, but higher concentrations before that date (Fig. 11A). Increasing CEC had a slight

and inconsistent effect on simulated BC horizon K^+ . The NuCM model predicted a decline in BC horizon Cl^- concentrations as was observed in streamwaters (Fig. 3C and 11C).

The general increase in streamwater SO_4^{2-} was mimicked by NuCM for the high CEC scenario, but not for the low CEC scenario (Fig. 3B and 11B). In the low CEC scenario, the increases in pH caused desorption of SO_4^{2-} from soils, resulting in a sharp increase in BC horizon SO_4^{2-} from 1959 to 1972, which was followed by a slow decline. By the end of the simulation, BC horizon SO_4^{2-} concentrations were similar in the low and high CEC scenarios, but there were differences in cumulative S budgets: there was a net gain of 7.2 kmol ha^{-1} with low CEC and 9.2 kmol ha^{-1} with high CEC, compared with 10.8 and 10.3 kmol ha^{-1} for the respective NO LIME scenarios. Thus, although no S was contained in the simulated LIME mineral, both LIME and CEC had substantial indirect effects on S cycling during the simulations.

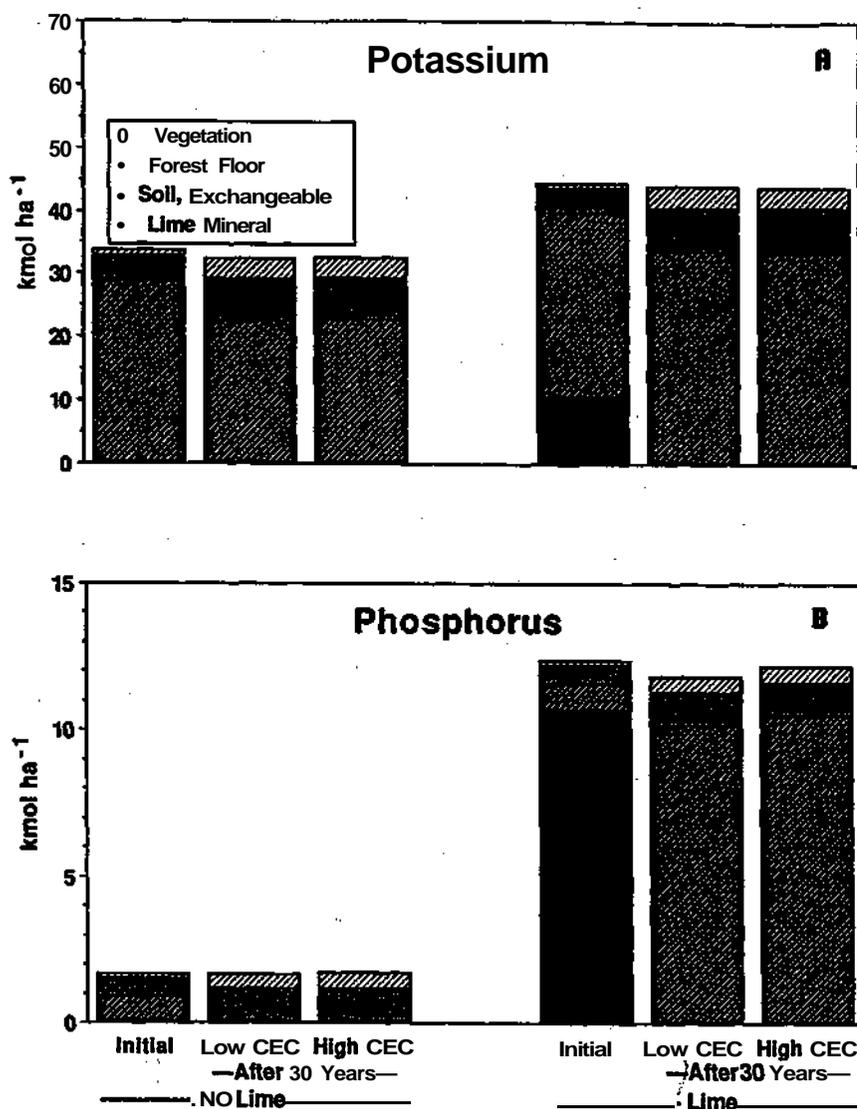


Fig. 13. Simulated (A) K and (B) P distributions at the beginning and end of the simulations.

Simulated Nutrient Pools and Fluxes

Figures 12 and 13 show the changes in simulated vegetation, litter, exchangeable, and lime mineral pools during the simulations. Changes in other mineral pools (not shown) were negligible because weathering rates were set to very low values. Total ecosystem pools of Ca, K, and P changed little over the simulation in the NO LIME scenarios, but there was a substantial redistribution of these nutrients from exchangeable to litter and vegetation pools. Total ecosystem Mg pools decreased by $\approx 20\%$ due to leaching in the NO LIME scenarios, and there was also a substantial redistribution from exchangeable to litter and vegetation pools (Fig. 12B). In this context, it is noteworthy that Knoepp and Swank (1994) have documented 70 to 80% reductions in exchangeable Ca^{2+} and Mg^{2+} in deciduous forest soils at Coweeta over the period 1970 to 1990.

Total ecosystem pools of K and P changed little over the simulation in the LIME scenarios, but for very different reasons. In the case of K^+ , LIME had only negligible

effects on leaching (Table 3) so that ecosystem pools were largely unaffected. In the case of P, LIME caused substantial increases in leaching, but P leaching rates were so low that ecosystem P retention remained very high nevertheless (Table 3 and Fig. 13B). Ecosystem Ca and Mg pools decreased significantly in the LIME scenarios (Fig. 12), but LIME had very different effects on the retention of these nutrients compared with the NO LIME scenarios. LIME caused increased Ca^{2+} leaching, especially with low CEC, resulting in relatively low (67%) retention in this particular scenario (Table 3 and Fig. 12A). Liming had no effect on Mg^{2+} leaching in the low CEC scenario, and thus the net ecosystem retention of applied Mg was 100%, despite the fact that there was a net loss of total ecosystem Mg (Table 3 and Fig. 12B). Liming caused increased Mg^{2+} leaching in the high CEC scenario, and thus Mg retention decreased to 85%.

Because soil exchangeable pools changed with time in both the LIME and NO LIME scenarios, simple budget calculations (inputs — outputs) would give misleading estimates of net retention of the applied nutrients. The

Table 3. Calculated retention of Ca, Mg, K, and P added in LIME simulations.

	Ca	Mg	K	P
	kmol ha ⁻¹ 30 yr ⁻¹			
Inputs				
Atmospheric deposition	2.8	1.0	1.3	0.1
LIME mineral	37.4	10.6	10.8	10.7
Leaching				
Low CEC				
NO LIME	1.6	9.6	2.7	0.03
LIME	13.9	9.6	2.4	0.57
High CEC				
NO LIME	4.3	9.3	2.6	0.03
LIME	5.3	10.8	2.4	0.24
Ecosystem retention of added nutrients^t				
Vegetation	0.4 (<1%)	<0.1 (<1%)	0.1 (1%)	<0.1 (<1%)
Litter	0.3 (1%)	<0.1 (<1%)	0.3 (3%)	0.1 (<1%)
Soil exchange sites				
Low CEC	24.2 (65%)	10.5 (99%)	11.1 (102%)	10.0 (94%)
High CEC	35.6 (95%)	9.0 (85%)	10.8 (100%)	10.3 (96%)
Soil minerals	0.3 (<1%)	<0.1 (<1%)	<0.1 (<1%)	0.1 (<1%)
Total ecosystem				
Low CEC	25.1 (67%)	10.6 (100%)	11.5 (106%)	10.2 (95%)
High CEC	36.6 (98%)	9.1 (86%)	11.2 (103%)	10.5 (98%)

^tLIME minus NO LIME pools.

simple budget would show little net Mg retention, for example, because leaching was, by coincidence, approximately equal to the total amount of applied Mg. The fact that Mg²⁺ leaching was only slightly affected by LIME belies this interpretation. The key point is that the untreated ecosystem was changing, and the effects of LIME must be assessed against such changes.

SUMMARY AND CONCLUSIONS

1. Field data suggested that most applied Ca²⁺ and Mg²⁺ was retained in the upper soil horizons 23 yr after liming, even in sites where leaching was accelerated by excess NO₃⁻ production under black locust. The hypothesis that NuCM simulations would also show most retention in upper horizons was supported in the case of Ca²⁺ but not Mg²⁺. Most applied Mg²⁺ was retained in the BC horizon, where the largest pool of exchangeable Mg²⁺ was initially located.

2. The hypothesis that increased CEC and exchangeable H⁺ in the model (simulating pH-dependent CEC) would cause increased retention of Ca²⁺ and Mg²⁺ was supported for Ca²⁺ but not for Mg²⁺. Although there was greater retention of applied Mg²⁺ in surface horizons with high CEC than with low CEC, this was outweighed by the lower retention of applied Mg²⁺ in the BC horizon, with the net result being a lower total retention of applied Mg²⁺.

3. Streamwater concentration data suggested that, beginning 12 yr after liming (1971), Ca²⁺, Mg²⁺, and Na⁺ concentrations were driven primarily by NO₃⁻ and Cl⁻. Sulfate increased steadily, just as in other watersheds in the basin, suggesting that soil adsorption sites were being filled. There were no overall patterns in K⁺ or pH. It is not known if there were pulses in the concentrations of any of these ions before 1971.

4. Simulated BC horizon soil solution concentrations mimicked the general Streamwater patterns in the cases

of NO₃⁻, Mg²⁺, Na⁺, Cl⁻, SO₄²⁻, and K⁺ but not in the cases of pH and Ca²⁺. The simulation results showed a large desorption of SO₄²⁻ from soils as a result of pH increases after liming. It is not known if liming resulted in an initial release of SO₄²⁻ in the field, but this effect is well-known in the literature (e.g., Mehlich, 1964).

5. Both simulations and field data suggest that changes in soil exchangeable cations over time can be substantial in untreated ecosystems. Assessments of treatment effects and calculations of nutrient retention that do not take these changes into account could be seriously misleading.

ACKNOWLEDGMENTS

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REFERENCES

- Adams, F., and C.E. Evans. 1962. A rapid method for measuring lime requirements of red-yellow podzolic soils. *Soil Sci. Soc. Am. Proc.* 26:355-357.
- Andersson, F.O., and H. Lundqvist. 1989. Long-term field experiments in forest management practices and site productivity. p. 125-138. In W.J. Dyck and C.A. Mees (ed.). *Research strategies for long-term site productivity. Proc., IEA/BE A3 Workshop*, Seattle, WA. August 1988. IEA/BE A3 Rep. 8. Ministry of Forestry, Forest Res. Inst., Rotorua, New Zealand.
- Barber, S.A. 1967. Liming materials and practices. p. 125-160. In R.W. Pearson and F. Adams (ed.). *Soil acidity and liming. Agron. Monogr.* 12. ASA, CSSA, and SSSA, Madison, WI.
- Coleman, N.T., and G.W. Thomas. 1967. The basic chemistry of soil acidity. p. 1-42. In R.W. Pearson, and F. Adams (ed.). *Soil acidity and liming. Agron. Monogr.* 12. ASA, CSSA, and SSSA, Madison, WI.
- Derome, J. 1990. Effects of forest liming on the nutrient status of podzolic soils in Finland. *Water Air Soil Pollut.* 54:337-350.
- Goldstein, R.A., S.A. Gherini, C.W. Chen, L. Mok, and R.J.M. Hudson. 1984. Integrated acidification study (ILWAS): A mechanistic ecosystem analysis. *Phil. Trans. R. Soc. Lond. B* 305:259-279.
- Henderson, G.S., W.T. Swank, J.B. Waide, and C.C. Grier. 1978. Nutrient budgets of Appalachian and Cascade region watersheds: A comparison. *For. Sci.* 24(3):385-397.
- Hibbert, A.R. 1969. Water yield changes after converting a forested catchment to grass. *Water Resour. Res.* 5:634-640.
- Jackson, W.A. 1967. Physiological effects of soil acidity. p. 43-124. In R.W. Pearson and F. Adams (ed.). *Soil acidity and liming. Agron. Monogr.* 12. ASA, CSSA, and SSSA, Madison, WI.
- Jenkinson, D.S. 1970. The accumulation of organic matter in soil left uncultivated. *Commun. Bur. Soil. Sci. Rothamsted Exp. Sta. Rep.*
- Johnson, D.W., and D.W. Cole. 1980. Anion mobility in soils: Relevance to nutrient transport from terrestrial ecosystems. *Environ. Int.* 3:79-90.
- Johnson, D.W., and S.E. Lindberg (ed.). 1991. *Atmospheric deposition and forest nutrient cycling. Ecological Ser. 91. Springer-Verlag*, New York.
- Johnson, D.W., W.T. Swank, and J.M. Vose. 1993. Simulated effects of atmospheric sulfur deposition on nutrient cycling in a mixed deciduous forest. *Biogeochem.* 23:169-196.
- Johnson, P.L., and W.T. Swank. 1973. Studies of cation budgets in the southern Appalachians on four experimental watersheds with contrasting vegetation. *Ecol.* 54:70-80.
- Knoepp, J.D., and W.T. Swank. 1994. Long-term soil chemistry

- changes in aggrading forest ecosystems. *Soil Sci. Soc. Am. J.* 58: 325-331.
- Liu, S., R. Munson, D.W. Johnson, S. Gherini, K. Summer, R. Hudson, K. Wilkinson, and L. Pitelka. 1991. Applications of a nutrient cycling model (NuCM) to northern mixed hardwood and southern coniferous forest. *Tree Physiol.* 9:173-182.
- Matzner, E., P.K. Khanna, K.J. Meiwes, and B. Ulrich. 1983. Effects of fertilization on the fluxes of chemical elements through different forest ecosystems. *Plant Soil* 74:434-458.
- Matzner, E., and K.J. Meiwes. 1990. Effects of liming and fertilization on soil solution chemistry in North German Forest Ecosystems. *Water Air Soil Pollut.* 54:377-390.
- Mehlich, A. 1964. Influence of sorted hydroxyl and sulfate on liming efficiency, pH, and conductivity. *Soil Sci. Soc. Am. Proc.* 27: 496-499.
- Mohamed, A.D., J. Ranger, E. Dabrine, M. Bonneau, D. Gelhaye, and A. Granier. 1993. The effects of limestone and of limestone plus NPK fertilization on the soil and mass balance of a spruce stand (*Picea abies* (L.) Karst.) in the Vosges mountains. *For. Ecol. Manage.* 60:291-310.
- Montagnini, F., B. Haines, L. Boring, and W. Swank. 1986. Nitrification potentials in early successional black locust and mixed hardwood forest stands in the southern Appalachians, USA. *Biogeochem.* 2:197-210.
- Montagnini, F., B. Haines, and W.T. Swank. 1991. Soil solution chemistry in a black locust, pine/mixed hardwood and oak/hickory forest stands in the southern Appalachians, USA. *For. Ecol. Manage.* 40:199-208.
- Munson, R.K., S. Liu, S.A. Gherini, D.W. Johnson, K.J. Wilkinson, R.J.M. Hudson, K.S. White, and K.V. Summers. 1992. NuCM Code Version 2.0: An IBM PC code for simulating nutrient cycling in forest ecosystems. Tetra-Tech, Hadley, MA.
- Oades, J.M. 1988. The retention of organic matter in soils. *Biogeochem.* 5:35-70.
- Pearson, R.W., and F. Adams (ed.). 1987. Soil acidity and liming. *Agron. Monogr.* 12. ASA, CSSA, and SSSA, Madison, WI.
- Persson, T., A. Wiren, and S. Andersson. 1990. Effects of liming on carbon and nitrogen mineralization in coniferous forests. *Water Air Soil Pollut.* 54:351-364.
- Reuss, J.O., and D.W. Johnson. 1985. Effect of soil processes on the acidification of water by acid deposition. *J. Environ. Qual.* 14:26-31.
- Swank, W.T., and J.B. Waide. 1988. Characterization of baseline precipitation and stream chemistry and nutrient budgets for control watersheds. p. 57-79. In W.T. Swank and D.A. Crossley (ed.) *Forest hydrology and ecology of Coweeta*. Springer-Verlag, New York.