A new mechanism for calcium loss in forest-floor soils

Gregory B. Lawrence*, **Mark B. David†**
& Walter C. Shortle‡

* US Geological Survey, 425 Jordan Road, Troy,
New York 12180, USA
† University of Illinois, W-503 Turner Hall,
1102 South Goodwin Avenue, Urbana, Illinois 61801, USA
‡ USDA Forest Service, Northeastern Forest Experiment Station,
Durham, New Hampshire 03824, USA

CALCIUM is the fifth most abundant element in trees, and is an essential component for wood formation and the maintenance of cell walls. Depletion of Ca from the rooting zone can result in acidification of soil[1] and surface water[2] and possibly growth decline and dieback of red spruce[3,4]. During the past six decades, concentrations of root-available Ca (exchangeable and acid-extractable forms) in forest-floor soils have decreased in the northeastern United States[5,6]. Both net forest growth and acid deposition have been put forth as mechanisms that can account for this Ca depletion[5,6]. Here, however, we present data collected in red spruce forests in the northeastern United States that are inconsistent with either of these mechanisms. We propose that aluminium, mobilized in the mineral soil by acid deposition, is transported into the forest floor in a reactive form that reduces storage of Ca, and thus its availability for root uptake. This results in potential stress to trees and, by increasing the demand for Ca, also decreases neutralization of drainage waters, thereby leading to acidification of lakes and streams.

Forest-floor soil is formed on top of mineral soil by the accumulation of nutrient-rich organic matter from roots and litter. Thick (>5 cm) forest floors develop in northern temperate and boreal forests, where cool temperatures retard decomposition. Because of their high nutrient content relative to the mineral soil, these soils are the primary rooting layer in forests where they are found. To evaluate mechanisms that cause Ca depletion in forest-floor soil, we collected soil and soil-solution samples in 12 undisturbed red spruce stands, and one stand that has received 1,800 equiv. ha^{-1} yr^{-1} of $(NH_4)_2SO_4$ since November 1989[7]. The stands, located in New York, Vermont, New Hampshire and Maine, were selected to represent the range of environmental conditions and stand health for red spruce in the northeastern United States. Soils were analysed for exchangeable Ca (by NH_4Cl extraction[8]), exchangeable Al and H (by KCl extraction[9]), pyrophosphate-extractable Al[8], acid-extractable Al (by 1:1 HNO_3 digest[10]), and total Al (by neutron activation[11]). Bulk densities of soils in the Oa horizon (which is part of the forest floor) were estimated with a model developed by Federer[12]; we used the methods of soil-solution collection and analysis described in refs 13 and 14, respectively).

Because net forest growth and acid deposition can involve exchange between adsorbed Ca and H, observed decreases in exchangeable-Ca concentrations in the forest floor were expected to be accompanied by an increase in exchangeable-H concentrations. Results indicated, however, that concentrations of exchangeable Ca in the soil Oa horizon were correlated with neither exchangeable-H concentrations (Fig. 1a) nor with soil pH ($P > 0.1$), but were inversely related to concentrations of exchangeable Al (Fig. 1b). This negative correlation between concentrations of exchangeable Ca and exchangeable Al in the forest floor suggests that forest-floor decreases in Ca may be associated with increases in concentrations of reactive forms of Al rather than H. This contention is supported by results of analysing archived Oa-horizon soil samples collected from red spruce-balsam fir (*Abies balsamea* (L.) Mill) stands at the Hubbard Brook Experimental Forest (HBEF), New Hampshire. These data indicated that concentrations of exchangeable and acid-extractable Al
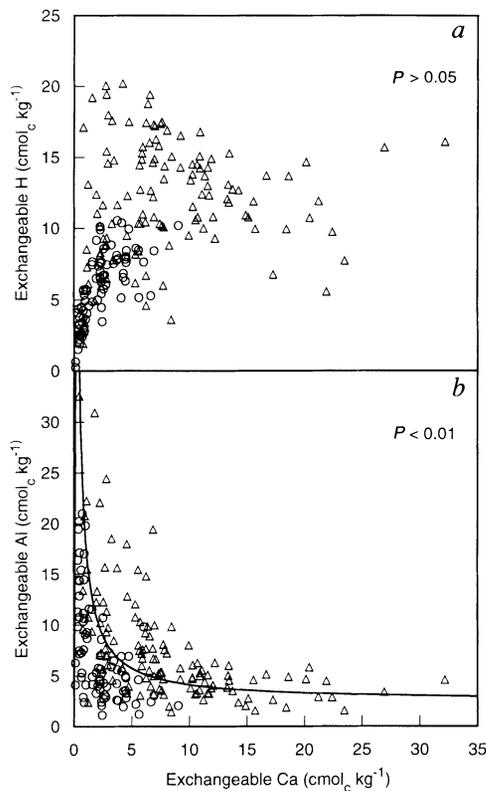
FIG. 1 Concentrations of exchangeable H (a) and Al (b) as a function of exchangeable-Ca concentrations in the Oa horizon of stands of red spruce (triangles) and mixed hardwood (circles); $cmol_c \, kg^{-1}$ indicates cmol of charge per kg soil. Red spruce data are based on analysis of 36 soil samples from each of eight sites, plus 18 samples collected at each of five additional sites. Each triangle represents the value for three soil samples that were combined before analysis. Hardwood data are based on 68 samples collected on Slide Mountain, New York at elevations ranging from 800 to 1,100 m. The curve in b represents the best fit for the model $y = 1.2(1/x) + 4.7$; ($R^2 = 0.41$). The significance probability (P) is listed in each panel.

have increased with a corresponding decrease in Ca concentrations over the past two decades, although the increase for exchangeable Al was not statistically significant (Table 1).

Mineral forms of Al which are physically mixed into the forest floor can be mobilized by naturally derived organic acids, although dissolved Al is typically highly undersaturated with respect to mineral solubility in the forest floor[15]. Acid deposition provides an additional source of H^+ that could possibly enhance dissolution of mineral Al; however, our results showed that exchangeable-Al concentrations were unrelated to mineral-Al concentrations, and dissolved inorganic Al concentrations were unrelated to soil-solution pH ($P > 0.10$). Despite the relative abundance of mineral Al in the forest floor (85% of total Al), exchangeable Al concentrations were probably controlled by organically complexed Al. Mineral saturation indices showed that dissolved inorganic Al concentrations in the forest floor were more than 1,000 times lower than would have been observed had any type of mineral known to occur in these soils been the primary control, and exchangeable Al was positively correlated ($P < 0.01$; $R^2 = 0.60$) with reactive-nonexchangeable Al, which consisted of 70% organically complexed Al. In organic soils, control by organically complexed Al, rather than mineral solubility, has often been demonstrated[15,16] and decreases in pH have been shown to cause decomplexation of Al from solid-phase organic matter[16]. The naturally low pH of forest-floor solutions[17], however, indicates that acid deposition has not enhanced dissolution of mineral Al or decomplexation of organic Al within these forest floor soils. Production of organic acids

causes solution pH values at these sites to range from 3.3 to 3.8 (Table 2); these values are below the pH of precipitation in this region which averages about pH 4.4 and is seldom less than 4.0 (ref. 18). There is no established mechanism to explain how the addition of precipitation with a pH above 4.0 could enhance dissolution of mineral Al in forest floors that have solution pH values naturally less than 4.0.

In contrast to the forest floor, soil-solution pH of the B horizon (which is part of mineral soil) is likely to have been lowered by acid deposition at these sites. The pH of mineral-soil solutions were higher than forest-floor solutions (Table 2) because organic acids leached from the forest floor tend to be removed from solution by sorption to mineral surfaces[19]. Strong acids derived from acidic deposition, however, are much less easily immobilized and therefore are more effective than organic acids at acidifying soil solutions and mobilizing Al in the mineral soil[20]. The influence of strong acids on Al mobilization in the B horizon is supported by the positive correlation we observed between solution concentrations of H^+ and inorganic Al ($R^2 = 0.54$; $P < 0.01$), typical for mineral soils receiving acidic deposition[21].

An alternative mechanism for increased exchangeable-Al concentrations in the forest floor is suggested by a strong positive correlation found between the Al/Ca ratio of soil solution in the B horizon and the exchangeable-Al content of the forest floor (Fig. 2). We propose that Al, mobilized in the mineral soil by acid deposition, is transported into the forest floor where it accumulates in a reactive mostly organically complexed form. Both biocycling and water movement have been established as mechanisms that can transport Al into the forest floor[22,23]. A recent study showed that biocycling (including Al transported from roots in the mineral soil to roots in the forest floor) plus atmospheric deposition was roughly 60% of forest-floor leaching losses at Tunk Mountain, Maine[22,24]. Root uptake of Al in the B horizon is likely at all of our study sites because the ratios of inorganic Al to Ca are greater than 1.0 (Table 2), the value above which root exchange sites readily adsorb Al at the expense of Ca (ref. 25). A rising water table provides an additional way to increase the pool of reactive Al in organic surface horizons, as does upward movement of water through rapid drying of the forest floor by evapotranspiration. When mineral-soil solution
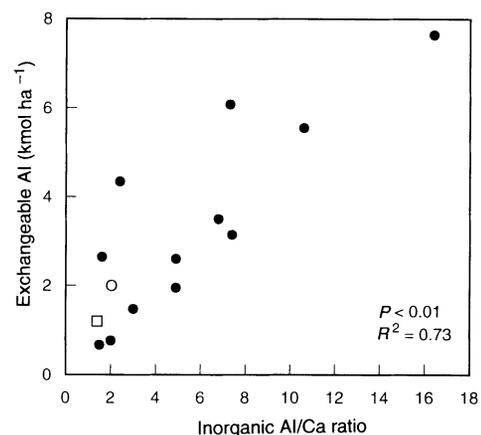

FIG. 2 Exchangeable-Al content of Oa horizons of red spruce stands as a function of the molar concentration ratio of inorganic Al to Ca in B-horizon soil solution. Exchangeable Al was expressed as content to normalize the data for varying forest-floor thickness. Each filled circle represents the mean of 18–36 soil and soil-solution samples (combined into 6–12 samples before analysis) collected at each of 12 sites. One of the 13 sites (Hubbard Brook) was omitted because there was insufficient B-horizon soil to sample. The open circle represents the mean of 68 soil samples and 31 seep-water samples, collected in a mixed hardwood forest on Slide Mountain, New York at elevations ranging from 800 to 1,100 m. The open square represents soil and seep-water concentrations measured at Tunk Mountain, Maine by Rustad[24]. The significance probability is given by P; the coefficient of determination is given by R^2.

TABLE 1   Al and Ca concentrations in Oa-horizon soils

Sampling period	Exchangeable (cmol$_c$ kg^{-1})		Acid-extractable (cmol$_c$ kg^{-1})	
	Al	Ca	Al	Ca
1969–70	2.5^a (1.1)	8.3^a (4.4)	19.3^a (10.2)	9.9^a (6.4)
1987, 1992	3.7^a (2.9)	3.5^b (2.1)	37.0^b (21.6)	4.6^b (2.9)

Samples were collected in spruce-fir stands at the Hubbard Brook Experimental Forest, New Hampshire, USA. Samples collected in 1969 and 1970 were averaged together, as were those collected in 1987 and 1992. Values are means based on 9–14 samples. Statistically significant differences ($P < 0.05$) between sampling periods, determined from the Wilcoxon nonparametric test and the Tukey means separation test, are indicated by superscripts with different letters. Standard deviations are given in parentheses.

that is enriched in Al relative to Ca moves into the forest floor, Al is more effectively retained than Ca owing to the high affinity of Al for organic binding sites[19]. When this same solution then drains back into the mineral soil, the Al to Ca ratio is decreased. Mulder et al.[23] found, in two Norwegian watersheds, Al-enriched organic surface horizons caused by upward movement of water from mineral horizons; simulation with the BROOK90 hydrological model[26] indicated that, in HBEF soils, movement of water from the mineral soil to the forest floor at a rate of 1 mm d^{-1} was common in the summer.

The quantitative importance of exchangeable Al in the forest floor relative to exchangeable Ca is shown by the exchangeable Al to Ca ratios in Table 2. Mobilization of Al in the mineral soil has significantly contributed to the documented decrease of root-available Ca in the forest floor by (1) reducing uptake of Ca from the mineral soil that could be biocycled into the forest floor, (2) providing a supply of reactive Al, that when transported into the forest floor, exchanges with Ca, enabling the latter to be leached, and (3) increasing Al saturation so that the number of exchange sites available for adsorbing added Ca is reduced (because Ca has minimal ability to displace adsorbed Al[19]). Increasing Al saturation in the forest floor is particularly significant in relation to the importance of atmospheric Ca as an input to the available pool of Ca. Recent work at a high-elevation red spruce stand indicated that about half of the Ca in the forest floor was of atmospheric origin[27], even though atmospheric inputs of basic cations have decreased over the past two decades[28]. A high degree of Al saturation will limit retention of Ca added from atmospheric deposition, increasing the likelihood that dissolved Ca will pass below the rooting zone before it can be taken up by roots.

Although this study has focused on red spruce forests, evidence of Al transport from the mineral soil to the forest floor can also be shown for hardwood forests. Relations among concentrations of exchangeable Al, Ca and H are similar for red spruce forests and a mixed hardwood forest on Slide Mountain, New York (Fig. 1), as are relations between mineral-soil solution and forest-floor exchangeable Al pools (Fig. 2). Transport of Al from the mineral soil to the forest floor is likely to occur in regions that are receiving acid deposition and have forest soils with well defined organic surface horizons overlying shallow mineral soils with an inherent low base saturation. Ecosystems of this type occur over large regions of eastern North America, Scandanavia and Russia.

By reducing the availability of Ca in the primary rooting zone, increases in reactive forms of Al will potentially slow growth and weaken the stress tolerance of trees. Increased demand for Ca by trees will also limit the neutralization of drainage waters because a greater fraction of available Ca will be retained within the terrestrial ecosystem. Reversing the accumulation of reactive Al in the forest floor by anticipated future decreases in atmospheric deposition of strong acids will be hindered by high Al to Ca ratios in mineral-soil solutions, the tendency for Al to strongly adsorb to organic matter, and continued decreases in atmospheric deposition of Ca. □

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TABLE 2   Soil-solution and soil chemistry in the Oa horizon and upper 10 cm of the B horizon

Site	Oa horizon				Upper B horizon			
	pH	Ca	Inorganic Al	Ex. Al/ ex. Ca	pH	Ca	Inorganic Al	Ex. Al/ ex. Ca
Sleepers River*, Vermont	3.7	60	<1.5	0.2	4.5	8	13	12
Groton, Vermont	3.3	98	2	0.3	4.8	6	8	5
Howland, Maine	3.3	142	13	0.4	4.5	5	14	22
Kossuth, Maine	3.4	85	9	0.8	4.6	5	11	34
Bartlett, New Hampshire	3.5	61	<1.5	0.5	4.5	2	16	25
Hubbard Brook*, New Hampshire	3.6	38	2	0.8	—	—	—	—
Whiteface Mtn*, New York	3.7	31	13	0.8	4.6	7	20	11
Crawford Notch, New Hampshire	3.3	47	3	1.1	4.4	4	19	27
Bear Brook ref.†, Maine	3.8	30	13	1.9	4.4	8	19	20
Big Moose Lake, New York	3.5	22	2	1.2	4.1	5	30	27
Cone Pond, New Hampshire	3.5	18	7	5.2	4.4	2	18	53
Mt Abraham*, Vermont	3.7	13	26	5.6	4.1	4	25	16
Bear Brook treat.‡	3.7	15	87	7.1	4.1	4.5	74	21

Concentrations of Ca and inorganic monomeric Al are in μmol l^{-1}. Units for the ratios of soil exchangeable Al to Ca are cmol$_c$ kg^{-1}. Each value represents the mean of 36 samples that were collected individually and then combined into 12 samples for analysis, except for sites followed by an asterisk, for which each value represents 18 samples collected individually and combined into six samples for analysis. Upper B-horizon soil-solution data were not collected at Hubbard Brook because of insufficient mineral soil development.
  † Site name refers to the undisturbed Bear Brook watershed.
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Simulation of abrupt climate change induced by freshwater input to the North Atlantic Ocean

Syukuro Manabe & Ronald J. Stouffer

Geophysical Fluid Dynamics Laboratory/NOAA, Princeton University, Princeton, New Jersey 08542, USA

TEMPERATURE records from Greenland ice cores[1,2] suggest that large and abrupt changes of North Atlantic climate occurred frequently during both glacial and postglacial periods; one example is the Younger Dryas cold event. Broecker[3] speculated that these changes result from rapid changes in the thermohaline circulation of the Atlantic Ocean, which were caused by the release of large amounts of melt water from continental ice sheets. Here we describe an attempt to explore this intriguing phenomenon using a coupled ocean–atmosphere model. In response to a massive surface flux of fresh water to the northern North Atlantic of the model, the thermohaline circulation weakens abruptly, intensifies and weakens again, followed by a gradual recovery, generating episodes that resemble the abrupt changes of the ocean–atmosphere system recorded in ice and deep-sea cores[4]. The associated change of surface air temperature is particularly large in the northern North Atlantic Ocean and its neighbourhood, but is relatively small in the rest of the world.

The coupled model[5,6] consists of general circulation models (GCMs) of the atmosphere and oceans and a simple model of land surface that includes the budgets of heat and water. It is a global model with realistic geography. The atmospheric GCM includes the seasonal variation of insolation and predicted cloud cover. It has nine vertical finite-difference levels. The horizontal distributions of predicted variables are represented by spherical harmonics (15 associated Legendre functions for each of 15 Fourier components) and by corresponding grid points. The oceanic GCM uses a finite-difference technique with a regular grid system which has horizontal spacing of $4.5°$ latitude $\times 3.75°$ longitude and 12 vertical levels.

The control experiment is a 1,000-year time integration of the coupled model[7] described above. The initial conditions for the control experiment have realistic seasonal and geographical distributions of surface temperature, surface salinity and sea ice, with which both the atmospheric and oceanic model states are nearly in equilibrium. When the time integration of the model starts from this initial condition, the model climate drifts towards its own equilibrium state which differs from the realistic initial condition described above. To reduce this drift, the fluxes of heat and water obtained from the atmospheric component of the coupled model are modified by given amounts before they
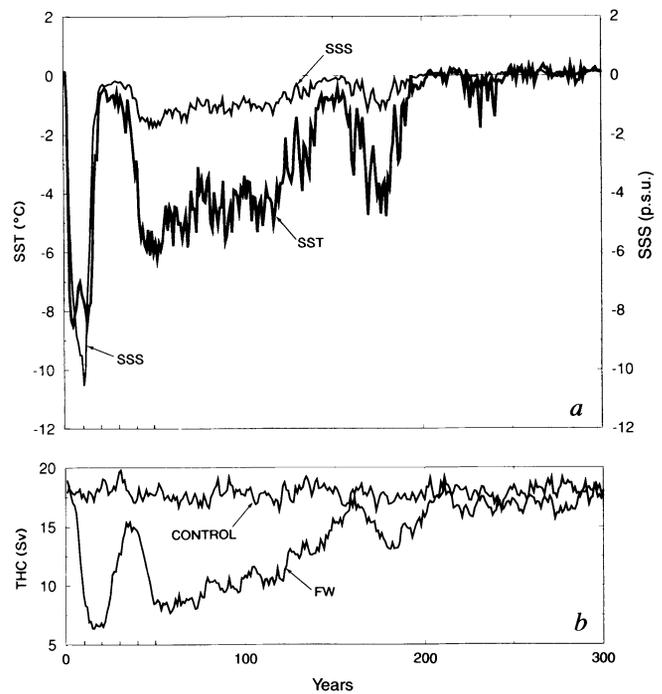

FIG. 1 a, Time series of the deviations of sea surface temperature (SST) and sea surface salinity (SSS; p.s.u., practical salinity units) from their initial values (that is, 7 °C and 35 p.s.u., respectively) at a grid point in the Denmark Strait (60.75° N, 37.50° W) obtained from the FW experiment. b, Temporal variations of the rate of THC in the North Atlantic obtained from the control and FW integrations. Here, the rate of THC is defined as the maximum value of the stream function of meridional circulation in the North Atlantic (Fig. 4).

are imposed at the oceanic surface. Because the adjustments are determined before the time integration of the coupled model, and are not correlated to the transient surface anomalies of temperature and salinity which can develop during the integration, they are unlikely to either systematically amplify or damp the anomalies. The adjustments do not eliminate the shortcomings of the model dynamics which could distort the simulated transients[8]. But the adjustments do prevent the rapid drift of the model state from the realistic initial condition, which could seriously distort the results of a numerical experiment. The identical adjustments are also applied to the freshwater (FW) experiment described below.
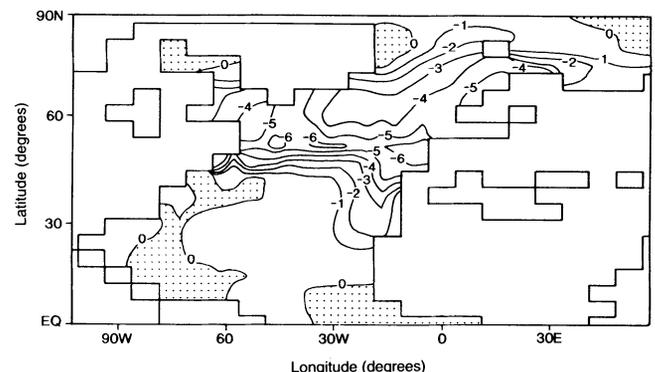

FIG. 2 Horizontal distribution of SSS anomalies (in units of p.s.u.) averaged over the 10-year period from year 11 to year 20 of the FW experiment. The areas of positive anomalies are shaded. Here, the anomaly represents the difference between the 10-year mean state of the FW integration and the 100-year (years 501–600) mean state of the control integration.