SOIL-CALCIUM DEPLETION LINKED TO ACID RAIN AND FOREST GROWTH IN THE EASTERN UNITED STATES

Since the discovery of acid rain in the 1970's, scientists have been concerned that deposition of acids could cause depletion of calcium in forest soils. Research in the 1980's showed that the amount of calcium in forest soils is controlled by several factors that are difficult to measure. Further research in the 1990's, including several studies by the U.S. Geological Survey, has shown that (1) calcium in forest soils has decreased at locations in the northeastern and southeastern U.S., and (2) acid rain and forest growth (uptake of calcium from the soil by roots) are both factors contributing to calcium depletion.

CALCIUM CYCLING IN FORESTS

Calcium is an essential nutrient for tree growth that is used in the formation of wood and in the maintenance of cell walls, the primary structure of plant tissue. Trees obtain calcium from the soil (fig. 1), but to be taken up by roots, the calcium (a positively charged ion) must be dissolved in soil.
The discovery of acid rain (acids deposited from the atmosphere in rain, snow, particles and gases, more accurately referred to as acid deposition) in the 1970’s prompted concern that deposition of acids could increase leaching of calcium, and other neutralizing cations, such as magnesium, sodium, and potassium (referred to as base cations) from forest soils. Acid deposition provides (1) hydrogen ions, which displace cations adsorbed to soil surfaces, and (2) sulfate and nitrate ions, which tend to keep these cations dissolved in soil water that eventually drains into streams and lakes. Results of preliminary research in the 1970’s suggested that elevated leaching might deplete soil calcium, decrease forest growth, and acidify surface-waters (Cowling and Dochinger, 1980). These concerns were somewhat alleviated in the Northeast by the discovery that the soil contained large amounts of calcium. Although most of the soil calcium was known to be in unavailable forms in rocks and minerals, the rate at which calcium was released by weathering was considered to be sufficient to offset increased leaching caused by acid rain (Johnson and others, 1982).

In the Southeast, the amount of calcium in soils was found to be generally less than in the Northeast, but was thought to be somewhat protected from cation leaching by the high capacity of these soils to adsorb sulfate, a negatively charged ion. The fine texture of soils in the Southeast enhances sulfate adsorption, which removes the negative charge from soil water that is necessary to leach the positively charged cations. Considerable uncertainty as to the status of soil calcium remained, through the 1980’s, however, because the processes involved in weathering and leaching were found to be extremely complex. At the close of the research phase of the National Acid Precipitation Assessment Program (NAPAP) in 1990, decreases in the availability of calcium in forest soils from either acid rain or forest growth had not been confirmed, although the possibility of future depletion from acid deposition was acknowledged (NAPAP, 1993).
since the 1970's, may also have contributed to the
decrease in the availability of soil calcium in the
East (Johnson and others, 1994b).

Investigations of forest health have identified
relations between low calcium availability and a
reduction in stress tolerance of red spruce (Shortle
and Smith, 1988; DeHayes, 1992; Schlegel and
others, 1992), and sugar maple (Wilmot and others,
1995; Long and others, 1997). Related studies have
also suggested that forest harvesting could reduce
calcium availability through the removal of calcium
stored in trees, which could lower the growth rates of
the regenerating stand (Federer and others, 1989;
Hornbeck and others, 1990). Relationships among
acid deposition, calcium availability, and forest
productivity remain uncertain, however.

Ongoing research by the U.S. Geological Survey, in collaboration with the U.S. Forest Service, the University of
Illinois, the Institute of Ecosystem Studies and Syracuse University, has provided new information on the causes
and magnitude of calcium depletion in soils of the eastern United States. Results of this research have been
detailed in four articles prepared for scientific journals. A general summary of each of these articles and a
description of current USGS calcium research follows.

1. DISCOVERY OF A NEW MECHANISM OF CALCIUM DEPLETION IN FOREST SOILS

Aluminum released to water in the mineral soil by acid rain decreases the availability of calcium in the
overlying forest floor, the primary layer for nutrient uptake by roots in forest soils.
Lawrence, G.B., David, M.B., Shortle, W.C., 1995, A new mechanism for calcium loss in forest-floor soils:

Decreases in concentrations of exchangeable
calcium are generally attributed to displacement by
hydrogen ions, which can originate from either acid
deposition or uptake of cations by roots (Johnson
and others, 1994a, Richter and others, 1994). A
regional survey of soils in northeastern red spruce
forests in 1992-93 (fig. 2) has revealed that
decreases in exchangeable calcium concentrations in
the Oa horizon (a layer within the forest floor,
where uptake of nutrients is greatest) can also result
from increased concentrations of exchangeable
aluminum, which originated in the underlying
mineral soil (Lawrence and others, 1995). By
lowering the pH of the aluminum-rich mineral soil,
acid deposition can increase aluminum
concentrations in soil water through dissolution and
ion-exchange processes. Once in solution, the
aluminum (although not a nutrient) is taken up by
roots and transported through the trees to be
eventually deposited on the forest floor in leaves
and branches. Dissolved aluminum in the mineral
soil can also be transported into the forest floor by a
rising water table, or during unsaturated conditions,
1. Kossuth, Me.
2. Bear Brook, Me.
3. Howland, Me.
4. Crawford Notch, N.H.
5. Bartlett, N.H.
6. Cone Pond, N.H.
7. Hubbard Brook, N.H.
11. Whiteface Mountain, N.Y.
12. Big Moose Lake, N.Y.
13. Neversink River, N.Y.
15. Oak Ridge, Tn.
16. Calhoun Forest, S.C.
17. Shenandoah National Park
18. Duke Forest, N.C.
20. Coweeta Hydrologic Lab, N.C.
22. Clemson, S.C.
23. Gainesville, Fl.

Figure 2. Locations at which soil-calcium assessments have been made in the papers by Lawrence and others, (1995,1997) and Huntington and others (USGS approved).

horizons, which contain little organic matter, tend to be removed from solution through further decomposition or by adsorption to mineral surfaces. Once removed from solution, they are incapable of acidifying the soil, which results in a higher pH in the mineral soil than in the forest floor. Unlike these natural organic acids, sulfuric and nitric acids from acid deposition neither decompose (because they are inorganic) nor adsorb to soil particles readily; rather, they tend to remain in solution within the mineral soil where they lower the pH, thereby releasing aluminum to soil water and causing the leaching of calcium.

The effects of these processes can be seen through a comparison of soils that have been acidified to varying degrees (table 1). The ratio of exchangeable aluminum to exchangeable calcium in the Oa horizon was lowest at Groton, Vt, where the pH of water in the mineral soil was highest, and the pH of soil water in the Oa horizon was lowest. At Big Moose Lake, N.Y. and Mt. Abraham, Vt. the pH of soil water in the B horizon was considerably lower than at the Groton site and the ratios of exchangeable aluminum to exchangeable calcium in the Oa horizons were greater than 1.0, the threshold above which aluminum can interfere with uptake of calcium by roots.

<table>
<thead>
<tr>
<th>Site location</th>
<th>Forest floor pH</th>
<th>Al/Ca*</th>
<th>Mineral soil pH</th>
<th>Al/Ca*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groton, Vt.</td>
<td>3.3</td>
<td>0.3</td>
<td>4.8</td>
<td>5</td>
</tr>
<tr>
<td>Big Moose Lake, N.Y.</td>
<td>3.5</td>
<td>1.2</td>
<td>4.1</td>
<td>27</td>
</tr>
<tr>
<td>Mt. Abraham, Vt.</td>
<td>3.7</td>
<td>5.6</td>
<td>4.1</td>
<td>16</td>
</tr>
</tbody>
</table>

* ratio expressed as centimoles of charge per kilogram Aluminum per centimole of charge per kilogram Calcium
2. STATUS OF SOIL CALCIUM IN THE OA HORIZON OF RED SPRUCE STANDS OF THE NORTHEAST

A regional assessment of forest-soil chemistry supports evidence of soil-calcium depletion in the Northeast; acid rain identified as a probable factor.


Decreases in available calcium in forest soils of the Northeast have been indicated in several studies in the 1990’s (Shortle and Bondietti, 1992; Bailey and others, 1996; Johnson and others, 1994a,b), but the results of these studies could not be directly related to each other because the measurements of soil-calcium concentrations were made with different methods of unknown comparability. To address this problem, soil samples collected by Lawrence and others (1995) in the survey of red spruce forests (fig. 2) were analyzed by the four most common methods currently used for measuring exchangeable calcium (Lawrence and others, 1997). A comparison was also done between the most common current method for determining acid-extractable calcium and the method used by Heimburger (1934), and also by Johnson and others (1994a) in resampling the plots first sampled by Heimburger 50 years earlier (Lawrence and others, 1997). The soil survey of Lawrence and others (1995, 1997) in red spruce forests entailed the selection of 12 sites that together encompassed the range of environmental conditions represented by red spruce stands in the Northeast.

Considerable variability in exchangeable-calcium concentrations was observed among the 12 sites; concentrations ranged from 2.1 to 22.0 centimoles of charge per kilogram in the Oa horizon, and from 0.11 to 0.68 centimoles of charge per kilogram in the upper mineral soil. The primary cause of this variability was mineralogical differences in parent material (rock that weathers to form soil), but results also suggested that acidic deposition had decreased concentrations of exchangeable calcium in the mineral soil at these sites (Lawrence and others, 1997).

Results of the methods-comparison tests were used to relate the long-term decrease documented in the study by Johnson and others (1994a) to the range of calcium variability measured in the study by Lawrence and others (1997). The average value determined by Johnson and others (1994a) for 38 red spruce stands in the Adirondack Mountains of New York, was near the middle of the range obtained by Lawrence and others (1997), and in the upper range of values obtained in a study by McNulty and others (1991). The average value obtained for Adirondack sites measured by Heimburger (1934) 50 years earlier was in the upper part of the range measured by Lawrence and others (1997). Although considerable variability was caused by local differences in environmental factors such as mineralogy of parent material, and acid deposition rates, the results support the probability indicated by the combined studies of Johnson and others (1994a,b), Shortle and Bondietti (1992), Lawrence and others (1995), and Bailey and others (1996), that concentrations of available calcium in northeastern red spruce forests have decreased in the second half of this century.

Figure 3. Acid-extractable calcium in Oa horizons of red spruce stands in the studies of Lawrence and others (1997), McNulty and others (1991), Heimburger (1934), and Johnson and others (1994a).
3. DEPLETION OF SOIL CALCIUM AFFECTS THE RESPONSE OF STREAM CHEMISTRY TO DECLINING RATES OF ACID DEPOSITION IN THE NORTHEAST


Rates of acid deposition have been declining in the Northeast since the 1970’s, but many acidified surface waters in the region have unexpectedly shown little or no corresponding increase in acid-neutralizing capacity, an integrated measure of the degree to which a water body is acidified. Long-term records of stream chemistry at the Hubbard Brook Experimental Forest in New Hampshire (fig. 2) showed that the ratio of base cations (calcium, magnesium, sodium, and potassium) to acid anions (sulfate, nitrate and chloride) decreased steadily through the 1970’s, then remained fairly stable through the 1980’s and early 1990’s (Likens and others, 1996). This response was interpreted as an indication that past declines in soil concentrations of calcium and other base cations were impeding recovery of acidified stream-water at this site.

Additional information on the relations between soil-calcium depletion and the status of acidified surface waters was obtained in a recent USGS study by Lawrence and others (in press) in the Neversink River Basin in the Catskill Mountains of New York (fig. 2). Results showed that rates of atmospheric deposition of sulfuric acid increased from the lowest elevations to the highest elevations of a subbasin, whereas the concentrations of exchangeable-base cations in natural soil decreased from lowest to highest elevations (fig. 4 a, b).

Relations between the elevational trends in atmospheric deposition rates and soil chemistry were further investigated through a procedure in which a large quantity of soil was collected at a low elevation in the basin, where exchangeable base-cation concentrations were somewhat higher than in the subbasin being studied. This soil was thoroughly mixed, placed in mesh bags, then buried in the soil in stands of mixed northern hardwoods at varying elevations within the subbasin. Analysis of the samples after 1 year, confirmed a distinct up-slope decrease in exchangeable base cation concentrations.
(fig. 4c), and in base saturation (the base-cation concentration as a percentage of total cation exchange capacity). Detailed analysis of other factors that could cause an elevational gradient in soil acidity and leaching of base cations indicated that the effects of these factors were either minimal or undetectable. These results led to the conclusion that the upslope increase in the rate of atmospheric deposition was the most probable cause of the upslope decrease in base-cation concentrations (and base saturation) in the soil.

The elevational trends in atmospheric deposition and soil chemistry were also reflected in an elevational trend in stream chemistry; the ratio of base cations to acid anions in stream water (an index of acidity) decreased with increasing elevation, which indicates an upslope increase in stream-water acidity (fig. 4d). A followup laboratory soil experiment demonstrated that this ratio in soil water was directly related to soil-base saturation. The upslope increase in atmospheric deposition can therefore be linked to the upslope increase in stream-water acidification through the elevational trend in soil-base saturation.

The effect of the upslope increase in atmospheric deposition on soil chemistry and stream chemistry may be analogous to the effect of past increases in acid deposition rates on temporal trends of soil and stream chemistry, and supports the explanation put forth by Likens and others (1996) that the observed minimal response of stream chemistry to declining acid deposition rates in New Hampshire was due to depletion of base cations in soil. Long-term trends in concentrations of calcium and acid-neutralizing capacity have both shown significant decreases (indicating increases in acidity) for 1984-97 in the Neversink Basin (fig. 5) despite a consistent decreasing trend in rates of atmospheric deposition during this period.

![Graph showing calcium concentrations and acid-neutralizing capacity (ANC) of stream water in a subbasin of the Neversink Basin, 1984-1997.](image)

**Figure 5.** Calcium concentrations and acid-neutralizing capacity (ANC) of stream water in a subbasin of the Neversink Basin, 1984-1997.

### 4. CALCIUM DEPLETION IN FOREST ECOSYSTEMS OF THE SOUTHEAST

Data from detailed site studies and regional surveys suggest that soil-calcium depletion is common in forests of the Southeast and could diminish long-term forest productivity.

Huntington, T.G., Hooper, R.P., Johnson, C.E., Aulenbach, B.T., and Cappellato, A., in review, Calcium depletion in forest ecosystems of the southeastern United States: Submitted for publication as an article in a technical journal (USGS Approved).

Accumulating evidence indicates possible depletion of soil calcium in forests of the Southeast, as well as the Northeast. Long-term studies at several southeastern forest sites have documented declines in the exchangeable-calcium concentration of soils. In these studies, calcium inputs from weathering and atmospheric deposition were found to be insufficient to replenish the losses that occur through uptake by vegetation and leaching (Johnson and others, 1988; Johnson and others, 1991; Knoepp and Swank, 1994; Richter and others, 1994).
Several factors suggest that the available calcium in southeastern soils is prone to depletion. These soils have weathered in place for a few hundred thousand to 2 million years and many of them have little weatherable calcium left in soil particles and rocks. Also, poor farming practices caused extensive loss of soil and nutrients on lands that are now used for commercial forestry (Nelson, 1957; Brender, 1974; Trimble, 1974). Forest growth places a continued demand on the remaining calcium in these soils, and when the stands are harvested, the calcium in the trees is removed from the ecosystem. Acidic deposition during the 20th century has placed further strain on soil calcium availability by enhancing calcium leaching rates at a time when the rates of atmospheric deposition of calcium have declined (Lynch and others, 1996).

The potential for calcium depletion in southern forest soils, was evaluated in detail through the development of a calcium budget for Panola Mountain watershed, in the Piedmont region near Atlanta, Ga. (Huntington and others, USGS approved); this budget was then compared with data from other watershed studies and soil surveys to assess the extent of calcium depletion within the Southeast. Calcium-budget calculations for Panola Mountain watershed (averaged over the roughly 90 year life of the current forest stand), indicate that the rate of calcium leaching from the soil approximates the rate of calcium input from atmospheric deposition. Also, chemical and mineralogical analyses of soil and saprolite (the highly weathered layer of residual rock beneath the soil) indicated that only trace amounts of weatherable mineral calcium remain, which suggests that inputs from weathering are negligible. The annual rate of calcium depletion in this watershed is, therefore, similar to the annual rate of uptake by trees of 10.7 kilograms per hectare. Continuous depletion at this rate for 150 years would reduce the total reserves of calcium in the soil to the approximate amount required by a hardwood stand to reach a marketable size.

Budget calculations for other forested study sites in the Southeast showed a wide variation in sensitivity to soil-calcium depletion (table 2). The most sensitive forests are dominated by hardwood species, which have a higher calcium demand than softwoods; at some sites more calcium is contained by the trees than by the soil. Stands that are the least sensitive tend to be dominated by softwood and are in areas that receive the highest amounts of calcium from atmospheric deposition. The rate of calcium depletion estimated for Panola Mountain watershed was in the middle of the range of values reported for other forested sites in the Southeast.

Lower availability of calcium in soils of the Southeast than the Northeast is suggested by surveys of exchangeable-calcium concentrations in soils. About 70 percent of the sites sampled in the Southern Blue Ridge region through the U.S. EPA Direct-Delayed Response Program (Church and others, 1989) had concentrations of exchangeable calcium less than 1000 kilograms per hectare, whereas in the Northeast, about 50 percent of the

Figure 6. Cumulative percentage of sites as a function of (A) exchangeable calcium concentrations in soil and (B) calcium concentrations in stream water in selected regions of the eastern United States. Figure A adapted from Turner and others (1993); Figure B adapted from Sale and others (1988).
sites sampled had calcium concentrations less than 1000 kilograms per hectare (fig. 6a). Calcium concentrations in southeastern streams also tended to be distributed toward low values, as indicated by the steeply ascending lines in fig. 6b.

The assessments of the calcium budgets at Panola Mountain watershed and other forested sites in the Southeast, in conjunction with the surveys of soil and stream chemistry, suggest that (1) depletion of calcium in soils is common, (2) the growth of some forests may be limited by insufficient amounts of calcium in soils, and (3) calcium availability will be lowered by forest harvesting of sites currently low in calcium.

<table>
<thead>
<tr>
<th>Table 2. Calcium (Ca) contents of soil, calcium fluxes, net calcium depletion, and sensitivity to calcium depletion at selected forest sites in the eastern United States.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(kg/ha, kilograms per hectare; (kg/ha)/yr, kilograms per hectare per year; ND, no data)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site location</th>
<th>Type of forest</th>
<th>Calcium content of soil (kg/ha)</th>
<th>Calcium flux (kg/ha/yr)</th>
<th>Ecosystem sensitivity to Calcium depletion</th>
<th>Source of data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Sites that are highly sensitive to calcium depletion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Great Smoky Mountains Nat. Park</td>
<td>Beech</td>
<td>57</td>
<td>2,500</td>
<td>15.9</td>
<td>high²</td>
</tr>
<tr>
<td>Oak Ridge, Tenn.</td>
<td>Oak</td>
<td>140</td>
<td>1,800</td>
<td>8</td>
<td>high²</td>
</tr>
<tr>
<td>Oak Ridge, Tenn.</td>
<td>Oak</td>
<td>110</td>
<td>1,180</td>
<td>17</td>
<td>high²</td>
</tr>
<tr>
<td>Calhoun Forest, S.C.</td>
<td>Pine</td>
<td>245</td>
<td>ND</td>
<td>7.5</td>
<td>high²</td>
</tr>
<tr>
<td>Shenandoah Nat. Park, Va.</td>
<td>Mixed pine, hardwood</td>
<td>380</td>
<td>ND</td>
<td>10</td>
<td>high²</td>
</tr>
<tr>
<td>Oak Ridge, Tenn.</td>
<td>Pine</td>
<td>820</td>
<td>2,500</td>
<td>16</td>
<td>high²</td>
</tr>
<tr>
<td>Coweeta Hydrologic Laboratory, N.C.</td>
<td>Mixed hardwood</td>
<td>1,370</td>
<td>11,500</td>
<td>12.2</td>
<td>high 97</td>
</tr>
</tbody>
</table>

| **B. Sites that are moderately sensitive to calcium depletion** |
|---------------------|-----------------|-----------------|----------------|--------------------------|----------------|
| Stewart Co.; Ga.    | Pine            | 840             | 840            | 6                        | 3.2            | med. 123 | 6 |
| Duke Forest, N.C.   | Pine            | 2,130           | 4,900          | 13.6                     | 8.1            | med. 130 | 1 |

| **C. Sites that are insensitive to calcium depletion** |
|---------------------------------|-----------------|-----------------|----------------|--------------------------|----------------|
| Clemson, S.C.                  | Pine            | 1,450           | ND             | 3.4                      | 2.9            | low 310 | 7 |
| Oak Ridge, Tenn., plot 1       | Pine            | 6,900           | 8,600          | 5.5                      | 5.4            | low 350 | 1 |
| Gainesville, Fla.              | Pine            | 240             | 758            | 5.9                      | 8              | low⁵    | 1 |
| Coweeta Hydrologic Laboratory, N.C. | Pine          | 667             | 3,770          | 3.9                      | 7.1            | low⁵    | 1 |
| Great Smoky Mountains Nat. Park | Spruce          | 230             | 1,800          | 1.2                      | 19             | low⁵    | 1 |

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¹ Value indicates number of years until current rates of depletion reduce exchangeable stores to twice the expected requirement for a marketable forest stand

² References:
4. Written commun. from J.R. Webb (University of Virginia), June 1995.

³ Soils already depleted to less than twice the calcium requirement for marketable timber

⁴ Estimated from typical forest growth rates in this area, on basis of USDA Forest Service—Forest Inventory Analysis data and calcium concentration for oak (Quercus spp.)

⁵ Either soils are accumulating calcium, or output equals input
**UNANSWERED QUESTIONS**

Much information has been obtained in the 1990's on the calcium status of forest soils in the East, but additional work is needed to define the current trends in soil calcium availability and to determine if these trends will continue into the future. Some specific questions that need to be addressed are:

1. Is the available calcium content of soils currently increasing, decreasing, or remaining stable?

2. How do rates of soil-calcium weathering and leaching vary throughout the East?

3. How is forest growth affected by low levels of available calcium?

4. How does forest harvesting affect the availability of soil calcium and long-term trends in stream chemistry?

**ONGOING USGS RESEARCH**

Unanswered questions regarding the current and future status of calcium in the East are being addressed through the USGS Hydrologic Benchmark Network (HBN) and the National Trends Network (NTN). The HBN sponsors monitoring of stream flow and chemistry, in undeveloped, medium-sized basins (100 to 200 km² drainage areas). The NTN, which is closely affiliated with the National Atmospheric Deposition Program (NADP), supports the monitoring of chemical deposition in rain and snow (wet-only deposition) at about 100 locations nationwide. The HBN and NTN programs are currently supporting investigations in three HBN watersheds in the Northeast (the Wild River, in New Hampshire and Maine, the Neversink River, in N.Y., and Young Womens Creek, in Pennsylvania) and two in the Southeast (Little River, in Tennessee, and Cataloochee Creek, in North Carolina). These investigations will (1) measure atmospheric deposition rates, stream chemistry, and soil chemistry, (2) determine soil-weathering rates, forest-growth history and past harvesting in these watersheds, and (3) assess the effects of future tree harvesting. A primary objective of this work is to gather detailed information on calcium cycling that can be used to assess current conditions for each of the five basins. This information will be integrated with the long-term monitoring data to better understand past and future changes in soil-calcium status in the eastern United States.

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By ¹Gregory B. Lawrence and ²T. G. Huntington

For more information contact:
¹Gregory B. Lawrence
U.S. Geological Survey
425 Jordan Rd.
Troy, NY 12180
E-mail address: glawrenc@usgs.gov

²T.G. Huntington
U.S. Geological Survey
3039 Amwiller Rd.
Atlanta, Ga 30360
E-mail address: thunting@usgs.gov

Copies of this report can be purchased from:
U.S. Geological Survey
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