6.0 MONITORING RECOVERY FROM CALCIUM DEPLETION AND NITROGEN SATURATION

Walter C. Shortle, Peter S. Murdoch, Kevin T. Smith, Rakesh Minocha, and Gregory B. Lawrence

Atmospheric emissions from industrial processes in the early part of the 20th century resulted in acidic deposition in the Northeastern U.S., a phenomenon known as "acid rain." Acid rain has been implicated in acidification of sensitive waterways, nitrate enrichment of surface waters, and fish population declines in poorly buffered mountain streams (Baldigo and Lawrence 2000, Murdoch et al. 1998). Scientists are also discovering that acid rain has had additional lasting and negative effects on soil and stream chemistry and that these chemical changes may slow tree growth (Hallett et al. 2006). The goals of this research and monitoring development project were to:

- Develop relationships between soil and foliar calcium (Ca), soil and stream Ca, forest nitrogen (N) saturation, and tree productivity at intensive monitoring and research areas (IMRAs) to quantify and verify the impact of Ca depletion on forest growth
- Develop methods for regional monitoring of forest and stream recovery from acidification, Ca depletion, and other stressors
- Develop methods for early detection of forest and ecosystem stress due to factors such as Ca depletion

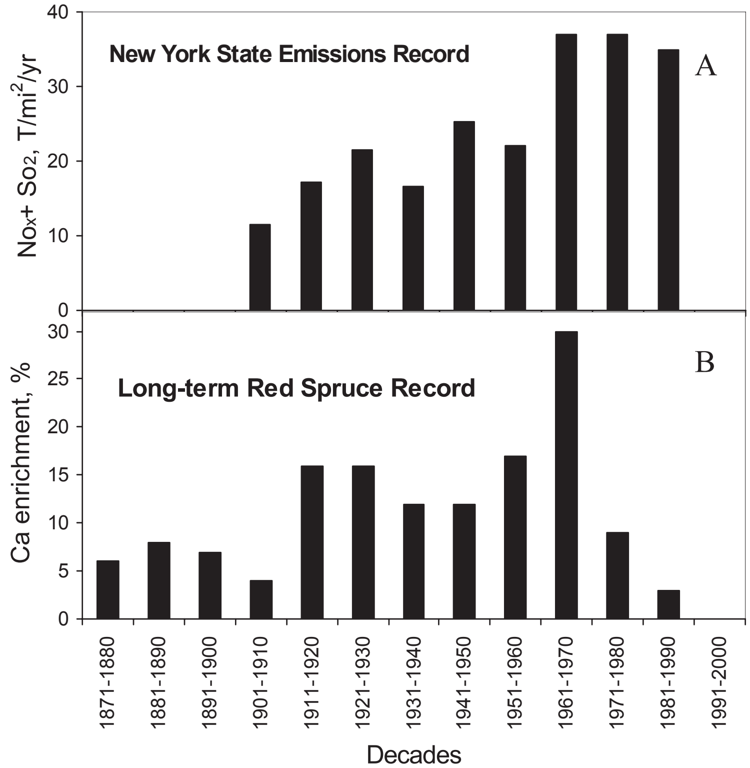
6.1 Background

Calcium is the fifth most abundant element in trees, after hydrogen (H), carbon (C), oxygen (O), and nitrogen (N). It occurs as part of the structure of wood, regulates acidity, and signals changes in various biological functions (McLaughlin and Wimmer 1999). For wood to form, a steady supply of Ca is needed.

Trees obtain Ca via their roots as they grow through forest soils. These soils have a topmost forest floor layer, derived from decaying leaves, branches, roots, and dead trees, and an underlying layer of mineral soil, derived from rock of varying mineral composition. Calcium and other essential elements in the forest floor are the result of decades of organic cycling as trees grow, shed, die, and decay, during which time some Ca is leached from the soil into streams where it is needed to support aquatic life. Some Ca is added back to the system from atmospheric deposition and weathering of the underlying minerals. In most cases the amount of Ca available to trees remains relatively constant because removal processes are offset by replacement processes. However, if a major disturbance occurs, the system can be disrupted and net losses can occur, reducing the amount of Ca available for tree uptake. The disturbances are various: major fires, heavy harvesting operations, or changes in the input of inorganic acidity brought about by industrialization in the 20th century.

The latter form of disruption of the organic cycling of Ca is of particular concern for the Northeastern United States, where the Delaware River Basin (DRB) is located. Oxides of sulfur (S) and N, emitted during industrial processes, can react with water to form strong inorganic acids, which are the basis of acidic deposition. Emission of sulfur and nitrogen oxides increased from the beginning of the century until 1970, when the Clean Air Act was

Figure 6.1.—Dendrochemical marker of calcium mobilization and coincident change in emissions of oxides of sulfur and nitrogen. A) Combined emissions of sulfur dioxide and nitrogen oxides for the State of New York from 1901 to 1990. B) Percent frequency of calcium enrichment by decade. For example, the frequency of calcium enrichment between 1961 and 1970 relative to the preceding decade (1951-1960) was 30 percent across all sample trees.



passed (Fig. 6.1A). Since 1970, emissions have not increased further, but have remained historically high. Since 1990 there has been about a 40-percent reduction in deposition of sulfur oxides, but little change in deposition of nitrogen oxides (Driscoll et al. 2001).

In some regions, N deposition has exceeded the biological demand for N in forested watersheds, leading to a buildup of N in the soil and the leaching of N from the watershed to surface waters (Aber et al. 1989). This phenomenon, referred to in the literature as "nitrogen saturation," appears to be occurring in parts of the northern DRB, where acidification of soil water and surface water by nitric acid has been evident (Murdoch and Stoddard 1992).

When deposited from the atmosphere, inorganic acids such as nitric acid remove Ca from where it is bound on decaying organic matter to make it soluble, or mobile. Mobile Ca is then absorbed by roots for use by the tree. Initially, the increase in mobile Ca helps trees to grow. However, this inorganic acidity can also mobilize aluminum (Al). When this occurs, Al does two things: it binds very tightly to soil particles, thereby displacing Ca from the soil, and it blocks the uptake of Ca by tree roots (Fig. 6.2). Forest soils can become depleted of Ca to the point where some tree species have Ca deficiency, which reduces growth. Prolonged growth suppression of mature trees can lead to mortality from a variety of causes.

6.2 Relationships Between Soil Calcium Depletion and Tree Growth

The problem of Al-induced Ca deficiency syndrome (Shortle and Smith 1988) and Ca loss from the forest floor (Lawrence et al. 1995) has been extensively studied in spruce forests to the north of the DRB (Lawrence et al. 2000, Shortle et al. 2000). In this research, chemical data from tree cores (dendrochemistry) were used to infer changes in soil chemistry in the past. Growth ring patterns (dendrochronology) were used to infer tree response to changing soil conditions and climate variables.

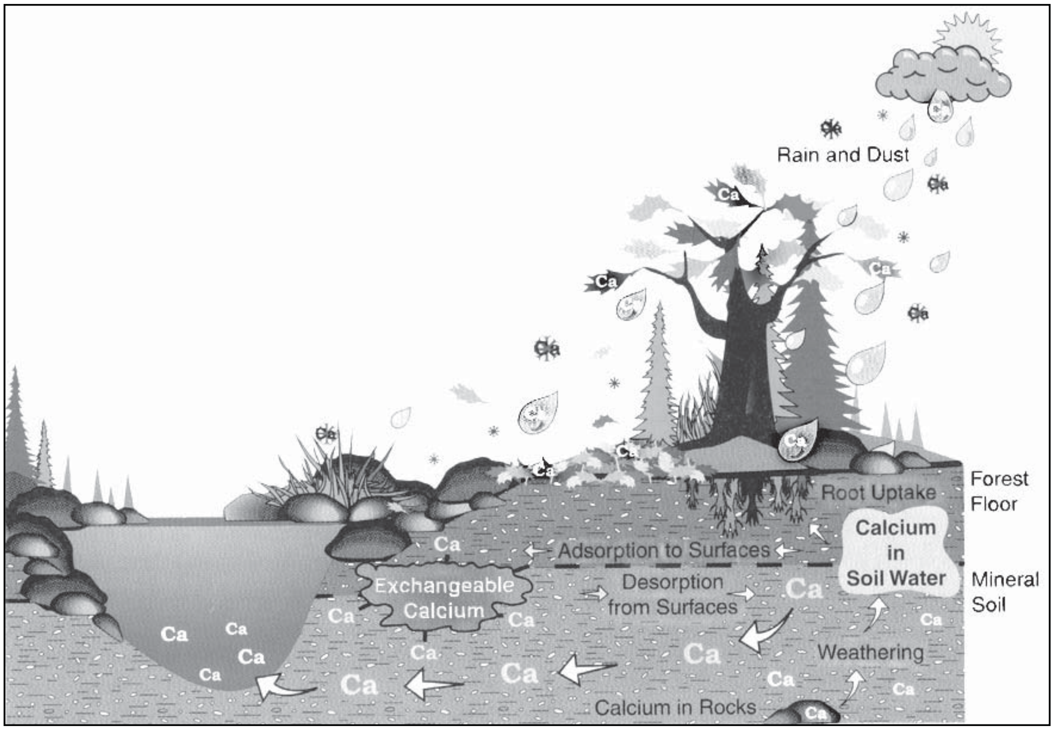


Figure 6.2.—Calcium cycle in a forest ecosystem. Inputs to the pool of available calcium in the soil result from weathering of rocks, atmospheric deposition, and litterfall. Outputs from this pool result from root uptake and leaching out of the soil. From Lawrence and Huntington (1998).

Calcium depletion from soil appears as Ca enrichment in wood because mobilization of Ca by inorganic acids increases the availability of Ca for root uptake as well as leaching. When we look at a 12-decade record in spruce (Fig. 6.1B), the 4 decades from 1871 to 1910 had a mean Ca enrichment (Ca concentration in a tree core formed in a particular decade, relative to the previous decade) frequency of 6 percent, which more than doubled in the 5 decades of 1911-1960 and doubled again in 1961-1970 before returning to 6 percent in 1971-1990. This pattern indicates a period of low soil Ca depletion and low wood enrichment followed by six decades of disruption, in which depletion and enrichment became more common after acidic deposition increased and reached a maximum in 1961-1970. After 1970, the pattern indicates a return to low depletion and low enrichment because much of the bound Ca in soil was replaced by Al as soil became acidified by acid rain. A buildup of Al on organic storage sites in the forest floor tends to block Ca uptake by the tree. Analysis of forest floor material indicated that bound Ca levels are related to bound Al levels, not to bound H levels as expected if only natural organic acidity was mobilizing Ca. These patterns are consistent with the concept that Ca storage and uptake before 1911 were governed primarily by organic acidity of trees and associated organisms, but that after a long period of elevated inputs of inorganic acidity, mobilized Al became a limiting factor in the Ca cycling of spruce forests.

Does this pattern exist in sugar maple and other species in the DRB? Does the tree ring record indicate growth reductions following Ca depletion? Did the growth relationship to climate variables change after Ca depletion? These questions were addressed by coring trees and analyzing dated tree ring tissue at the Neversink IMRA.

6.3 Early Detection of Stress Using Foliar Indicators

Early detection of changes in soil chemistry and resulting changes in physiological and biochemical processes in trees, before the appearance of visual symptoms, can point to geographic areas needing special attention and can enable the early abatement of emerging forest health problems. The relationship of altered soil chemistry to foliar biochemical indicators has been studied in spruce forests (Minocha et al. 1997) and in field experiments with maple, pine, and oak (Minocha et al. 2000). One group of indicators showing special promise for early detection of increasing environmental stress in trees are nitrogenous compounds, such as polyamines and amino acids.

Putrescine (a polyamine) has been shown to increase in foliar samples of healthy spruce under conditions of increasing Al and decreasing Ca in soil (Fig. 6.3). When Ca was experimentally added to deficient soils, the health of sugar maples was restored and foliar putrescine levels were reduced (Figure 6.3A,B). Additions of nitrate to stands of pine, maple, and oak at Harvard Forest to simulate the effect of increased nitrate inputs by acid rain resulted in decreased soil Ca and increased foliar putrescine (Fig. 6.3 C,D). It appears that foliar polyamine analysis, coupled with inorganic analysis of soil and foliage, indicates that altered soil chemistry produces stress in trees before symptoms of declining health appear.

Polyamines like putrescine are not specific indicators of a particular kind of stress, such as Ca depletion, which makes them very useful for detecting a broad range of environmental stress. To determine the cause of the stress detected, other analyses of soil and foliage are needed. Arginine, an amino acid, appears to be a specific indicator of high N input which can be a serious tree health problem in Ca-depleted soils.

6.4 Existing Monitoring Programs and Regional Assessment Capability

Federal and State monitoring programs operating within the DRB collect data on individual components of the forest ecosystem that are important to a regional Ca-depletion assessment. Information about air quality, surface water quality and quantity, and forest growth has been collected by the U.S. Environmental Protection Agency (EPA), the U.S. Geological Survey (USGS), the U.S. Forest Service (USFS), and State agencies. A brief summary of the existing databases used to assess the N-saturation and Ca-depletion issues follows.

6.4.1 Soil Chemistry

Information on soil chemistry is routinely collected at the Forest Inventory and Analysis (FIA) phase 3 plots, which are randomly and sparsely scattered through the DRB (as well as other regions of the U.S.), and USGS researchers collect soil chemistry information associated with their individual research projects in the Neversink IMRA. The resulting dataset on soil chemistry and condition, however, is inadequate for generating accurate maps of soil chemistry within the IMRAs or the upper DRB.

6.4.2 Forest Condition

Research on foliar chemistry and biochemical indicators of tree stress is developing promising tools for tracking forest condition, but foliar measurements have not yet been implemented as part of routine monitoring in state or national forest-monitoring programs. Foliar N and Ca data have been collected at a few scattered research sites in the DRB, but the number of points represented is inadequate for developing a map of regional condition. Remote sensing products from MODIS were used to estimate forest net primary production (NPP) in the DRB, by parameterizing the interpretive models for eastern forest species (Pan et al. 2006). Remote sensing of foliar Ca was in the development stages during the Delaware CEMRI.

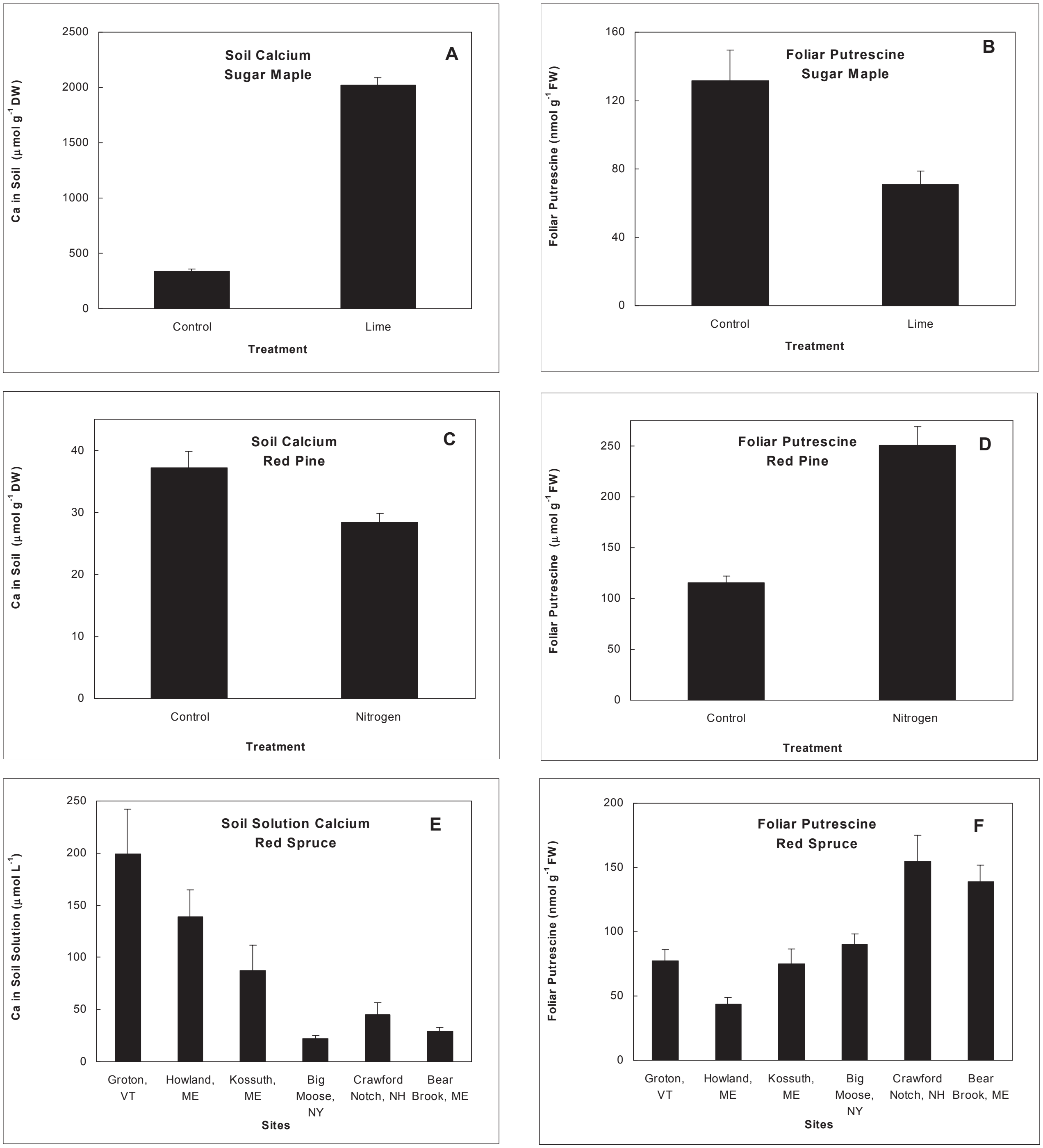


Figure 6.3.—Inverse correlation between foliar stress indicators (putrescine) and calcium in soil in three different tree species under different growth conditions. A-B) Impact of liming treatment on exchangeable calcium in sugar maple stands on the Allegheny Plateau, PA. Data for putrescine are mean +/- SE (n=100) and for soil (n=16). C-D) Effects of chronic nitrogen addition (as ammonium nitrate) on exchangeable calcium in organic soil and foliar putrescine in red pine trees at Harvard Forest, MA. Data for putrescine are mean +/- SE (n=100) and for soil (n=18). E-F) Calcium in soil solution of organic soil and foliar putrescine in red spruce trees growing at six sites across the Northeastern U.S. Putrescine data are mean +/- SE (n=40 except for Kossuth, ME, and Big Moose, NY, for which n=20) and soil data are mean +/- SE (n=12).

6.4.3 Water Quality

Water quality monitoring funded by EPA is primarily conducted through State monitoring programs and is focused on areas of human disturbance and associated pollution runoff. The EPA has collected scattered data in the upper DRB on streams draining forested watersheds as part of its Ecological Monitoring and Assessment program (EMAP), but that sampling occurred over a limited time and had an insufficient density to provide estimates of Ca concentrations in streams draining undeveloped landscapes in the DRB. State water quality monitoring in the basin includes some sampling of forested watersheds as indicators of background conditions for assessing the effects of human disturbance. The New Jersey Department of Environmental Protection (DEP) recently established a 73-site network of ecoregion reference stations that is generating data primarily on invertebrate populations and habitat conditions. The New York City DEP monitoring program in the Catskills includes several streams draining forested watersheds. Of the few streams sampled that have drainage areas measuring less than 25 km^2 in the northern DRB (i.e., first- or second-order drainages), reported Ca + magnesium (Mg) concentrations range from 0.8 to 20 mg/L, and nitrate concentrations range from 0 to 4 mg/L (0 to 64 uEq/L: Ward Hickman, NAWQA program 2001, written communication). Forest and soil condition measurements are not systematically tied to these stream monitoring networks, and the stream samples are typically collected at base flow when root-bearing soils are not hydrologically connected with streams. The association of streamwater quality with forest and soil condition could not be assessed with pre-CEMRI data.

6.4.4 Deposition

The National Atmospheric Deposition program (NADP) and State deposition chemistry monitoring stations either within or near the DRB have been used in models to create regional maps of deposition in the Northeastern United States. The accuracy of those maps for specific subregions of the DRB is uncertain, but the general pattern of N deposition can be used with reasonable confidence.

6.4.5 Summary of Gaps in Current Data Collection

The greatest gap in current monitoring systems is the lack of a multiresource monitoring effort, particularly surveys of soils and surface waters, needed to understand the interrelated nature of atmospheric deposition, soil and stream Ca status, and tree growth. The lack of these data on a regional scale precludes all but the most simplistic regional assessments of Ca depletion or N saturation at this time.

Table 6.1.—Key variables and analyses for assessing forest recovery from calcium depletion and nitrogen saturation

Tier 1: Intensive sites
Relationships between foliar and soil nitrogen and calcium (Neversink IMRA only)
Relationships between tree growth (net primary production-NPP) and soil/ foliar chemistry
Relationships between soil N and Ca, forest NPP, and water quality (Neversink IMRA only)
Relationship between forest stress factors and soil chemistry
Tiers 2 and 3: Gradient sites and regional surveys
Forest NPP and crown condition
Soil chemistry
Soil physical parameters
Tier 4: Remote sensing and mapping
Atmospheric deposition: N and Ca
Remote sensing of foliar chemistry: foliar N and foliar Ca
Forest type, species classification
Remote sensing of forest productivity (from MODIS satellite)

6.5 The CEMRI Monitoring and Assessment Approach for Nitrogen Saturation and Calcium Depletion

6.5.1 Intensive Site Research (Tier 1)

A summary of the key research and monitoring components needed for a regional assessment of the extent and effects of N saturation and Ca depletion is presented in Table 6.1. A brief description of the current information base for a regional assessment is provided below.

The relationship between soil chemistry and tree stress, and the development of indicators that reveal disturbance of that relationship, was the focus of IMRA activity related to Ca depletion and N saturation in forested watersheds. Specific process-level questions that were addressed included the following:

- What are the thresholds of Ca availability in soil below which NPP is decreased and trees show stress characteristics?
- Is there a spatial or elevational gradient of Ca depletion and associated tree stress that can be related to deposition rates and soil fertility?
- How does Ca depletion affect tree growth (leaf area, root area, survivorship, and reproduction), C sequestration, nutrient uptake, and adjacent aquatic ecosystems?
- What combination of soil characteristics, deposition rates, and forest conditions results in nitrate leaching from forest soils?
- What indicators of Ca-depletion stress on an ecosystem can be used to assess the regional extent of the N-saturation and Ca-depletion issues?

Based on this list of questions, foliar chemistry, growth and dendrochemical history, wood polyamine content, soil chemistry, and drainage water quality were the primary components of the ecosystem measured as indicators of Ca and N stress at the IMRAs.

One goal of this research was to determine whether Ca depletion and retarded tree growth are related in Appalachian Plateau hardwoods and to assess whether stream Ca concentrations are an indicator of forest nutrient status. These were tested at the IMRAs by applying dendrochronological and dendrochemical techniques and integrating those data with soil chemistry and streamwater quality data in the same landscapes (Table 6.1). Relationships between changing soil Ca and tree response determined at the Tier 1 study sites were applied across a region using the combination of data describing atmospheric deposition, soil condition, tree species, and tree health available from Tier 3 regional surveys. To further assess the relative importance of these potential controls on current tree growth at the regional scale, repeat measurements of growth over a 3-year period at selected plots in the IMRAs and randomly located within the broader basin were used to confirm growth patterns.

Research by the USFS was also conducted at the Neversink IMRA to develop methods for detecting stress using foliar polyamine content in trees exposed to Ca depletion before visible signs of stress appear. Foliar samples were collected from plots where soil Ca status and tree growth rates are known with certainty. Results from these intensive sites were then applied across the region to determine if they could be correlated with remote sampling of foliage by near-infrared spectrometry. In previously published data from Harvard Forest, a high correlation was seen between putrescine level and foliar N numbers obtained by near-infrared spectroscopy (Minocha et al. 2000). Collection of foliage from mature trees was difficult to incorporate into extensive plot sampling, because of the time-dependent nature of the sampling technique.

6.5.2 Gradient Surveys (Tier 2)

Regionally extensive data collection for addressing the N-saturation and Ca-depletion issues incorporated measurement of forest, soil, and water conditions as well as deposition volume and chemistry. Gradient surveys relating soil, stream, and foliar Ca were conducted within or near the DRB before the Delaware CEMRI and proved adequate for relating the intensive site research results to the regional probability-based survey. Foliar C and N, soil chemistry, NPP, and nearby stream chemistry were also computed for 16 regional plots distributed throughout the Appalachian Plateau of the upper DRB, and for 10 plots within each of the IMRAs (for a total of 30 IMRA plots) representing a range of soil Ca and forest types. All plots were integrated in the broader FIA plot grid for the United States and were thus easily scalable to survey data collected at the FIA plots within the basin.

6.5.3 Regional Probability Surveys (Tier 3)

Regional probability surveys were linked to the IMRA intensive datasets through measurement of these same components on a less intensive but more widely distributed scale. Some measurements, such as polyamine content in wood, were still at the experimental stage and were not available for use in broad surveys. Forest condition assessments relied on data from the USFS FIA plot networks. Data on current NPP, canopy condition, species distribution, presence/absence of key pests, and historical information on forest growth were used where available. To make inferences about soil Ca status and tree growth at the regional scale, monitoring methods were developed to enable the regional mapping of soil Ca status. Soil samples collected from the O horizon and two depths in the B horizon at each phase 2 and phase 3 FIA plot within the Appalachian Plateau portion of the DRB were analyzed for soil Ca and other related constituents.

Because large-scale soil monitoring is extremely time consuming and costly to implement, one goal of the research at the IMRAs was to compare soil chemistry from each plot to nearby stream chemistry. If water chemistry and soil chemistry were found to be closely linked, then water samples could be used to infer soil chemistry. A stream survey is preferable to a soil survey for implementation as an extensive monitoring program for soil Ca status because stream samples are simpler and faster to collect, less costly to process, and integrate the chemical signal of large areas of the upper soil. To develop these regional soil/water relationships, streamwater samples were collected by the USGS district research and monitoring program at the nearest first-order stream to the FIA plots where soils have been collected. First-order stream chemistry, especially during periods of high flow when the flowpath of water through the watershed is through the shallow soil, can serve as an integrator of soil condition and can thus reveal where N is leaching from soils and Ca depletion in soils is starting to affect runoff water quality. A survey of first-order streamwater quality that was linked to survey measurements of NPP, foliar chemistry, soil chemistry, and forest condition (crown density, pest presence/absence, etc.) provided the major parameters needed for the first comprehensive regional assessment of Ca depletion in the study area.

Data from this experimental survey linking terrestrial and aquatic information were also compared with data from the USGS National Water Quality Assessment program (NAWQA) stream gradient survey and fixed-site monitoring networks, thus allowing an assessment of the downstream extent of forest soil-stream chemistry relationships and the relative importance of forest soil conditions to downstream water quality.

6.5.4 Remote Sensing and Maps from Fixed-Point Measurements (Tier 4)

Several coverages of spatially extensive data were developed for the region with existing or developing methodologies to address the N-saturation and Ca-depletion issue. Critical coverages that could be derived from interpolable fixed-point measurements and remote sensing imagery include

- Topography and hypsography
- Air temperature and precipitation maps
- Deposition rates of Ca, N, and other related constituents
- Forest species, species distribution and fragmentation (derived from Landsat imagery)
- Foliar C, N, and Ca, and forest NPP (derived from MODIS and AVIRIS imagery where available within the basin or from the FIA plot data)

The intensification of the FIA network within the DRB provided an unprecedented opportunity for large-scale validation of remote sensing tools, including MODIS for forest biomass and NPP, and Landsat-TM for characterizing patterns of forest fragmentation and land use. Indicators of Ca depletion and N saturation in forests from remote sensing data were in the development stage during the Delaware CEMRI.

New experimental methods for determining foliar N and Ca from remote sensing were concurrently being developed by researchers at the University of New Hampshire and the USFS research laboratory in Durham, New Hampshire. The methods being tested used AVIRIS imagery, which was available for the northern Catskill Mountain region of the DRB (Hallett et al. 2006). Maps of forest species derived from the USFS FIA plot data, and NPP from remote sensing interpretation were also developed for a thorough regional Ca-depletion monitoring program. Maps of deposition rates were generated through modeling of data from the several deposition monitoring stations in the DRB by researchers at Pennsylvania State University (James Lynch, 2003, written communication). This development of a linked deposition, aquatic forest, and soil chemistry database for the upper DRB should improve our ability to infer and model large-scale patterns of forest recovery from acid deposition.

These combined measurements provide the first regional database in the United States that integrates forest condition, soil condition, and associated surface water quality. Determining regions within the DRB where N saturation and associated Ca depletion are most acute will allow resource managers to plan forest harvest and development in those areas in ways that limit the further degradation of the ecosystem.

6.5.5 Modeling

Models that specifically address the extent of Ca depletion for a given region, or the likelihood of Ca depletion occurring in a specific watershed, were still in their development stages during the Delaware CEMRI and were further developed as part of the initiative. The PnET-II and PnET-BGC models are designed to determine the extent of, and potential for, development of N saturation and Ca depletion, respectively, for specific instrumented watersheds. The CEMRI provided a spatially and temporally integrated dataset that was used to develop and verify those models on a regional scale and to test the use of the models in support of a regional or national monitoring strategy.

6.6 Preliminary Results

Collaborative research between USGS and USFS research laboratories revealed important biogeochemical correlations among foliar chemistry, tree stress indicators, and both stream and soil Ca concentrations in the Neversink IMRA (Murdoch et al. 2003) (Fig. 6.4). A significant addition to our understanding of soil Ca's influence on forest condition, made possible through the CEMRI strategy, was concurrent mapping of forest condition, soil chemistry, and first-order stream chemistry for the northern half of the DRB (the area underlain by the Appalachian Plateau). These maps, when compared with regional nitrate deposition maps, indicate a common pattern of low soil Ca concentrations and low stream acid neutralizing capacity in the western Pocono Mountains and the eastern Catskill Mountains, the areas of the basin hardest hit by acidic deposition (Fig. 6.5). The CEMRI effort therefore created the first regional picture of soil Ca depletion and its relation to acidic deposition and stream acidification through integrating and augmenting existing USGS and USFS programs.

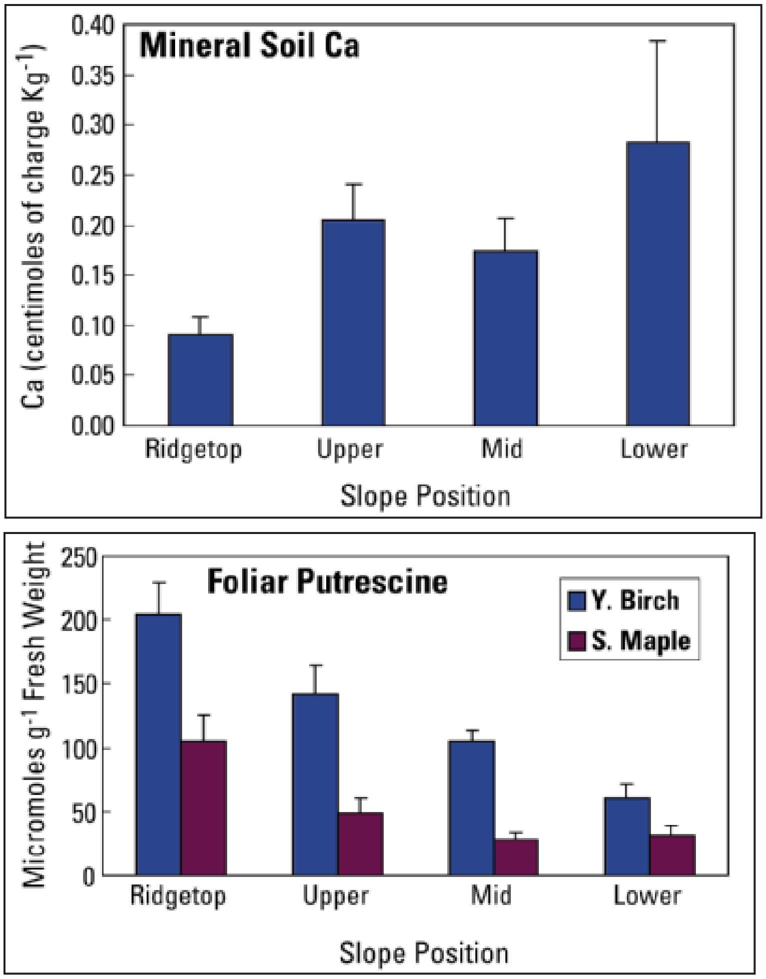


Figure 6.4.—Correlations among foliar chemistry, tree stress indicators, and both stream and soil calcium concentrations. Top: lower elevations have more available calcium (G. Lawrence, U.S. Geological Survey, written communication, 2003). Bottom: lower elevations have less foliar putrescine, an indicator of tree stress (R. Minocha, U.S. Forest Service, written communication, 2003).

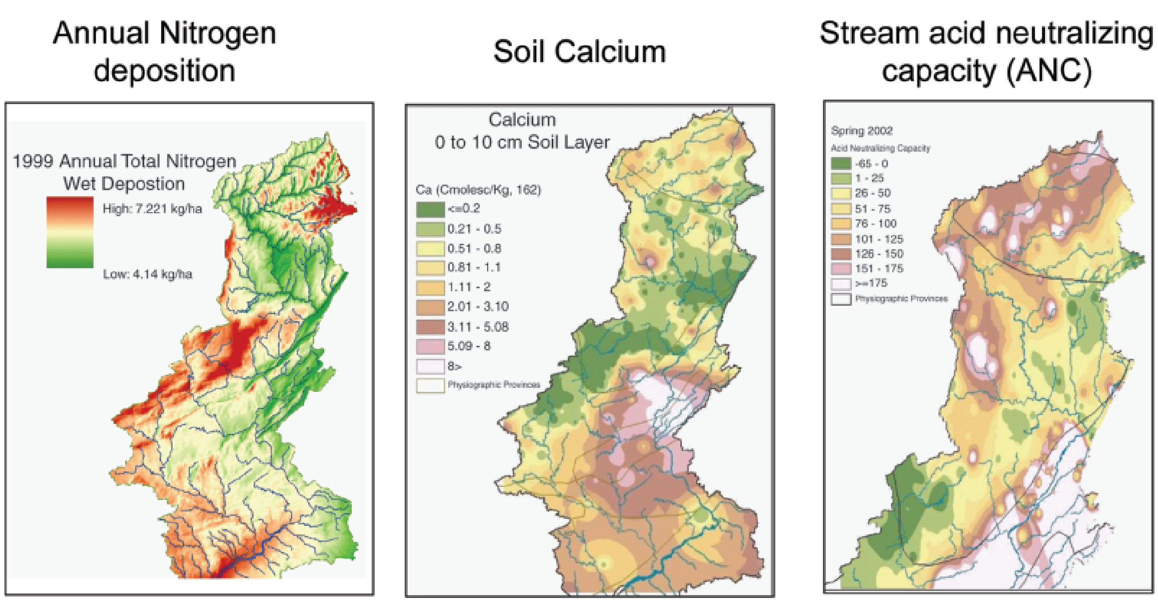


Figure 6.5.—Correlation between deposition, soil calcium, and stream chemistry.