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PD 98-1128　　　　　　07/10/02	**NSF PROPOSAL NUMBER**

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DEB - Ecosystem Studies

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(See GPG II.C For Definitions)　☐ FOR-PROFIT ORGANIZATION　☐ SMALL BUSINESS　☐ MINORITY BUSINESS　☐ WOMAN-OWNED BUSINESS

TITLE OF PROPOSED PROJECT　**Biotic Control of Calcium Supply: Distinguishing Sources to Regrowing Forests**

REQUESTED AMOUNT	PROPOSED DURATION (1-60 MONTHS)	REQUESTED STARTING DATE	SHOW RELATED PREPROPOSAL NO., IF APPLICABLE
$　602,071	36　months	01/01/03	

CHECK APPROPRIATE BOX(ES) IF THIS PROPOSAL INCLUDES ANY OF THE ITEMS LISTED BELOW

☐ BEGINNING INVESTIGATOR (GPG I.A)
☐ DISCLOSURE OF LOBBYING ACTIVITIES (GPG II.C)
☐ PROPRIETARY & PRIVILEGED INFORMATION (GPG I.B, II.C.6)
☐ HISTORIC PLACES (GPG II.C.9)
☐ SMALL GRANT FOR EXPLOR. RESEARCH (SGER) (GPG II.C.11)
☐ VERTEBRATE ANIMALS (GPG II.C.11) IACUC App. Date _____

☐ HUMAN SUBJECTS (GPG II.C.11)
Exemption Subsection _____ or IRB App. Date _____
☐ INTERNATIONAL COOPERATIVE ACTIVITIES: COUNTRY/COUNTRIES INVOLVED (GPG II.C.9)
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☐ HIGH RESOLUTION GRAPHICS/OTHER GRAPHICS WHERE EXACT COLOR REPRESENTATION IS REQUIRED FOR PROPER INTERPRETATION (GPG I.E.1)

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Biotic Control of Calcium Supply:

Distinguishing Sources to Regrowing Forests

The effects of forest age and succession have not been given sufficient emphasis in studies of environmental stress in forested ecosystems. In the case of Ca cycling, changes associated with stand age and species composition have confounded interpretation of the effects of acid rain on stream water, soils, and ecosystem sustainability. Calcium budgets indicate that young northern hardwood stands (<30 yrs old) transfer Ca from mineral soil into aboveground vegetation, forest floor, and drainage water, whereas older stands are in approximate steady state. This difference in Ca cycling between young and old stands has important implications for our understanding of the threat of Ca depletion from acid rain and forest harvest. Our objectives are to describe differences in Ca cycling with stand age, and to determine the source of Ca mobilized from mineral soil in young stands. To meet these objectives, we will test the following hypotheses:

1. Young stands are acquiring Ca from the mineral soil at a more rapid rate than are old stands.
2. There is a significant pool of Ca in forest soils that is associated with apatite or other non-silicate minerals, especially in deeper soil horizons.
3. Rates of (a) apatite or (b) silicate weathering in young forest stands are higher than in older stands.
4. Tree species differ in their ability to access soil Ca pools, and this difference explains the observed change in Ca status with forest succession.

We will use Sr isotopes and element ratios to identify the relative contributions of different soil Ca pools to forest vegetation as a function of species and stand age. Our experimental approach involves an extensive survey of 13 stands of different ages, in which we have already observed patterns in Ca accumulation, and an intensive study of replicate stands of three ages (15, 30, and 80 years) in a single site, all in the White Mountains of New Hampshire.

Understanding how stand age influences patterns of biogeochemical cycling is key to the development of sustainable forest harvesting and effective environmental policies. In addition to the intellectual impacts of the study, this project will provide long-term infrastructure for studies of succession and forest age in the northern hardwood forest. Finally, we will contribute to future research by training five undergraduate and three graduate students in an interdisciplinary collaboration of forest ecologists, geochemists, and soil scientists that allows us to take a new view of biotic influences on weathering processes.

History of this Proposal

Earlier versions of this proposal were submitted to NSF Ecosystems in December 2000 and January 2002. The most recent set of reviews included 3 excellents, 2 very goods, 1 good and 1 fair. The panel summary noted that "the proposal would significantly improve our understanding of Ca dynamics and effects of acid precipitation on sensitive Northeastern forests... It draws upon state-of-the-art tools and expertise in geochemistry to address an important ecological question."

The panel summary recommended "focusing on answering the central questions posed: Do younger trees have access to Ca sources that older trees do not?" In response we have dropped from the proposal the exploration of the mechanisms by which young stands acquire Ca, and achieved considerable cost savings. We focused the revised proposal on describing patterns of Ca cycling with stand age and species succession and the nature of the Ca source.

A few reviewers expressed uncertainty as to whether Sr isotopes and element ratios would be sufficient to distinguish the sources of Ca to biotic cycles. Since the last proposal was submitted, our latest results using this approach have been successful, and some of the results have been published in NATURE (Blum et al. 2002). We have also included more background in the proposal on the ubiquity of apatite inclusions in silicate rocks. The elucidation of non-silicate weathering supply of Ca may be the single most important potential contribution of the proposed work. The role of stand age in mobilizing this pool in particular has important implications for understanding the potential for repeated harvesting and acid rain to deplete soil available Ca and limit ecosystem productivity.

Introduction

There is growing concern that base cations are being depleted from forest soils in the northeastern United States as a result of acid rain (Baes and McLaughlin 1984, Shortle and Bondietti 1992, Likens et al. 1998). These losses from soil are likely to be compounded by timber harvesting and the associated loss of nutrients, with Ca the element most likely to become limiting (Federer et al. 1989). Recent studies have reported dramatic declines in pools of exchangeable base cations (Johnson et al. 1994, Knoepp and Swank 1994, Huntington et al. 2000). The loss of cations in general and Ca in particular over past decades is thought to have adversely affected forest productivity and health in eastern North America (Baes and McLaughlin 1984, Shortle and Bondietti 1992) and Europe (Ulrich et al. 1980, Graveland et al. 1994).

Environmental stresses such as acid rain may not be the only factors influencing changes in soil Ca over time. We suggest that forest age needs to be considered when interpreting Ca cycling patterns. Our Ca budgets indicate that young northern hardwood stands (<30 yrs old) transfer Ca from mineral soil into aboveground vegetation, forest floor, and drainage water, whereas older stands are in approximate steady state. This suggests that young stands tap a pool of soil Ca that is not as available to older stands. Identification of this pool is essential to predicting the consequences of acid rain and forest management on ecosystem productivity. Our proposed research will explore the effect of forest age on Ca cycling in the northern hardwood forest. Our objectives are to describe differences in Ca cycling in stands of different ages, and to determine the sources of Ca mobilized from mineral soil as a function of stand age.

Calcium limitation and aging forests

It can be difficult to distinguish the effects of environmental stress, such as acid rain, from other changes in forested ecosystems (Arthur and Yanai 2000). The hardwood forests of the northeastern US are primarily second growth forests, largely originating from post-Civil War abandonment of agricultural land and logging in the late 1880's and early 1900's (Whitney 1994). Because large portions of the landscape are vegetated by forests of a similar age, we might observe

synchronous changes in biogeochemical cycling, and attribute them solely to environmental stresses such as air pollution. For example, the change in stream-water export of Ca observed over time at HBEF has been thought to result from the changing base status of the soils resulting from the addition of strong acid anions through acid rain (Likens et al. 1996). However, the Ca export of young stands compared to old stands shows the lasting influence of disturbance on Ca export in stream water (Figure 1) and the relationship of base-cation exports to strong acid anion concentrations in stream water (data not shown). Except for the first few years, when disturbance causes high nitrate export, this elevated Ca export is not balanced by strong acid anions, contrary to predictions based on acid rain as the key determinant of patterns of cation loss (Likens et al. 1996).

The water draining regrowing forests at HBEF is enriched in base cations compared to the undisturbed watershed, even though both systems have been exposed to acid rain for decades and the regrowing watershed has much higher vegetative demand for base cations. To better understand the potential for ecosystems to become Ca limited (Federer et al 1989), more thorough investigation of age-related changes in Ca cycling is required.
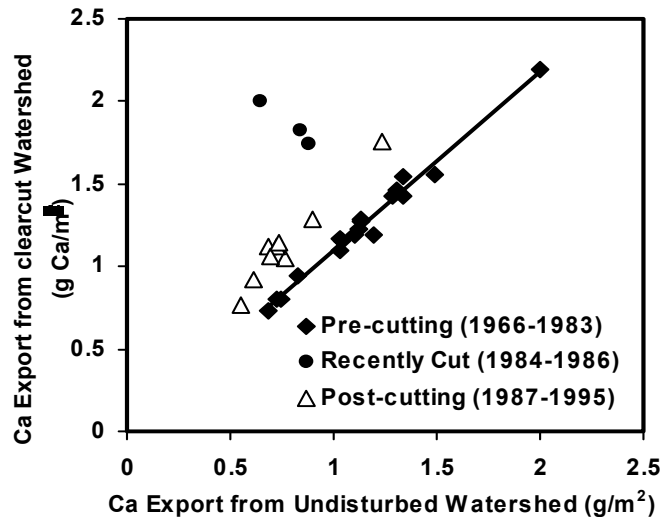

Figure 1. Stream water exports of Ca from a disturbed and undisturbed watershed at the Hubbard Brook Experimental Forest were linearly related until the disturbed watershed was whole-tree harvested in the winter of 1983-1984. Exports of Ca remain high in the clearcut watershed to this day, 18 years later (G.E. Likens, unpublished data).
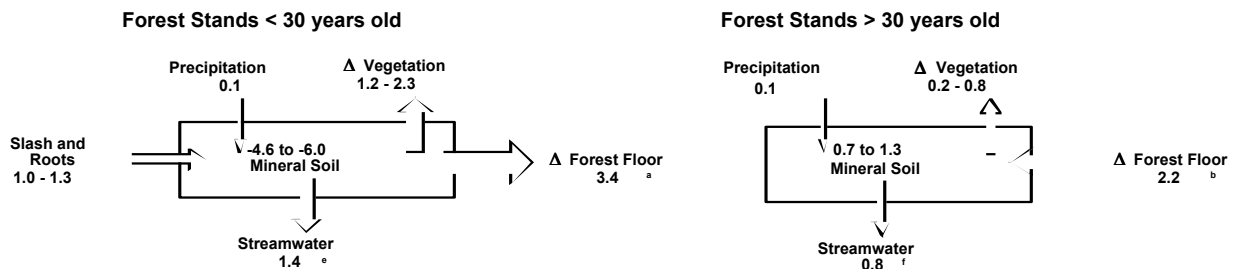
The importance of stand age

Although acid rain has been identified as an important potential cause of Ca loss from soil over time, our studies show that forest age is likely to be at least equally important in explaining observed differences in Ca availability.

Repeated sampling of stands of different ages in the White Mountains of New Hampshire produced a mass balance model of Ca flux showing that young forests, or early successional species, mobilize Ca from the mineral soil (Hamburg et al. 2002). In stands < 30 years old, the large accumulation of Ca in the forest floor (3.4 g Ca m^{-2} y^{-1}) and in vegetation (1.2-2.3 Ca m^{-2} y^{-1}) over the first 30 years of forest regrowth following harvesting exceeds the inputs of Ca from slash and precipitation (Figure 2). This accumulation as well as the greater loss of Ca in stream water (Figure 1) over this same period of time is possible only if the mineral soil is a large net source of Ca (4.6 to 6.0 g Ca m^{-2} y^{-1}) to the ecosystem.

Figure 2. Budgeted net flux of calcium into and out of the mineral soil (g/m2/yr). Calcium fluxes in vegetation of young stands are from data from the late 1960's and 1988-1994; data from the old forests are from the periods 1964-1969 and 1987–1992; precipitation data are from 1980-1992; stream-water data are from 1984-1992; forests floor data are from 1979-1994 to 1980-1995 (Yanai et al. 1999). Data on stream water, precipitation and vegetation dynamics are from the the Hubbard Brook Experimental Forest.

Despite the accumulation of Ca in the forest floor (Figure 3a) and in living biomass, young forests still mobilize enough Ca to elevate concentrations of exchangeable Ca in soils (Johnson et al. 1997). Litterfall Ca concentrations are higher in young stands (Figure 3b), as are changes in the abundance of snails (Figure 3c), which are sensitive to Ca availability (Wareborn 1992, Graveland et al. 1994, Hotopp 2002). This enhanced Ca cycling continues for three decades after disturbance, much longer than the two or three years of enhanced nitrification (Fisk and Fahey 1990) that could stimulate cation release from exchange sites.

These observations suggest that effects associated with forest age or succession may contribute to the declining soil and stream-water Ca concentrations observed in maturing second-growth forests. The effect of forest age on nutrient cycling is likely to be particularly important in regions where historic patterns of forest management have resulted in large proportions of the landscape undergoing a synchronous transition from young to old forest, such as the northeastern United States.

In northern hardwoods regenerating after clearcutting, several biotic changes take place that could influence the mobilization of Ca from mineral soil and the changes in Ca cycling we observed (Figures 1-3). Tree species composition changes dramatically, with pin cherry dominating early, then
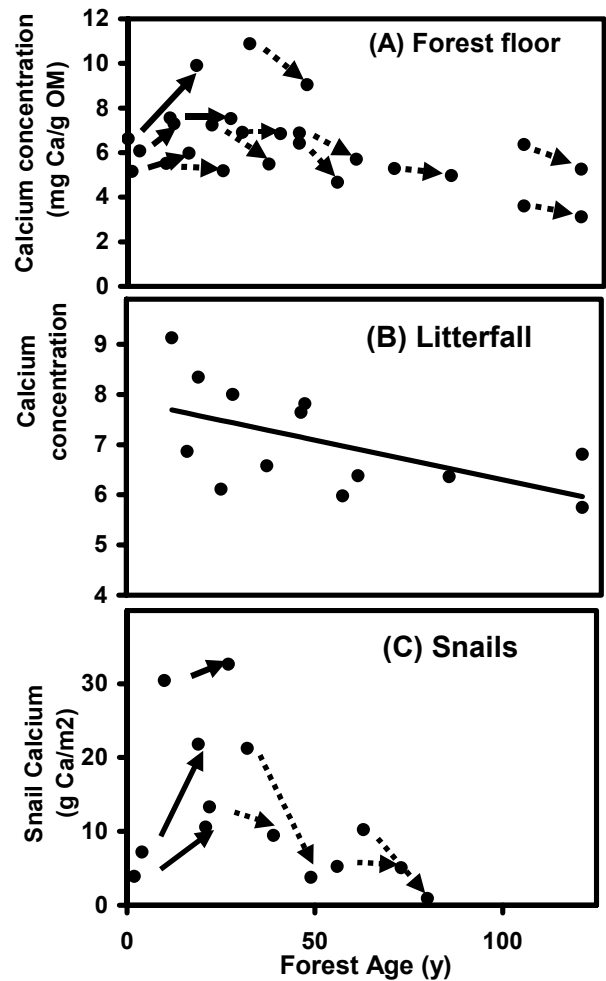

Figure 3 (a) Changes in concentrations of Ca in the forest floor of thirteen northern hardwood stands from across the White Mountains measured in 1979 or 1980 and again in 1994 or 1995 (Yanai et al. 1999). (b) Concentrations of Ca in leaf litter in the same thirteen stands sampled for forest floor changes, measured for three years from 1994-96. (c) Changes in calcium content of snails in seven northern hardwood stands from across the White Mountains, NH, measured in 1980 and again at the same sites in 1996-98. Arrows connect data from a single stand at two points in time; solid lines represent

declining after 30 to 40 years (Marks 1974, Fahey et al. 1998). Pin cherry has high tissue Ca compared with other northern hardwood, species (Likens and Bormann 1970); hence this species may have mechanisms of Ca acquisition that are absent in other species. Independent of changes in species composition, rapid tree growth and canopy closure cause a transient high demand for soil resources early in succession (Fahey et al. 1998), which is likely reflected in root distribution and function. An early successional peak in belowground allocation might be expected in response to high nutrient limitation and could influence Ca mobilization in several ways. Higher root biomass and activity could mineralize Ca from readily weatherable pools. Higher allocation to nutrient acquisition via mycorrhizal associations also would be expected. Patterns of mycorrhizal infection over time in succession could include more abundant infection, changes in vertical distributions of infection, and changes in fungal species composition. Other factors, such as the changing character of root exudates or soil organic matter, may be important to the release of organically bound Ca as well as mineral weathering rates. Transpiration moves solutes to root surfaces and therefore has a positive effect on nutrient uptake (Williams and Yanai 1996); transpiration rates are thought to decrease as a forest gets taller (Ryan and Yoder 1997).

Testing the full range of these possible mechanisms is beyond the scope of a single proposal, but we will seek additional funding, and encourage proposals by others, to coordinate with the proposed studies.

The importance of a non-silicate pool of weatherable Ca

The plant-available pool of soil Ca has commonly been equated with the salt-exchangeable fraction (1 M NH_4Cl), and the non-exchangeable pool has been assumed to be dominated by slowly-weathered silicate minerals. However, our experiments suggest that soil Ca pools need to be characterized in greater detail. To assess the validity of previous assumptions regarding the non-exchangeable pool, we have examined soils from 65-90 year-old northern hardwood forests (on WS-1 and WS-5 of the Hubbard Brook Experimental Forest) using sequential extractions and digestions of the soil (Blum et al, 2002; Hamburg et al, 2002). The salt-exchange removed small amounts of Ca (Figure 4), as well as Na , Mg and K, as expected. However, when this treatment was followed by a cold acid leach, (1 M HNO_3), a relatively large pool of Ca (65 g Ca/m^2 in E and B horizons and 6 g Ca/m^2 per cm of depth in the C horizon) was removed, which was at first surprising to us. The major Ca-bearing minerals present in the soil parent material are plagioclase, K-feldspar, hornblende, pyroxene and apatite ($Ca_5(PO_4)_3OH$). To identify the Ca source in this acid leach we examined the molar ratios of P/Ca versus Na/Ca in C-horizon sequential digestions in comparison with the average composition of the major Ca-bearing minerals (Figure 5). We conclude that the cold acid leach dissolved mainly apatite, consistent with the >10^3 faster dissolution rate of apatite compared to hornblende, plagioclase and K-feldspar. A hot 1 M HNO_3 digest following the cold acid leach dissolved mainly hornblende and pyroxene (Figure 5) and an HF total digest dissolved mainly plagioclase and K-feldspar. Application of this sequential extraction procedure to the C-horizon
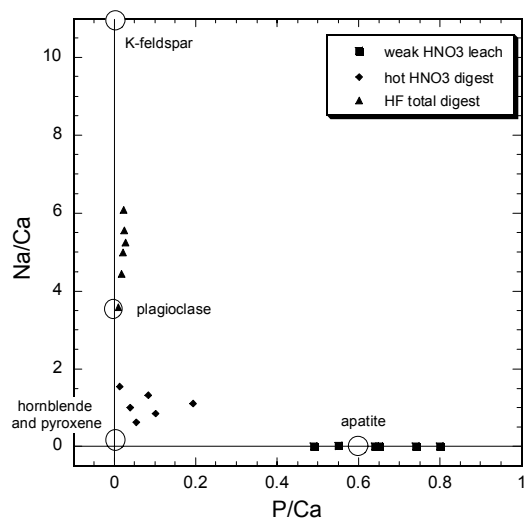
Figure 5. Major element ratios of digests of six composite C-horizon soil samples and soil minerals.
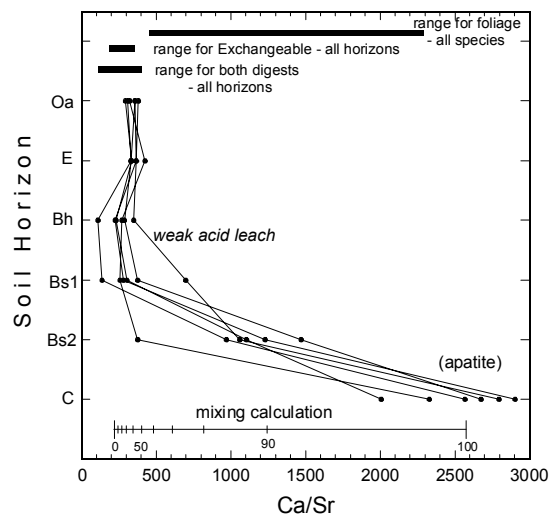
Figure 6. Ca/Sr ratios of the Digest-1 for each soil horizon. The bars at the top of the diagram show the total range of Ca/Sr ratios for all foliage, and the Exchangeable, Digest-1, Digest-2, and Digest-3 for all horizons. The line at the bottom of the diagram shows the results of mixing calculation between the Bs1 horizon Exchangeable and the average C horizon Digest-1 (i.e., apatite) with tick marks for each 10% addition of Ca from apatite.

material reveals that about 12% of the Ca in the soil parent material occurs in apatite, another 12% is in hornblende and pyroxene, and 76% is in feldspars. The contrast in Ca/Sr ratio between the cold acid leach and the more aggressive digestions is due to differences in Sr substitution for Ca in silicate versus phosphate minerals—which provides a tracer of apatite-derived Ca. The Ca/Sr ratio of the cold acid leach for each soil horizon suggests that apatite was depleted from the Oa, E, Bh and Bs1 horizons, but is present in the Bs2 and C horizons (Figure 6). A Ca/Sr mixing calculation shows that about 86% of the Ca released from the Bs2 horizon soils by the acid leach is derived from apatite, based on the C horizon cold acid leach as an end member for apatite (Figure 6). Apatite was observed to be ubiquitous as small inclusions in the silicate minerals of the soil parent material, as revealed by cathodoluminescence imaging and optical microscopy of soil and stream sediment thin sections.

These studies have for the first time identified apatite as an important calcium source in base-poor New England forest ecosystems (Blum et al, 2002; Hamburg et al, 2002). The importance and fate of apatite in soils has been studied widely, however, because apatite is the only significant primary mineral source of phosphorus in rock and soil parent material. Virtually all igneous, metamorphic and sedimentary rocks contain phosphorus in concentrations of 0.1 to 1 wt %, and this phosphorus is held primarily in apatite (Deer et al., 1992). Soil chronosequence studies (Walker and Syers, 1976; Gardner, 1990; Crews et al., 1995; Schlesinger et al., 1998) and studies of lake sediments (Filippelli and Souch, 1999) have used sequential leaching of soils and sediments to show that primary (ie, 1 M cold acid-leachable) apatite dominates the P pool in very young soils and is depleted from surface horizons over thousands of years of soil development. Thus we are confident that our observations concerning apatite weathering made at Hubbard Brook (HBEF) will be equally relevant to the broader geographic study area outlined in this proposal, which is underlain by granitic and high grade metamorphic rocks similar to those at Hubbard Brook. In fact, we argue that our investigations of apatite weathering will find broad application to young soils developed on virtually all soil parent materials. Aubert et al. (2001) recently demonstrated that most of the Sr (and Ca) in the streamwaters of the Strengbach catchment in France, which has similar bedrock and soil parent material, is derived from apatite dissolution.

Several recent studies of European soils developed on granitic parent materials have demonstrated that apatite inclusions in silicate minerals, such as those we observed in New England soils, are selectively dissolved by low molecular weight organic acids exuded by mycorrhizal hyphae (Van Breemen et al, 2000; Wallander, 2000). We suggest that roots and associated rhizosphere organisms may access the non-silicate mineral reservoir of Ca revealed by the cold acid extraction, and that this pool may be preferentially accessed by early successional forests. We will test whether young and old forests differ in their use of silicate minerals as well as non-silicates, although we believe silicate weathering to be very slow.

Distinguishing among sources of Ca to forests

We pose two alternate hypotheses for the source of the Ca mobilized by young forest stands. First, young stands may accelerate the weathering of minerals, either the silicate minerals that dominate the parent material, or the non-silicate apatite pool we identified using acid leaching. If this is the case, repeated forest harvesting should not be expected to cause rapid depletion of plant-available Ca in young soils with abundant Ca-bearing minerals, even if exposed to current levels of acid precipitation. Alternatively, if the supply of Ca from weathering is not biologically controlled but instead remains constant, the Ca mobilized by young stands must come from the depletion of already weathered Ca pools in the mineral soil, such as the exchangeable or organically bound pool. If the amount of Ca that can be mobilized by young stands is limited by the size of these much smaller pools, then the frequency of disturbance and the amount of Ca lost from the ecosystem as

a result of acid precipitation will control the amount of Ca available for regrowth. The similar biogeochemical behavior of Ca and Sr (Graustein, 1989; Blum et al, 2000), yet contrasting crystal-chemical behavior (e.g., Jacobson and Blum, 2000) provides a tracer that can help distinguish between the sources of increased Ca supply from mineral soils in young stands. The ratio of $^{87}Sr/^{86}Sr$ can be used to separate the Sr (and Ca) derived from mineral weathering from that deposited from the atmosphere (Åberg 1995, Bailey et al. 1996, Clow et al. 1997, Miller et al. 1993; Vitousek et al., 1999). The Ca/Sr ratio can be used to separate the Ca derived from the weathering of more weathering-resistant Ca-bearing silicate minerals from less resistant apatite. By measuring both the $^{87}Sr/^{86}Sr$ and Ca/Sr ratio in the various soil and vegetation pools, we will be able to distinguish differences between stands in the relative proportion of Sr and Ca supplied from various mineral weathering sources versus remobilization

Figure 7. The combined use of 87Sr/86Sr and Ca/Sr ratios will allow us to differentiate between the three potential sources of Ca (silicate weathering, non-silicate weathering, and atmospheric deposition) to biotic pools and cycling soil pools.

from soil exchange pools and organic matter, as we have demonstrated at Hubbard Brook (Blum et al., 2002; Figure 7). Because strontium isotope ratios cannot be fractionated at all by plant uptake (e.g., Blum et al., 2000; Dambrine et al. 1997) and Ca/Sr ratios are probably changed by less than a factor of 1.4 during plant uptake (Blum et al., 2002), they largely reflect the value of the plant nutrient source and have been used to determine the source of Ca within the soil that is taken up by plants. Mixtures between end member compositions fall along straight lines on plots such as Figure 7, and the proportional source of Ca for any point that falls within the triangle defined by the end members can be easily calculated.

To identify the sources of Ca in various ecosystem pools at Hubbard Brook, we defined the Ca/Sr and $^{87}Sr/^{86}Sr$ ratios of three ecosystem endmembers. For the apatite weathering endmember, we used the average of the C horizon cold 1 M HNO_3 leach fractions. For the silicate weathering endmember we used the average value of the soil C horizon hot 1 M HNO_3 digest, because it is the most readily weathered soil silicate fraction. The atmospheric deposition endmember at Hubbard Brook has been measured directly (Bailey et al., 1996). The exchangeable fractions of soil Oa and Bs1 horizons had Ca/Sr similar to atmospheric and silicate values, but $^{87}Sr/^{86}Sr$ close to apatite values and intermediate between atmospheric and silicate values (Figure 7). Thus the soil cation exchange pool is dominated by a mixture of Ca and Sr from silicate weathering and atmospheric deposition.

In contrast to the soil cation exchange pool, foliage samples collected in the vicinity of the soil samples plot along a line connecting the soil cation exchange pool and apatite, with different species occupying distinct fields (Figure 7). The Ca/Sr ratios were relatively low for sugar maple, intermediate for yellow birch and American beech, and high for balsam fir and red spruce. In contrast, foliar $^{87}Sr/^{86}Sr$ was nearly identical for all tree species and consistent with both the soil cation exchange pool and apatite weathering values (Figure 7). Wood ferns, which are shallowly rooted and reflect forest floor values, had Ca/Sr ratios in the same range as maple and birch foliage. Analyses of bolewood for each species reflected the same trends in Ca/Sr shown for foliage (Blum et al, unpublished data). Throughfall from the dominantly spruce/fir areas of the mixed conifer-hardwood canopy is a mixture of atmospheric deposition and spruce/fir foliage, whereas throughfall from the dominantly hardwood areas shows a stronger hardwood foliage influence. The range of soil and stream water Ca/Sr and $^{87}Sr/^{86}Sr$ are also shown for comparison and allow calculation of exports of Ca originating from each identified Ca pool (Figure 7).
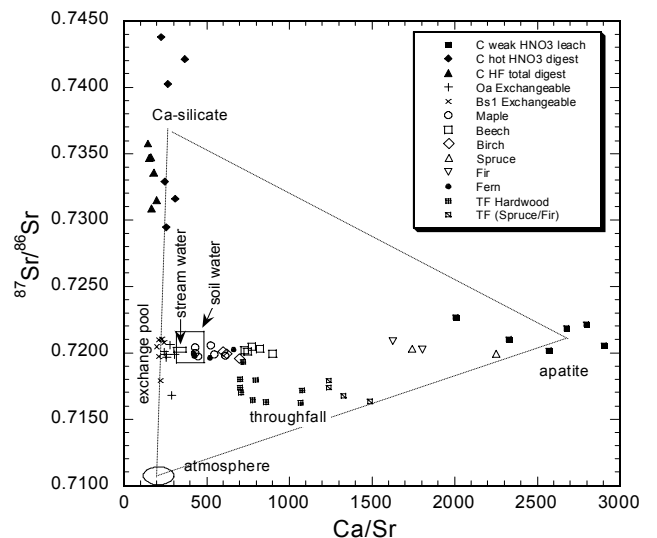
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The analysis of Sr isotopes in tree rings provides a record of changes in the source of Sr during the lifetime of a tree (Aberg et al., 1990; Aberg, 1995). We have demonstrated that for many species of trees, mobile Ca and Sr can be removed from the wood by leaching in a very dilute acid solution (pH 4), leaving behind a more robust signal of Ca/Sr and $^{87}Sr/^{86}Sr$ obtained during the growth year (Blum et al., unpublished data). Some chemical changes observed in tree rings have been associated with environmental change. For example, $^{87}Sr/^{86}Sr$ measurements of trees from three locations in the northeastern US showed significantly greater atmospheric contributions of Sr in tree rings laid down after about 1930-1940 (Blum et al., unpublished data). This is consistent with the pattern of increased deposition of Ca and Sr from anthropogenic sources such as fly ash, road dust, and cement production in the 1930s and 1940s (Miller et al., 1993; Likens et al., 1996). This relatively recent addition of atmospheric Sr is important to our study, because it has labeled the vegetation and the actively cycling soil pools with a $^{87}Sr/^{86}Sr$ signature against which the contribution from mineral weathering can be quantified. The change in $^{87}Sr/^{86}Sr$ we observed in tree rings could also be due in part to enhanced weathering of apatite or deeper rooting in young stands. Our experimental design will allow us to distinguish the biotic from the anthropogenic effects because we can sample wood laid down at the same historical time by trees of different ages.

Objectives

Our overall objectives are to describe differences in Ca cycling with stand age, and to determine the source of Ca mobilized from mineral soil in young stands. We will test our hypotheses using two experimental approaches: an extensive one involving 13 stands that we have previously studied (Extensive), and an intensive one using replicate stands of three ages at a single site (Intensive).

Hypotheses

1. Stand Age

Hypothesis 1: **Young stands are acquiring Ca from the mineral soil at a more rapid rate than are old stands.**
Corollary: As stands age, Ca status of soils and stream water tend to decline, and these changes confound the interpretation of the effects of acid rain in systems observed over time.

This hypothesis is based on budgets (Figure 2) that were estimated from a variety of sources (Figure 3) but have not been tested using data from a single set of sites. The proposed Intensive Approach (described below) at the Bartlett Experimental Forest allows us to better test this hypothesis by constructing Ca budgets in three replicate stands of each of three ages (15 yr, 30 yr, and >80 yr). We will estimate the accumulation rate of Ca in vegetation and the forest floor, and measure Ca fluxes in leaching via lysimetry.

Alternate Hypothesis: **The association between Ca cycling and stand age in our previous chronosequence work is spurious, caused by a coincidence between recent harvesting and inherent soil fertility.**

If the differences we have observed between stands are caused by differences in parent material, rather than stand age, we would predict the differences in Ca status to be stable over time. In contrast, if young stands improve their Ca status over time, while older stands undergo Ca depletion, we predict age-related changes in the stands over time. We can test these alternate hypotheses because we have archived samples of litter collected in our chronosequence stands in

1994, 1995 and 1996, and we can repeat the collection of samples in 2003-2004. The test should be sensitive to small changes, because we distinguish litter by species as well as by stand age. Most importantly, the repeated sampling of a chronosequence controls for variation between sites not related to their age.

If the alternate hypothesis is true, mapping the patterns in parent material that are responsible for differences in Ca status between sites will be essential to predicting susceptibility of stands to Ca depletion and designing sustainable management practices.

2. Soil Sources

*Hypothesis 2***: There is a significant pool of Ca in forest soils that is associated with apatite or other non-silicate minerals, especially in deeper soil horizons.**
Corollary: Weathering rates calculated based on the assumption of stoichometry with Na in silicate minerals may underestimate the rate of mineral weathering in northern hardwood forest soils.

*Alternate Hypothesis***: The non-silicate pool that we have seen in preliminary studies at Hubbard Brook is not common to the region.**
Corollary: Mapping the presence of this pool in the broader region will be essential to predicting forest sensitivity to Ca depletion.
Corollary: Observations about Ca cycling, forest management, and acid rain should not be extrapolated from Hubbard Brook to the northern hardwood forest in general.

We will test for the presence and magnitude of a non-silicate pool of weatherable Ca with depth using elemental and isotopic analysis of sequential soil extractions and microscopic imaging of soil thin sections in thirteen sites (Extensive Approach) distributed across the White Mountain National Forest (WMNF). We expect to demonstrate that our preliminary results showing the importance of this pool are not restricted to Hubbard Brook but are widespread in the region. Testing for the presence of this pool at the Bartlett Experimental Forest is also an important preliminary step in selecting sites for the Intensive study design.

3. Sources by Stand Age

*Hypothesis 3***: Rates of (a) apatite or (b) silicate weathering in young forest stands are higher than in older stands.**
Corollary: Contrary to predictions based on the exchangeable Ca pools, neither timber harvesting nor acid precipitation is likely to result in Ca deficiency in the northern hardwood forest in the near future.

*Alternate Hypothesis***: Young stands mobilize Ca from already weathered (exchangeable and/or organic) soil pools.**
Corollary: Forest harvest in combination with acid precipitation will induce Ca limitation within the next rotation as has been predicted (Likens et al. 1998).

Based on our observation that Ca mobilization is higher in young stands than in old stands (Figure 2, Hypothesis 1), we expect to find the highest Ca weathering rates in young stands. This hypothesis will be tested by comparing the $^{87}Sr/^{86}Sr$ and Ca/Sr of vegetation to weathering and atmospheric end members (Figure 7), and to cycling soil pools. We can test this hypothesis widely across the region (Extensive Approach, using 13 stands of various ages) and in a tightly controlled site of replicated stands with little variation in parent material (Intensive Approach). We will also

test whether ratios change over time as stands age, by comparing contemporary samples of leaf litter with archived samples from the Extensive stands.

4. Change by Age or Species

Hypothesis 4: **Species differ in their ability to access different Ca pools, as evidenced by different Ca/Sr and $^{87}Sr/^{86}Sr$ ratios.**

Alternate hypothesis: **Trees of the same species change in their dependence on different Ca pools as they age.**

We will test these hypotheses by analyzing samples of litter as a function of species and stand age, using the 13 Extensive study sites. We will compare the $^{87}Sr/^{86}Sr$ and Ca/Sr of fresh leaf litter to weathering and atmospheric end members (Figure 7), and to cycling soil pools. Analyses of tree ring chemistry will reveal changes as a tree ages in the sources of Ca obtained by different species.

Methods

Experimental Design and Study sites

Extensive: Chronosequence of 13 stands widely distributed across the WMNF.
The extensive approach will allow us to test the presence and magnitude of a previously unrecognized pool of Ca (Figures 4 and 5) in a variety of sites, whereas our preliminary studies have focused on the Hubbard Brook Experimental Forest. We will use thirteen stands of varying ages, all located in the central White Mountains of New Hampshire (Table 1). One is at Hubbard Brook, in a different part of the forest (W101) from our preliminary studies (W1 and W5). Six are at the Bartlett Experimental Forest, 40 km distant. The other six are scattered across the WMNF. This 60-km geographic coverage is sufficient to demonstrate that the importance of the non-silicate Ca pool is not a peculiarity of Hubbard Brook.
There is a second reason for us to use these specific stands for our test of the regional significance of the non-silicate Ca pool. They represent a chronosequence of time since logging, and have been used to test for patterns of forest floor and vegetation development after forest harvest (Federer 1984). They were resampled after an interval of 15 years (Yanai et al. 1999, 2000), which allowed us to describe greater rates of Ca accumulation in the forest floor and higher concentrations of Ca in litter in young than in old stands (Figure 6). It is important to rule out the possibility that this association between Ca cycling and stand age is a spurious result, occasioned by a coincidence between recent harvesting and greater importance of this non-silicate Ca pool. If the pattern turns out to be due to variations in soil parent material rather than stand age, we will revise Objective 2 to contrast sites with and without this available Ca pool, rather than stratify our study by stand age. The importance of predicting the likelihood of Ca depletion and the need to develop guidelines for sustainable forest management will not be diminished by such a result, but would refocus our attention on the spatial distribution of the apatite pool as that influences forest productivity. We believe this result unlikely because the sites were carefully selected when the chronosequnce was established with respect to soil series, drainage characteristics and bedrock geology. If there is a systematic bias it would challenge a large body of research dependent on similar approaches to establishing comparable sites.

Intensive: Replicate stands of three ages at a single study site

The proposed intensive study sites are located in the Bartlett Experimental Forest in Bartlett, New Hampshire. The area is situated in a large expanse of granitoid bedrock of the White Mountains Plutonic Suite. The geology of this area is ideal for studies that involve characterization of mineral weathering in base poor soils, because with such a large area of granite bedrock, the glacial till cover (derived from bedrock "upstream" in the former icesheet) has a simple mineralogy and a chemical composition similar to the bedrock. In addition, the high potassium (and rubidium) content and antiquity of these granitoid rocks results in high $^{87}Sr/^{86}Sr$ ratios for weathering-derived cations, in sharp contrast to $^{87}Sr/^{86}Sr$ ratios in atmospheric deposition, which are dominated by a marine aerosol influence in New England. To assure the suitability of the area for using the strontium isotope method, we performed Sr isotope analyses on total digests of C-horizon soils from three soil pits separated by about 1.5 km in the proposed study site. The average $^{87}Sr/^{86}Sr$ ratio was 0.7301 (close to the average value of 0.7339 measured by us at the Hubbard Brook Experimental Forest), and is in sharp contrast to the atmospheric value of 0.7100. The difference between the rock-derived and atmospheric values is over 1000 times greater than the precision with which we can routinely measure the $^{87}Sr/^{86}Sr$ ratio of soils and vegetation (+/-0. 000015).

We will study nine stands, three replicate stands in each age class: 10-15, 30-35, and 80-100 yrs. All of the stands in the study have similar soils (coarse loamy, mixed, frigid, Typic Haplorthods), derived from relatively shallow basal tills (70 cm to C horizon with intermittent hardpan), elevation (300-550 m) and topographic position (midslope, generally north facing). Each stand will be approximately 1 ha in size. To test the suitability of these stands for using the Sr isotope technique, we measured the $^{87}Sr/^{86}Sr$ ratio of composite foliage samples from a 15-year-old, a 33-year-old, and a >80-year-old stand. The results were $^{87}Sr/^{86}Sr$ of 0.7143, 0.7151, and 0.7164 respectively. Thus the values are intermediate between the soil parent material and atmospheric inputs. The increase in $^{87}Sr/^{86}Sr$ with increasing stand age is intriguing and will be further investigated, but a conclusion as to whether there is an age effect cannot be made with these limited data.

If young stands obtain Ca from the exchangeable pool, which is small relative to vegetative demand, we will detect depletion in young stands compared to older stands, especially after 30 years of rapid growth. Our alternate hypothesis is that Ca is obtained from a non-silicate pool that can be leached with cold acid (described above). The magnitude of this pool, like the silicate pool, is too large to detect differences in size with stand age, but the Sr isotope and element ratios of these pools are quite distinct (Figures 5-7). We will determine the isotopic and elemental composition of vegetation to calculate the fraction of plant Ca obtained from three end members: silicate weathering, non-silicate weathering, and atmospheric deposition.

Measurements

Ca in vegetation (Intensive only). We will inventory basal area and species composition in each of the nine stands (3 ages x 3 sites) in summer 2004. We will lay out 10 20x20 m plots in each stand, leaving a minimum of 10 m buffer around the edges of the stand, and marking the grid corners with stakes. We will measure all the trees greater than 10-cm dbh in all plots. Trees 2-10 cm dbh will be measured in the NE 10x10m quadrant of each 20x20m subplot. Stems <2 cm dbh will be measured in a 1x1 m corner at the SW of each NE quadrant of each subplot. GPS coordinates will be recorded for all plots.

Tree biomass, by component part, will be estimated for all trees in each of the 9 stands using the allometric equations developed in the White Mountains for the northern hardwood species (Whittaker et al. 1974, Siccama et al. 1994, Arthur et al. 2001). We will collect samples of leaves, wood, bark, branches and large roots for all of the dominant species (3-5 depending on stand age) at

each site. The Ca content of the biomass on each plot will be estimated by multiplying the mass of each tree component times the nutrient concentrations from material collected at each stand. Litter material for chemistry will be collected from tarps during rain-free periods. We will collect leaf material using a shotgun or pole pruner (depending on the size of the tree) from 20 trees representing the range of tree diameters on the 16 plots and in numbers proportional to the diameter frequency of each species in the stand. Branch and wood plus bark will be collected from trees <5 cm dbh in the 15 and 30 year old stands using standard allometric sampling techniques (Hamburg et al. 1997) to sub-sample the material for nutrient analyses. Material will be broken into smaller pieces using a clean chisel and then ground in a #4 Wiley mill. Root samples will be obtained during the collection of soil, described below. Vegetation samples will be analyzed for $^{87}Sr/^{86}Sr$, Ca/Sr and major elements (see Analytical Methods below for details).

At each of the nine stands, wood cores will be taken at breast height from 20 trees of a species composition and diameter proportional to their importance in the stand. Individual annual growth increments will be sampled from tree rings at five-year intervals from individual cores. Previous studies (Aberg et al., 1990; Blum et al., unpublished data) indicate that tree rings preserve annual variation in the assimilation of Ca/Sr and $^{87}Sr/^{86}Sr$. The canopy foliage samples will indicate the Ca/Sr and $^{87}Sr/^{86}Sr$ taken up in the year of collection.

Ca leaching from the rooting zone (Intensive only). Soil solutions will be collected at two soil depths (just below the forest floor and near the bottom of the B horizon) using ceramic cup lysimeters made by Soilmoisture Equipment Corp. (www.soilmoisture.com). The lysimeters consist of a PVC tube with a ceramic cup at the base. Lysimeters will be installed in fall 2003, to allow for equilibration before monitoring begins in 2004. They will be installed by coring a hole with a soil auger. A slurry of silica flour and water in the hole will ensure good contact with the soil when the tubes are installed.

Samples will be collected biweekly during the growing season, and approximately monthly during the dormant season. A hand pump with a pressure gauge will be used to apply low tension (0.05 MPa). A stopper assembly with a pinch clamp allows samples to be collected from the bottom of the tube after 24 hours of suction.

Ca in soils (Extensive and Intensive). Soil samples will be collected using the quantitative pit method (Hamburg 1984, Johnson et al. 1997), which will allow us to reduce the variance in our estimates of soil Ca pools. Three 0.5 m^2 pits will be dug within each plot. Soils will be excavated quantitatively (precise measurements of pit volumes are made) such that the weight and volume of soil, roots, and rocks can be measured directly. The soils will be sampled to the C horizon using five strata: O horizon, 0-10 cm, 10-20 cm, 20+ cm, and the C horizon. In the field, soils will be sieved using 0.6 mm screening and all roots not passing the screen collected, as well as all rocks weighed and sub-sampled for later mineralogical analysis. A subsample of the sieved rocks will be returned to the lab to determine the amount of soil and absorbed nutrients retained on the surface of the rocks. The sieved soils will be weighed, thoroughly mixed and sub-samples collected, dried and returned to the lab for chemical and root content determinations. These soil samples will be subjected to a series of extractions for Ca availability, Ca/Sr, and Sr isotopic composition, as described below.

Ca in leaf litter (Extensive and Intensive). We will collect litter material for chemistry from tarps during rain-free periods in the fall of 2003 and sort by species. This is the same method used in 1995 -1997 in the chronosequence stands (Extensive), which will allow us to test for change over time in foliar chemistry as stands age (Hypothesis 4).

Laboratory

Tissue analysis – Samples of litter, ground tree cores, and roots (0.4 to 1 g dry weight) will be digested in concentrated nitric acid using high pressure microwave digestion (at 200°C) and then diluted to a 10% nitric acid solution for analysis using ICP-OES.

Sequential extractions of soil Ca pools – We will analyze four operationally defined soil base-cation pools. There is no perfect solution to separating various soil cation pools, but through experimentation with soils from the Hubbard Brook Experimental Forest we have arrived at a preferred method. Each pool is extracted in sequence from a 5 gram soil sample, and the solid residue is separated from the solution by centrifugation after each of four steps. (1) First the soil is exchanged overnight with 5 ml of 1M NH_4Cl (pH=7) to remove the exchangeable cations. (2) The residue is treated overnight with 10 ml H_2O_2 to oxidize organic matter. This solution dissolves most (but not all) organic matter and allows us to determine the relative ratios of cations in organic matter. We choose not to ash the sample because some non-silicate minerals would be dissolved in the process of dissolving the ash into solution. (3) The residue is next leached overnight in 5 ml of 1M HNO_3 to remove non-silicate minerals such as apatite and calcite. Our previous studies have shown that this treatment dissolves >75% of the apatite and calcite in Hubbard Brook soils, yet dissolves <0.3% of the silicate fraction. (4) Finally, the residue is totally digested in 10 ml of a mixture of concentrated HF, HNO_3 and HCl at high pressure and 210°C in a microwave digestion apparatus to digest the silicate mineral fraction. Analyses of major and trace elements will be carried out on all of the solutions using ICP-OES and ICP-MS with both internal and external calibration.

Strontium Isotope Analyses – Subsets of all types of samples analyzed for Ca will be analyzed for Sr concentration by ICP-MS and then analyzed for $^{87}Sr/^{86}Sr$ ratio. Digested sample solutions will be evaporated to dryness and re-dissolved in 1 ml of 3 N HNO_3. Strontium will be separated by ion exchange chromatography in quartz columns using Sr-Spec ion specific resin, and loaded on to tungsten filaments with Ta_2O_5 powder. The $^{87}Sr/^{86}Sr$ ratio will be measured using a multi-collector thermal ionization mass spectrometry in static mode (Finnigan MAT 262) and normalized to $^{86}Sr/^{88}Sr$ = 0.1194.

Statistical analysis

Hypothesis 1: Calcium budgets will be constructed for each of 9 stands (3 ages) in the Intensive Approach, based on independent measurements of vegetation mass and Ca concentration. Forest floor will be measured in the quantitative soils pits. Leaching losses will be estimated from lysimeter solution concentrations and modeled solution fluxes (Yanai 1991). Variation in net Ca supply from the mineral soil will be tested against stand age using ANOVA.

We will test the change in Ca concentration of litter in the 13 chronosequence stands against our predictions of a declining trend with stand age using regression on the paired differences as a function of stand age (Extensive Approach).

Hypothesis 2: We will test for the presence of a non-silicate acid-extractable Ca pool using 13 stands representing a range of ages and locations (Extensive Approach). We expect to find that this previously unappreciated Ca pool is present in the parent material across the region, with no significant effect of stand age in linear regression.

Hypothesis 3: The relative contribution of the three end members (atmospheric, silicate, and non-silicate) to each ecosystem Ca pool (vegetation, soil organic matter, and the exchangeable Ca pool) as a function of stand age can be analyzed by regression, with 13 stands of different ages (Extensive). For the Intensive sites, we will use ANOVA with stand age as the independent variable, as there are three replicates of each of three ages of stand. In both cases, we will analyze the relative contribution from each end member, rather than the isotopic or elemental ratios of each pool, which protects us from variation in the isotopic composition of the end members. We will also test whether

the exchangeable Ca pool is significantly depleted in younger stands using 9 stands, ages 15, 30 and 80, in the Intensive study sites.

Hypothesis 4: The analysis described for determining sources of Ca to vegetation (Hypothesis 3) can be applied to samples of litter from 10 tree species from 13 stands of different ages (Extensive Approach). We can test whether species differ significantly from one another (and whether these differences explain the observed differences in ecosystem Ca status) and whether species differ across sites as a function of stand age (linear regression).

Timeline

	Project Timeline											
	Year 1 2003				Year 2 2004				Year 3 2005			
	Wi	Sp	Su	Fa	Wi	Sp	Su	Fa	Wi	Sp	Su	Fa
Extensive Approach												
Soil Sampling			■									
Litter collection								■				
Intensive Approach												
Forest Service approvals	■	■										
Plot layout		■	■			■						
Vegetation sampling						■						
Soil Sampling						■						
Install lysimeters				■								
Litter collection								■				
Tree coring								■				
Collect lysimeter samples					■	■	■	■	■	■		
Laboratory Analyses												
Soil sample preparation				■	■			■	■			
Soil Ca extraction					■	■	■	■	■			
Sr isotopes					■	■	■	■	■	■	■	
Tissue/litter chemistry							■	■	■	■	■	
Tree core analysis									■	■	■	■
Analysis of lysimeter water					■	■	■	■	■	■	■	■

Collaborative Arrangements

Due to the complexity of the problem posed, an interdisciplinary approach is required. We have brought together a team composed of a geochemist and ecologists specializing in forest structure, soils, and modeling. The perspectives and skills represented in this collaboration allow us to address issues fundamental to ecosystem nutrient cycling. The assembled group of PIs have worked together previously, meet quarterly at Hubbard Brook LTER meetings, and hold regular conference calls. We have an excellent working relationship and are well poised to complete this research. We have developed a work plan in which each of the PIs have direct responsibility for a section of the proposed research and we have detailed how each of these responsibilities will intersect. Primary responsibility for each of the PIs are as follows: Yanai – overall coordination, sampling of the chronosequence (Extensive); Arthur – litter analysis, comparison to previous chronosequence study; Blum – chemical analysis of soil and vegetation including Sr isotopes; Hamburg – plot establishment (Intensive), sampling of vegetation and soil. In order to facilitate coordination, the three graduate students and one technician from four different institutions, who will be doing much of the laboratory work, will be in the field working together during the field season. Similarly, all of the PIs will be on site together for site selection and plot establishment.

Broader Impacts of the Study

The proposed study addresses the question of Ca depletion in northeastern forests, which is critically important for both policy formulation and forest management. At the nearby Hubbard Brook Experimental Forest, exchangeable Ca in soil is predicted to be depleted in less than one harvest cycle, which means that either the productivity of re-growing forests will very soon be limited by Ca availability (Likens et al. 1998), or forests obtain Ca from previously unrecognized pools. The proposed experiment will improve our ability to predict the long-term implications of acid precipitation in the context of forest succession.

Geologists have traditionally put biology in a black box, minimizing the importance of biotic processes to geochemistry, while ecologists have put weathering in a black box, often ascribing to it whatever flux was necessary to balance a budget. The lack of a dialectic between weathering and biotic processes has limited our understanding of how nutrient cycling relates to ecosystem productivity and environmental stress.

In this proposal, we will make measurements that will allow us to define the importance of biotic processes on altering weathering and Ca availability. Understanding the importance of this interaction is key to defining sustainable forest management practices. We need to know how intensively we can manage northern hardwood forests before nutrient depletion limits forest productivity. The proposed research will contribute to identifying sustainable forestry practices in the northern hardwood forests of the northeastern United States.

Quantification of non-silicate mineral sources of Ca (apatite and calcite) to northeastern forest soils is important in calculations of Ca depletion because these Ca sources do not contain Na, which is often used to estimate the rate of Ca release by weathering. For example, Likens et al. (1998) calculated Ca weathering release based on stream sodium fluxes and an assumed Ca/Na weathering release ratio of 0.24 to 0.33. If non-sodium-bearing minerals contribute significant amounts of Ca to the soil, as we suggest, then rates of plant available Ca depletion could be significantly overestimated.

In addition to the intellectual impacts of the study, this project will provide long-term infrastructure for studies of succession and forest age in the northern hardwood forest. Previous advances in our understanding of long-term changes in ecosystem structure and function have relied heavily on chronosequence studies. Such studies are subject not only to random sources of error but also systematic ones: changes in technology and markets for wood products have altered the nature of harvest treatments over time (Arthur and Yanai 2000, Yanai et al. 2000). The proximity and similarity of our experimental study area to the Hubbard Brook Experimental Forest will magnify its utility to a broad spectrum of researchers. Finally, we will contribute to future research through training undergraduate and graduate students. There will be two undergraduates involved in field work in each of the first field seasons and one in the third. Many of these students will use this research opportunity to develop their own ideas for the required year-long senior thesis project for environmental science students at Brown University. Over the past six years, Hamburg has mentored 36 such students, 70% women and 15% minority. In addition, three graduate students will be trained on this project.

Results of prior NSF Support

R.D. Yanai: DEB-0087263 $300,000, 2000-2003.
Testing nutrient uptake models against ecosystem budgets.

In the first year of the project, we excavated roots of mature trees and measured their nutrient capacity in situ. This method worked for some species and nutrients, but for others, efflux exceeded influx, and net uptake was negative. This year, one graduate student is testing modifications of the

method that reduce disturbance to the roots; another is developing a method for measuring uptake from undisturbed root cores. Four undergraduate students are also involved in the project.

J.D. Blum: EAR 93-50262 $500,000, 1993-2000
Presidential Faculty Fellowship Award
      My mainstream geology research has been funded by a series of grants from the NSF. The PFF award allowed me the flexibility to investigate research problems that would otherwise have been risky endeavors for a geologist, and I took the opportunity to pursue (1) the application of Sr isotopes to biological and hydrological systems, and (2) investigations of the origins of meteorite impact glasses. With the support of this grant I have published twenty-two articles that fall in the first category (see Bio for a list of 10 of these papers) and seven articles in the second category.

T. Fahey and C. Driscoll (**S.P. Hamburg**, R.D Yanai et al. co-PIs): DEB-9810221 (Hamburg subcontract $129,170) 1998-2004 **Long Term Ecological Research at the Hubbard Brook Experimental Forest**.
      Three projects have been undertaken, (1) Snail densities have been remeasured in forests of different ages, showing that young forests have increasing snail densities and older forests declining densities and Ca availability. (2) A field experiment examined the influence of beech bark disease on declining sugar maple seedling survival. Shading and alellopathy appear to be the most important modes of influence. (3) We have monitored the impacts of the 1988 ice-storm on canopy structure showing that recovery was delayed, spatially variable, and favored beech.

Rhoads, A.G. S.P. Hamburg, T. J. Fahey, T.G,. Siccama, E.N. Hane, J. Battles, C. Cogbill, J. Randall and G Wilson. 2002 Effects of a large ice storm on the structure of a northern hardwood forest. *Canadian Journal of Forest Research*. (in press)

Hane, E.N., S.P. Hamburg, J. Plaut and A. Barber Allelopathic effects of American Beech (*Fagus grandifolia*) on sugar maple (*Acer saccharum*). *Canadian Journal of Forest Research* (accepted pending revision)

Hamburg, S.P., R.D. Yanai, M.A. Arthur, J.D. Blum and T.G. Siccama. Biotic Control of Calcium Cycling in Northern Hardwood Forests: Acid Rain and Aging Forests *Ecosystems* (accepted pending revision)

Hane, E.N. Indirect effects of forest disease: the effect of beech bark disease on sugar maple seedling survival *Canadian Journal of Forest Research* (accepted pending revision)

G.M. Lovett, **M.A. Arthur**, M.C. Carreiro, K.C. Weathers: DEB-9981503, $974,748, 2000-2003.
Effects of an introduced pest on the C and N dynamics of a northern hardwood forest.
    This project examines the potential role of shifting tree species composition from beech to sugar maple in the northern hardwood forests of the Catskill Mountains, in response to mortality caused by the beech scale insect. We are examining nitrogen and carbon cycling, and decomposition dynamics, in response to increasing sugar maple composition in a series of 20 forest stands with varying beech bark disease impacts.

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Lovett, G.M., K.C. Weathers and M.A. Arthur. 2001. Is nitrate in stream water an indicator of forest ecosystem health in the Catskills? *In:* M.S. Adams, ed., Catskill Ecosystem Health, Purple Mountain Press, Fleichmanns, NY, pp. 22-30.

Two additional papers are currently in review.

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FACILITIES AND EQUIPMENT

Facilities at SUNY-ESF

The equipment to be used at SUNY College of Environmental Science and Forestry include the following:
1. Perkin-Elmer "Optima" 3000DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)
2. Bran+Luebbe AutoAnalyzer 3, Dual Channel System, compact sampler

Facilities at Brown University

All the facilities and major equipment necessary to prepare samples for later elemental analysis and analyze the chemistry of soil water samples associated with the proposed research are housed in the Center for Environmental Studies analytical facilities in MacMillan Hall, Brown University: (http://envstudies.brown.edu/Dept/places/MacMillan/equip.html)
1. Milestone ETHOS 1600 microwave digestion labstation
2. Dionex DX500 Ion Chromatograph – dual column
3. CE Instruments NC2100 elemental analyzer
4. JY2000 Ultrace ICP Atomic Emission Spectrometer
5. Perkin Elmer 4100ZL Graphite Furnace Atomic Absorption Spectrophotometer
6. #4 Wiley Mill, intermediate Wiley Mill, mixer mill, Wiggle Bug
7. Drying ovens, drying racks, cold room, scales

Facilities at the University of Michigan

All the facilities and major equipment necessary to carry out the proposed
Sr isotope studies are housed in the Department of Geological Sciences at
the University of Michigan:
1. Class 100 clean room facilities for low trace element blank level
        digestion and Sr separation chemistry.
2. CEM "Mars5" High-Pressure Microwave Digestion System
3. Finnigan MAT 262 Multi-Collector Thermal Ionization Mass Spectrometer-TIMS
4. Perkin-Elmer "Optima" 3300DV Inductively Coupled Plasma Optical Emission
        Spectrometer (ICP-OES)
5. Finnigan MAT "Element" magnetic sector (high-resolution) ICP-MS

Facilities at the University of Kentucky
The facilities and equipment necessary to process the vegetation samples are available in the Forestry Department at the University of Kentucky, as follows:
1. Wiley mills for grinding material
2. Dry lab for sorting leaf litter
3. Storage space for archived samples
4. Drying ovens
5. Scales