Effects of tree species on soil properties in a forest of the northeastern United States

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To Helen

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Chapter 1

General Introduction

Introduction

The effect of trees on soil formation and nutrient cycling has been recognized for a long time (e.g. Shear and Stewart, 1934; Zinke, 1962; Challinor, 1968; Alban, 1982; Crozier and Boerner, 1986; Mladenoff, 1987; Boerner and Koslowsky, 1989; Boettcher and Kalisz, 1990; France *et al.*, 1989; Johnson and Todd, 1990; Binkley *et al.*, 1992; Hobbie, 1992; Gower and Son, 1992; Nordén, 1994; Binkley, 1995; Bockheim, 1997; Finzi *et al.*, 1998*a*,*b*; Amiotti *et al.*, 2000). Tree species effects on nutrient cycling, ranging from effects on mineral weathering (e.g. Bouabid *et al.*, 1995; Tice *et al.*, 1996), to nutrient uptake and litterfall (e.g. Alban, 1982; Johnson and Todd, 1987, 1990), to leaching (e.g. Johnson *et al.*, 1985), have been well documented. In return, these processes influence the fitness of trees and the spatial and temporal dynamics in a mixed forest. With continuing stress imposed by human activity, such as acid rain, there is an urgent need to incorporate tree-soil interactions into a better understanding of the long-term dynamics of nutrient cycling in forest ecosystems.

Tree-soil interactions

Tree-soil interactions and their influence on tree fitness and forest community dynamics are complex. Many current theories on spatial heterogeneity and species diversity of forest communities are based on the premise that species interaction is controlled by competition for resources (light, water, nutrients, Tilman, 1982, 1988; Goldberg, 1990). Although these resources are largely constrained by the physical environment, the influence of canopy trees on resources can be of significant importance in forest ecosystem dynamics. This biotic control over resources has received little attention until recently in understanding forest ecosystem dynamics.

Several authors have demonstrated the existence of a close interaction between plant and soil (Hobbie, 1992; Van Breemen, 1993; Van der Putten, 1997). Van Breemen (1993) reviewed studies on the influence of plants, soil animals and microorganisms on their physical substrate. He concluded that in many cases these organisms appear to affect soil fertility, soil moisture content and other soil properties in such a way that with time the substrate becomes more favorable for the growth of plants and soil organisms. Recent field studies show evidence of positive feedbacks of biota on soil processes. As a consequence, positive feedbacks seem to play a significant role in the structure and dynamics of ecosystems. Berendse (1994) studied the competition between two heathland plant species, the dwarf shrub *Erica tetralix* L. and the perennial grass *Molinia caerulea* (L.). While the slow growing *Erica* was much more competitive at low N levels, the fast growing *Molinia* dominated at high N levels. He concluded that these species could remain dominant, each at their own N level, because of positive feedbacks on soil N availability. *Erica* produced litter with low decomposability and therefore N availability in the soil remained low while *Molinia* produced litter of high quality keeping high levels of N in the soil. Van Breemen (1995) showed how *Sphagnum* formed an adverse environment for many plant species (such as poorly drained soils with low pH and low nutrient levels) in order to gain competitive advantage for its own growth.

Frelich *et al*. (1993) found that sugar maple and hemlock trees in a forest in Upper Michigan formed very stable patches of singular tree species. They concluded that competitive interactions, such as effects of mature trees on seedbed conditions, between sugar maple and hemlock could lead to spatial separation into monodominant patches over long time periods. Northup *et al*. (1995) reported that a pygmy forest along the Californian coast, growing on extremely infertile and acidic soils, synthesized large quantities of low decomposable compounds. Ectomycorrhizal fungi associated with this forest were able to use the organic N in these compounds, thus short-circuiting the N cycle and minimizing losses or use by other microorganisms in the ecosystem. The efficient use of N by this pygmy forest-soil fungi symbiosis prevented other tree species from growing there.

   The evidence above suggests that tree-soil feedbacks need to be incorporated into the concept of species diversity and spatial heterogeneity in forest ecosystems in order to gain more insight in long-term forest dynamics.

Acid rain

Acid rain still remains an important thread to many ecosystems in the United States (Krajick, 2001). Recent studies reporting changes in forest ecosystems in North America and Europe affected by acid rain highlight the need for a better understanding of forest ecosystem functioning (e.g. Likens *et al*., 1996, 1998; Binkley and Högberg, 1997).

   The acidity of precipitation is caused by a surplus of acid anions, such as sulfate and nitrate. Although the deposition of acid anions has declined both in Europe and North America during the last few decades, so has the deposition of base cations (Hedin *et al*., 1994). The decline in atmospheric base cations has been attributed to declining point-source emissions from fuel combustion and industrial processes as well as declining open-source emissions associated with traffic on unpaved roads and agricultural tillage practices.

   Atmospheric deposition is an important source of base cations for forests growing under nutrient-poor conditions such as those found on many soils in northern Europe and northeastern United States. Hedin *et al*. (1994) concluded that the declining trend they observed in atmospheric base cation content may have ecological consequences relevant to these forest ecosystems.

   Moreover, many temperate forest ecosystems of North America and Europe have shown high losses of base cations in the past, and in particular Ca (Åberg *et al.*, 1989; Federer *et al*., 1989; Johnson and Lindberg, 1992; Joslin *et al*., 1992; Lawrence *et al*., 1995; Bailey *et al*., 1996; Likens *et al*., 1996, 1998). Likens *et al*. (1996, 1998) calculated the Ca budget for a watershed in the Hubbard Brook Experimental Forest (New Hampshire, USA) and demonstrated that large quantities of Ca have been lost from the soil complex during the last few decades. Inputs from atmospheric deposition and mineral weathering were not able to make up for these losses, resulting in a depletion of Ca in the watershed. Long-term depletion of Ca and other nutrients in eastern US forests have been attributed to leaching losses caused by acid deposition (Federer *et al*., 1989; Lawrence *et al*., 1995; Likens *et al*., 1996, 1998).

Tree responses to Ca depletion in the soil

Calcium depletion in the soil may affect tree growth directly, simply by becoming deficient for growth. Several investigators report decreased primary production, increased canopy dieback and tree mortality because of Ca deficiencies in the soil for many forests of the northeastern United States (Wilmot *et al.*, 1995, 1996; Likens *et al.*,1996, 1998). The loss of Ca (and other base cations) and the resulting pH decrease in poorly buffered soils may adversely affect N mineralization, and consequently N availability in the soil. Giesler *et al.* (1998) suggested, based on a regional survey in Norway, that the soil pH and the supply of base cations affects plant productivity and community composition mainly via their effects on N supply. Finally, loss of Ca and pH decrease in the soil will increase Al mobilization. Lower Ca and higher Al concentrations in soil solution may inhibit Ca uptake, however there is also the potential for direct toxic effects of inorganic Al (Cronan and Grigal, 1995). Based on the Ca and Al contents measured in sugar maple wood and in the soil, Mohamed *et al.* (1997) concluded that trees were suffering from high Al concentrations in the soil causing a decline of sugar maple trees in Ontario, Canada.

In conclusion, Ca appears to play, both directly and indirectly, a key role in controlling the distribution of tree species in nutrient poor temperate forests of North America and Europe.

Biotic control over soil Ca availability for different tree species

Studies in the Great Mountain Forest (GMF), Connecticut, USA, showed significant differences in soil Ca availability under different tree species (Finzi *et al.*, 1998*a*). The tree species studied in this forest were sugar maple (*Acer saccharum*), white ash (*Fraxinus americana*), beech (*Fagus grandifolia*, Ehrh.), red maple (*Acer rubrum*, L.), northern red oak (*Quercus rubra*, L.) and eastern hemlock (*Tsuga canadensis*, Carr.). The soils where these investigations were conducted were sandy loamy, acidic inceptisols with low Ca content (ranging between 0.5 and 3.6% CaO, Van Breemen *et al.*, 1997). Figure 1 represents the relationship between the soil available Ca pool (exchangeable Ca extracted with 0.1 M $BaCl_2$) and the total mineral Ca content of the soil (Ca fixed in minerals not readily available for plant uptake, but potential available after mineral weathering) for the different tree species. Sugar maple showed increasing amounts of available Ca in the soil with increasing total mineral Ca contents, while the amounts of available Ca in the soil remained low under hemlock and red maple.
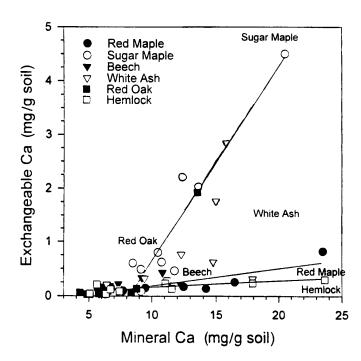
Figure 1. Species-specific linear regressions of exchangeable Ca as a function of the mass of total soil Ca (from Finzi *et al.*, 1998*a*).

This study also showed that sugar maple, hemlock and red maple were found on soils under a wide range in total mineral Ca contents, while red oak and beech were only found at the lower end and white ash at the higher end of total mineral Ca content (Figure 1, Van Breemen *et al.*, 1997). This suggests that the distribution of sugar maple, hemlock and red maple were not constrained by total mineral Ca contents in the soil in this forest. The strong correlation with the available Ca pool however suggests that these tree species may play an active role in altering the size of the available Ca pool in the soil. The total mineral Ca content in the soil may have differentiated the distribution of red oak, beech and white ash. Their role in altering the available Ca pool in the soil is less clear.

Above results imply that changes in the distribution and abundance of tree species that are growing in mixed forest stands, will change the temporal and spatial pattern of soil acidity and Ca cycling in this forest. In return, these temporal and spatial alterations in soil acidity and Ca cycling may, together with human induced stresses caused by acid rain, affect tree fitness and forest community dynamics.

Biogeochemical processes controlling soil Ca availability

Several mechanisms control soil Ca availability. Some of these mechanisms are closely linked to tree-growth while others are more related to a-biotic factors (climate, soil parent material, relief), while often there is an interaction of both biotic and a-biotic factors. In figure 2 the Ca fluxes and pools in a forest ecosystem are illustrated, which control the available Ca in the soil.
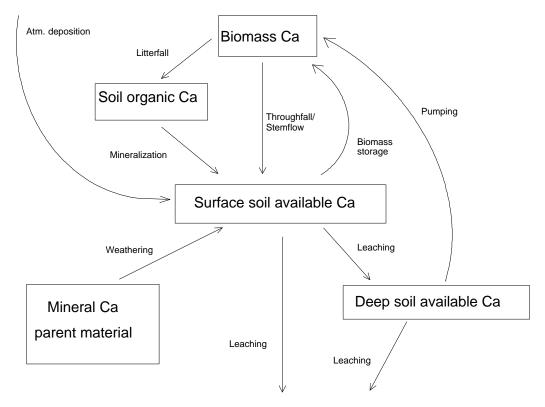
Figure 2. The Ca fluxes (arrows) and pools (boxes) within the tree-soil system controlling the exchangeable Ca pool in the soil.

The main biogeochemical processes that are likely to regulate the amount of available Ca in nutrient-poor soils are:

- *Atmospheric deposition*: As discussed earlier, atmospheric deposition is an important source of Ca for forests growing on nutrient-poor soils. There is no direct evidence that tree species alter the Ca atmospheric deposition in northeastern U.S. forests.
- *Mineral weathering*: The other important source of Ca is mineral weathering. The rate of Ca mineral weathering depends on a-biotic factors like the Ca content and the type of minerals in the soil. However, trees may affect weathering rates by producing organic acids in the soil, thus lowering soil pH and stimulating mineral weathering. Some investigators have reported different weathering rates under different tree species (Bouabid *et al*., 1995; Tice *et al*., 1996). Differences in weathering rates beneath different tree species may be mediated by hyphae of ectomycorrhizal fungi that penetrate primary minerals, presumably through the release of organic acids (Jongmans *et al*., 1997; Van Breemen *et al*., 2000).
- *Calcium biomass storage*: The storage of Ca in the living biomass can vary substantially for different tree species and for species with different age. Alban (1982) and Johnson and Todd (1987, 1990) showed that some tree species showed high losses of exchangeable Ca in the soil due to storage in living biomass.
- *Immobilization in soil organic matter*: The amount of Ca immobilized in soil organic matter can be significantly variable for different tree species. The immobilization of Ca depends on Ca contents of litter and on litterfall and mineralization rates of Ca.

The rate of Ca mineralization from decomposing leaf litter is generally closely related to mass loss (Gosz *et al*., 1973; Likens *et al*., 1998). The decomposition rate for leaf litter differs widely for tree species due to differences in litter quality (e.g. Melillo *et al*., 1982; Aber *et al*., 1990). Tree species with slow litter decomposition rates that build up thicker forest floors (e.g. Finzi *et al*., 1998*b*) may have higher amounts of Ca immobilized in the forest floor.

- *Vertical movement of exchangeable Ca*: Calcium is lost through leaching with soil water. Leaching losses of cations may vary under different tree species as a result of the release of organic acids and phenolic compounds from litter (Mollitor and Raynal, 1982; Boettcher and Kalisz, 1990; Likens *et al*., 1998). These products may acidify the soil, increasing Al solubility, and ultimately enhancing Ca leaching by the increased Al removing Ca from the binding sites on the exchange complex. Some tree species have deeper root systems than others and may be able to 'pump' Ca from deeper soil layers to the soil surface where the Ca eventually will return as leaf litter or with throughfall/stemflow (e.g. Johnson *et al*., 1985).

Objectives

The general objectives of this research are 1) to identify and quantify specific biogeochemical processes that are responsible for the differences in Ca availability in the surface soil (forest floor and upper 20 cm of the mineral soil) and other related soil properties under different tree species and 2) to separate tree species effects from soil effects on soil properties in the surface soil. The intention of this thesis is to improve the understanding of the influence of different tree species on soil Ca availability and other soil properties and to provide tools to be able to predict future forest community dynamics under the continuing stress of acidic deposition.

Study site

This study was done in the 3000 ha Great Mountain Forest on the Canaan Mountain Plateau (elevation 300-500 m) in northwestern Connecticut, USA (42°N, 73°15'W). The species that were studied are: sugar maple (*Acer saccharum*), hemlock (*Tsuga canadensis*, Carr.), American beech (*Fagus grandifolia*, Ehrh.), red maple (*Acer rubrum*, L.), white ash (*Fraxinus americana*) and red oak (*Quercus rubra*, L.), which are also the dominant canopy tree species in this mixed hardwood forest. Mean annual precipitation is 1400 mm and mean annual temperature is 7°C (-5°C in January and +20°C in July). Soils are acidic, well-drained sandy loams derived from glacial till over mica-schist bedrock. The dense glacial till at all sites starts approximately at 60-cm depth. The sites have not been cleared for agriculture while some selective logging has occurred. A sparse and scattered understory vegetation is present consisting primarily of hayscented fern (*Dennstaedtia punctilobula*) while no major shrub or sub canopy tree species is present. Within this forest, sampling sites were selected, consisting of patches that were

dominated by a cluster of 4 to 10 mature trees for each of the six studied tree species (~80-130 years old).

Outline of this thesis

In chapter 2 I describe tree species effects on Ca weathering in the soil. I analyzed primary minerals in soils at three different soil depths from sugar maple and hemlock sites. By comparing the relative abundance of soil minerals that differ in specific weathering rate, I interpreted the overall soil weathering beneath sugar maple and hemlock sites. In addition, I used stable Sr isotopes as a marker for Ca to quantify Ca weathering rates in the surface soil. By measuring $^{87}Sr/^{86}Sr$ ratios in atmospheric deposition, soil, soil solution, and tree biomass, I was able to separate sources of Sr and Ca from atmospheric deposition and soil weathering, and moreover, to calculate Ca weathering rates in the surface soil at each sampling site.

In chapter 3 I describe the role of organic acids on base cation leaching from the surface soil. Little is known about organic acid properties and production in surface soils beneath different tree species, which may have significant impact on base cation leaching from the surface soil. I determined the quantity, nature, and degree of neutralization of organic acids in forest floor solutions under different tree species, and attempted to relate properties of specific organic acids to certain tree species and their importance for Ca leaching.

In chapter 4 I evaluate the effect of tree species on Al solubility and mobility in the surface soil. Because Ca and Al are highly interrelated in soils through exchange reactions, Ca could be removed from the soil by displacement of Ca with Al on the exchange complex. I compared concentrations of exchangeable and organic-bound solid Al and of aqueous Al species among the different tree species at different soil depths. Factors controlling the binding of Al to organic compounds were determined to estimate their importance on Al speciation and mobility for each tree species.

In chapter 5 I describe *in situ* Ca mineralization in the forest floor and upper 15-cm of the mineral soil beneath different tree species. A large amount of Ca is released in the soil through organic mineralization each year, contributing substantially in the availability of Ca for plant uptake. I estimated *in situ* Ca mineralization by measuring changes in exchangeable Ca from forest floor and mineral soil samples incubated in plastic bags that were buried in the field.

In chapter 6 I evaluate the role of Ca uptake from deep soil layers (below 20-cm depth) on Ca availability in the surface soil between sugar maple and hemlock. I studied Ca uptake from deep soil layers by comparing Ca inputs in the surface soil from atmospheric deposition and soil weathering with Ca outputs below the surface soil through leaching. With support of root density measurements below both sugar maple and hemlock and a simple model, the effect of Ca uptake from deep soil layers on Ca availability in the surface soil is discussed.

Finally, in chapter 7 I state general conclusions of this thesis.

Chapter 2

Calcium weathering in forested soils
and the effect of different tree species

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Abstract.

Soil weathering can be an important mechanism to neutralize acidity in forest soils. Tree species may differ in their effect on or response to soil weathering. We used soil mineral data and the natural strontium isotope ratio $^{87}Sr/^{86}Sr$ as a tracer to identify the effect of tree species on the Ca weathering rate. The tree species studied were sugar maple (*Acer saccharum*), hemlock (*Tsuga canadensis*), American beech (*Fagus grandifolia*), red maple (*Acer rubrum*), white ash (*Fraxinus americana*) and red oak (*Quercus rubra*) growing in a forest in northwestern Connecticut, USA. Three replicated sites dominated by one of the six tree species were selected. At sugar maple and hemlock sites the dominant mineral concentrations were determined at three soil depths. At each site soil, soil water and stem wood of the dominant tree species were sampled and analyzed for the $^{87}Sr/^{86}Sr$ ratio, total Sr and Ca content. Atmospheric deposition was collected and analyzed for the same constituents. Optical analysis showed that biotite and plagioclase concentrations were lower in the soil beneath hemlock than beneath sugar maple and suggested species effects on mineral weathering in the upper 10 cm of the mineral soil. These results could not be confirmed with data obtained by the Sr isotope study. Within the sensitivity of the Sr isotope method, we could not detect tree species effects on Ca weathering and calculated Ca weathering rates were low at all sites (< 60 mg m^{-2} yr^{-1}). We found a positive correlation between Ca weathering and the total Ca concentration in the surface soil. These results indicate that the absolute differences in Ca weathering rate between tree species in these acidic surface soils are small and are more controlled by the soil parent material (plagioclase content) than by tree species.

Introduction

There is substantial evidence that acid rain has depleted exchangeable Ca pools in many soils of forests of the northeastern United States during the last century (e.g. Lawrence *et al*., 1995; Likens *et al*., 1996, 1998), and consequently has decreased the capacity of soils to neutralize acidity. However, numerous studies showed some biologic control over the status of the exchangeable Ca pool and pH in surface soils (Alban, 1982; Klemmedson, 1987; Boettcher and Kalisz, 1990; Johnson and Todd, 1990; Nordén, 1994; Bockheim, 1997). Except for replicated experiments where trees were planted (Challinor, 1968; Binkley and Valentine, 1991; Eriksson and Rosen, 1994), it is not easy to determine whether trees cause changes in soil exchangeable Ca and pH, or whether these soil properties reflect differences in parent material, which in turn influences tree distribution. Van Breemen *et al*., (1997) and Finzi *et al*., (1998*a*) tried to separate effects by tree species from effects by parent material, by measuring soil parent material properties (soil texture and elemental composition) and soil properties easily affected by trees as well (exchangeable Ca and pH). These studies, at Great Mountain Forest, northwestern Connecticut, concluded that the soils' parent material and its effect on tree distribution must be considered in determining tree species effects on exchangeable Ca and soil pH.

   Trees may affect the exchangeable Ca pool in surface soils through their influence on chemical weathering. Several authors have reported apparent differences in mineral

weathering caused by different tree species (Spyridakis *et al*., 1967; Bergkvist and Folkeson, 1995; Bouabid *et al*., 1995; Quideau *et al*., 1996; Tice *et al*., 1996; Augusto *et al*., 2000). Species-induced weathering has been related to the production of organic acids in the soil and the ability of these acids to complex metals or affect soil pH (Tan, 1980; Antweiler and Drever, 1983; Kodama *et al*., 1983; Lundström and Öhman, 1990; Raulund-Rasmussen *et al*., 1998; Van Hees and Lundström, 1998). Other workers have argued that exudates by roots or ectomycorrhizal fungi promote mineral weathering in the rhizosphere (Ochs *et al*., 1993; Gobran *et al*., 1998; Van Breemen *et al*., 2000). Trees may also increase soil weathering rates by modifying the soil pH through CO_2 production (Cawley *et al*., 1969), by net cation uptake from the soil, or by enhancing deposition of atmospheric acids (Fölster, 1985; Bergkvist and Folkeson, 1995). We predict that tree species grown on soils poor in base cations and that are able to lower soil pH through mechanisms mentioned above and/or are associated with ectomycorrhizal fungi, have a larger impact on the Ca weathering rate in the soil than tree species that do not have these characteristics.

Many studies concerning biologic control of mineral weathering have been done under laboratory conditions or with manipulated field experiments. Determining weathering rates in the field remains difficult (e.g. Likens *et al*., 1998). Recently the strontium isotope ratios, $^{87}Sr/^{86}Sr$, have been used as a tracer to separate the Sr input derived from soil weathering and the Sr coming from the atmosphere. The similar geochemical behavior of Ca and Sr (Graustein, 1989) has led to the use of Sr isotopes to estimate Ca weathering rates in natural terrestrial ecosystems (Åberg *et al*., 1989; Wickman and Jacks, 1992, 1993; Miller *et al*., 1993; Bailey *et al*., 1996; Clow *et al*., 1997). This method i) provides estimates of *in situ* Sr and Ca weathering rates; ii) is not affected by weathering from deeper unconsolidated material; iii) requires no site specific Sr or Ca mass balance calculations. However, in soils with high mineralogical heterogeneity where minerals have distinct $^{87}Sr/^{86}Sr$ ratios and Sr weathering rates, this method becomes more difficult.

The objective of this research was to identify the effect of different tree species on the chemical weathering rate of Ca in the soil and to quantify Ca weathering rates at sites differing in tree species composition and soil parent material using Sr isotopic and soil mineral data.

Methods

Study site

This research was done in a watershed near Camp Pond in Great Mountain Forest (GMF), northwestern Connecticut, USA (see Canham *et al*., 1994; Pacala *et al*., 1994). During the last ice age a thin mantle of compacted clayey sandy micaceous till covered more than 90% of the mica schist bedrock surface of the area. Following deglaciation, large masses of stagnant ice occupied current swamp areas (Colton, 1968). The soils formed on the glacial till at Camp Pond are acidic, well-drained, sandy loams classified as Typic Dystrochrepts (Hill *et al*., 1980) with depths ranging between 50-70 cm.
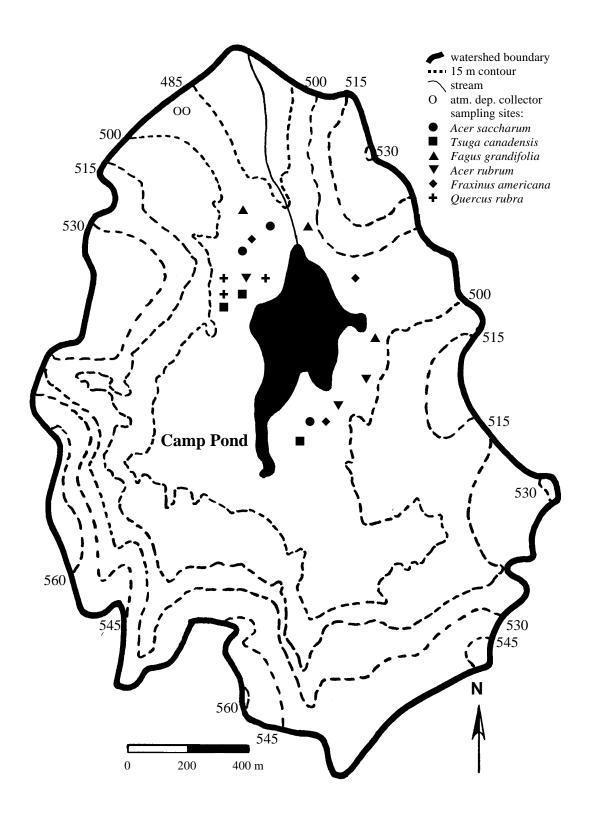
Figure 1. Camp Pond watershed and the site locations at Great Mountain Forest.

X-ray diffraction showed that significant amounts of plagioclase, alkali-feldspars and mica (biotite) are present in the soil (F.A. Dijkstra, unpublished). The uneven surface is scattered with numerous glacially transported boulders. A mixture of hardwood and coniferous trees covers the soils. We considered three endomycorrhizal trees (sugar maple -*Acer saccharum*-, red maple -*Acer rubrum*, L.-, and white ash -*Fraxinus americana*) and three ectomycorrhizal trees (eastern hemlock -*Tsuga canadensis*, Carr.-, American beech -*Fagus grandifolia*, Ehrh.-, and northern red oak -*Quercus rubra*, L.). For each tree species three sites were selected where each site was dominated by one of these six species (Figure 1). Four to ten mature trees of one of the six tree species dominated each site in an area with a diameter of approximately 25 m. The study site at Camp Pond is in a second growth (~80-130 yr. old) stand with a history of logging but not of agriculture.

Sampling

Atmospheric deposition was collected in two collectors at a clearing close to Camp Pond (see Figure 1). Collectors, 1 m above the ground, were made of a polyethylene funnel (diam. 20 cm), connected to a neoprene tube draining into a partially buried polyethylene bottle. A plug of polyester fiber in the funnel prevented particulate debris entering the bottle. Atmospheric deposition was collected weekly from May until October in 1997, 1998, and 1999 and stored in the dark at 4°C prior to analysis.

At each site three soil cores (diam. 4.5 cm) were taken at depths of 0 to 20 cm and 50 to 70 cm in the spring and summer of 1997, and at depths of 0 to 10 cm and 20 to 30 cm in the summer of 2000. Soil samples were bulked for each depth and for each site, then dried for 48 hours at 105 °C and sieved (mesh size 2 mm). For soil micromorphological observations thin sections were prepared according to FitzPatrick (1970), from soil samples taken at 0- to 10-, 20- to 30-, and 50- to 70-cm depth beneath sugar maple and hemlock sites.

Tension lysimeters (Rhizon SMS, Eijkelkamp) were installed at each tree sampling site at a depth of 20 cm in the summer of 1997. The lysimeters were above groundwater level during the whole year. The lysimeters were produced from a hydrophilic porous polymer connected to PVC tubing. Soil solutions were obtained by connecting evacuated bottles (40 kPa) to the lysimeters. Soil solution samples were collected during the spring of 1998. All materials for solution sampling were cleaned in 50% hydrochloric acid and rinsed with nanopure water before use. Blanks were determined in 200 ml of nanopure water rinsed through the lysimeters and the atmospheric deposition collectors. Strontium contamination from the lysimeter contributed < 0.04% of the Sr in the soil solution concentration, and the atmospheric deposition collectors released < 0.2% of the Sr found in atmospheric deposition.

Wood samples (three cores, diam. 0.5 cm, to the center of the stem at breast height of the dominant tree) were taken from one tree at each site. At one site with an area of approximately 15×15 m, six individual beech trees that differed in age between 40 and 130 years were sampled separately. Wood cores were dried for four days at 70 °C.

Chemical and mineralogical analyses

Weekly atmospheric deposition and soil solution were analyzed for Ca with a Perkin-Elmer Inductively Coupled Plasma Emission Spectrometer (ICP). To obtain enough Sr from the atmospheric deposition for analyses, weekly samples were bulked, so that four samples were obtained over the sampling period in 1998. Atmospheric deposition and soil solution sub samples were measured for Ca content with the ICP. To analyze the Sr content and the $^{87}Sr/^{86}Sr$ ratio, atmospheric deposition and soil solution samples were spiked with ^{84}Sr and afterwards evaporated. To minimize blank contributions all reagents were distilled in Teflon and sample processing was done in acid-cleaned Teflon. Samples were dissolved in concentrated HNO_3 and evaporated. Samples then were dissolved in 3 *N* HNO_3 and transferred into centrifuge tubes and centrifuged for 4 minutes at 9000 rpm. Strontium was separated by ion exchange chromatography in pre-cleaned quartz columns containing SrSpec resin. All metals, except Sr, were stripped from the column with 20 column volumes of 3 *N* HNO_3 and afterwards Sr was collected with 10 column volumes of H_2O. Samples were evaporated and nitrated twice with concentrated HNO_3 to reduce organic material.

The organic matter content of soils from 0- to 10-, 20- to 30-, and 50- to 70-cm depth was measured by loss on ignition. Approximately 10 g of oven-dried soil was combusted in a muffle oven at 450°C for 8 hours. The soil texture of these same samples was analyzed on a Coulter LS230 laser grain-sizer with a 5-mW, 750-nm laser beam (after Buurman *et al.*, 1997). Soil samples from 0- to 20-cm depth were analyzed for total Sr and Ca with X-ray fluorescence (XRF). Ground samples (0.6 g) were melted with 2.4 g of $Li_2Br_4O_7$ at 1100°C for four hours. The resulting glass beads were analyzed using a Philips PW 1404 XRF Spectrometer, using standard reference samples prepared similarly (after Buurman *et al.*, 1996).

Mineral surface areas, rather than mineral concentrations, need to be considered in predicting soil weathering rates (White *et al.*, 1996). We measured surface areas of minerals in soil samples taken from 0- to 10-, 20- to 30-, and 50- to 70-cm depth at sugar maple and hemlock sites. We expected these two tree species to be most divergent in their effect on soil weathering. To estimate surface areas of individual weatherable minerals, we considered the grain size fractions of 10-50 (separated by sedimentation, using Stokes Law) and of 50-500 μm (separated by sieving), after removing soil organic matter by adding 10% H_2O_2 at 80 °C until dissapearance of dark staining by humus, followed by ultrasonic treatment. Subsamples of the fractions were impregnated and cut and polished into 30-μm × 1-cm × 1-cm sized thin sections. The uncovered thin sections from the 50- to 500-μm fraction were stained with K_3CoNO_2 and hemateine to detect plagioclase and alkali-feldspars respectively according to Van der Plas (1966). On digital petrographic microscope pictures of the thin sections (COOLSNAP, Roper Scientific Inc.) two-dimensional surface areas of all minerals, and of biotite, plagioclase, and alkali-feldspar separately, were measured with digital image analysis software (Image-Pro Plus, Media Cybernetics). Because the grain size distributions hardly differed between the different samples, the relationship between two-dimensional surface areas and actual three-dimensional mineral surface areas is the same for each sample.

Minerals of the 50- to 500-μm fraction of the soil samples from 50- to 70-cm depth were separated using heavy liquids and magnets prior to hand picking under a binocular

microscope. The 10- to 50-mg mineral separates were better than 99% pure. The predominant soil minerals were separated (quartz, plagioclase, alkali-feldspar, biotite, muscovite, and vermiculite). Sub samples of the bulk soil (from 50- to 70-cm depth) and stem wood were ground with a KLECO Pulverizer (model 4200). Ground soil samples and stem wood samples were ashed at 600 °C in platinum crucibles. Bulk and mineral samples were treated with 40% HF and concentrated HNO_3, evaporated and dissolved in 6 N HCl in Teflon beakers. An aliquot of the samples was taken and diluted ten times for measurement of Sr and Ca concentrations by ICP. Another aliquot was evaporated and dissolved in 3 N HNO_3 and Sr was separated in the same way as for the atmospheric deposition and soil solution samples.

Total Sr and the $^{87}Sr/^{86}Sr$ ratio were measured by thermal ionization mass spectrometry (Finigan Mat 261 and 262 RPQ-Plus). All samples were loaded on annealed rhenium filaments. Dynamic triple jump measurements were performed on the non-spiked samples (soil and stem wood samples) while the spiked samples (solution samples) were measured in static mode providing both total Sr and the $^{87}Sr/^{86}Sr$ ratio. Mass fractionation during the measurements were corrected by normalizing to the $^{86}Sr/^{88}Sr$ ratio, set at 0.1194. Each mass spectrometer run consisted of at least 50 individual measurements and the standard error of the final $^{87}Sr/^{86}Sr$ ratio was smaller than 0.00002. The $^{87}Sr/^{86}Sr$ ratio measured in the spiked samples was corrected for the amount of spike added. The international standard NBS 987 was measured periodically. Typical values for the dynamic and static runs were 0.710243 ± 0.000012 (n>50) and 0.710231 ± 0.000018 (n=24) respectively. Total Sr blanks for the chemical separation procedure were <200 pg or generally < 0.02% of the Sr loaded for each sample.

Calculations and statistical analyses

The proportion of Sr measured in the stem wood derived from weathering $X_{B,W}$ can be calculated with a linear mixing equation using the two sources of Sr in the tree-soil system, soil weathering and atmospheric deposition, as the end members (Graustein and Armstrong, 1983; Graustein, 1989):

$$X_{B,W} = \frac{Sr_B - Sr_D}{Sr_W - Sr_D} \tag{1}$$

where Sr_W is the Sr isotope ratio $^{87}Sr/[^{87}Sr + {}^{86}Sr]$ of the weathering end member, Sr_B is the isotope ratio measured in the stem wood and Sr_D is the isotope ratio of the atmospheric end member. This equation assumes that there is a single weathering end member in the rooting zone of the soil. Because concentrations of weatherable minerals, each with different Sr isotope ratios and weathering rates, vary with soil depth at our site, no single weathering end member can be identified in these soils. This problem can be dealt with in different ways. Some studies have tried to simulate soil weathering under laboratory conditions. By leaching rock or soil with an inorganic or organic acid the $^{87}Sr/[^{87}Sr + {}^{86}Sr]$ ratio for the weathering end member was obtained from the leachates (Wickman and Jacks, 1992, 1993; Miller *et al*., 1993; Wickman, 1996). Organic extractions however, are easily contaminated with Sr. Moreover, leaching with strong

inorganic acids is a poor substitute for natural weathering, and in fact is not much different than completely dissolving soil minerals. Earlier studies did not tackle the problem of variable soil mineralogy with depth. Bailey *et al.* (1996) based the $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratio of the weathering end member on the abundance and distribution of different minerals at various depths, and calculated an isotope ratio for the weathering end member that happened to be close to the Sr isotope ratio of the bulk soil.

We used the Sr isotope ratio of the organic-poor, but mineral-rich soil at 50- to 70-cm depth for the weathering end member to minimize contamination from exchangeable Sr with a partly atmospheric Sr signature. At the same time we estimated the weathering end member in the soil based on measured surface areas of soil minerals that have extreme $^{87}Sr/^{86}Sr$ ratios. We did a sensitivity analysis on the weathering end member where we varied the relative weathering rates of soil minerals and the relative abundance of these minerals coming from different soil depths. The weathering end member was calculated as if only these minerals were present in the soil.

Ca weathering rates were calculated according to (after Wickman, 1996, see derivation in the Appendix):

$$W_{Ca} = \frac{Sr_O - Sr_D}{Sr_W - Sr_O} D_{Sr} \frac{r_{Ca}}{r_{Sr}} \qquad (2)$$

where W_{Ca} is the Ca weathering rate (mg m^{-2} yr^{-1}), Sr_O is the isotope ratio of the Sr lost from the soil, D_{Sr} is the Sr in atmospheric deposition (mg m^{-2} yr^{-1}), and r_{Ca}/r_{Sr} is the ratio of Ca to Sr released by mineral weathering. During the life span of a tree the loss associated with Sr_O is equal to the loss through water drainage or leaching and the increment stored in living and dead biomass (see Figure 2). The ratio r_{Ca}/r_{Sr} was taken as the Ca/Sr mass ratio in the soils at 0- to 20-cm depth. Annual atmospheric deposition of Sr was estimated from the water volumes and concentrations of Ca in weekly sampled bulk deposition, the average volume-adjusted Ca/Sr ratios from the four pooled atmospheric deposition samples, and precipitation data collected at a weather station within ten kilometers of our site, in Norfolk, Connecticut. We could find no direct evidence that tree species affect Ca or Sr dry atmospheric deposition. According to Lindberg *et al.* (1986) most of the dry deposition in Temperate forests of the northeastern US is in particles >2 μm in diameter and occurs under the influence of gravity. Assuming similar behavior of Ca and Sr in atmospheric deposition, we therefore believe that atmospheric Sr will not be significantly different among tree species. The isotope ratio of Sr lost from the soil (Sr_O) has been estimated as follows. Since organisms do not differentiate between the two Sr isotopes (Gosz and Moore, 1989), the $^{87}Sr/^{86}Sr$ or $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratio of the living and dead biomass will be indistinguishable and equal to the ratio in the stem wood. Strontium lost from the soil is the sum of leaching plus living and dead biomass storage, so Sr_O can be calculated from a relationship similar to mixing equation (1) using the $^{87}Sr/[^{87}Sr + ^{86}Sr]$ ratios of leaching Sr_L and stem wood Sr_B as the end members:

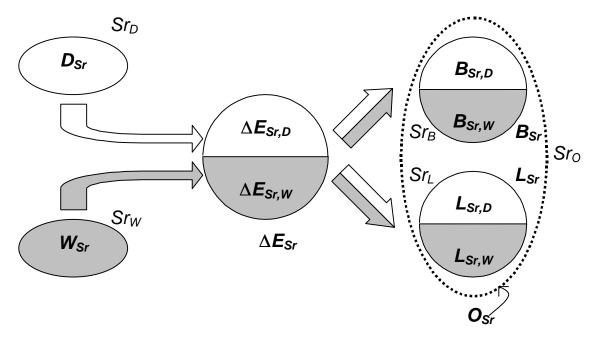$$Sr_O = Sr_L - \frac{B_{Sr}}{O_{Sr}}(Sr_L - Sr_B) \qquad (3)$$

Figure 2. The flow of atmospheric (white) and weathered (gray) strontium through a forest ecosystem. D_{Sr} = atmospheric deposition, W_{Sr} = mineral weathering, ΔE_{Sr} = the net change in the exchangeable soil pool, B_{Sr} = net biomass storage, L_{Sr} = leaching, O_{Sr} = Sr lost from the soil. Sr_x = the Sr isotope ratio in flow X.

In equation (3) O_{Sr} is the Sr lost from the soil and B_{Sr} is the net storage of Sr in the living and dead biomass (in mg m^2 yr^{-1}). When B_{Sr} is relatively small compared to O_{Sr} (i.e. leaching $\gg$ biomass increment) and/or when Sr_L is close to Sr_B, then Sr_O can be substituted with Sr_L (see equation (3)).

Differences in soil mineralogy between sugar maple and hemlock sites were statistically analyzed by t-tests. Linear regression models were fitted for each combination of dependent variable (Ca weathering rate and Sr in wood derived from weathering) and tree species, as a function of the Ca or Sr content (covariate) using the General Linear Model procedure in SPSS (version 7.5). Total Ca, Sr and Ca/Sr ratios in stem wood appeared to be independent of Ca, Sr and Ca/Sr ratio in the soil respectively. To test differences in total Ca, Sr and Ca/Sr ratios measured in stem wood between tree species, Post Hoc one-way ANOVA analyses (Tukey's test) were done.

Results

Soil texture was similar across sites. All soils were high in sand and loam, and showed a small but significant decrease in clay content with depth (Table 1). Soil texture did not differ significantly under different tree species. Besides quartz, alkali-feldspar, plagioclase and biotite were the dominant minerals in soils at the sugar maple and hemlock sites and the variation between sites and with depth was high (Table 2).

The average proportion of alkali-feldspar, plagioclase and biotite (% of total mineral surface area) in the 50- to 500-μm fraction and of biotite
ns: not significant, *: . $P < 0.1$, and **: $P < 0.01$ (t-test).

(cm)	Alkali-feldspar (%) 50-500 μm		Plagioclase (%) 50-500 μm		Biotite (%) 50-500 μm		10-50 μm	
	Acer saccharum	*Tsuga canadensis*	*Acer saccharum*	*Tsuga canadensis*	*Acer saccharum*	*Tsuga canadensis*	*Acer saccharum*	*Tsuga canadensis*
	13.8 (5.3)	13.7 (5.1) ns	15.7 (2.7)	6.9 (1.8) *	6.5 (4.2)	1.3 (0.4) ns	9.1 (3.6)	0.5 (0.2) *
	6.2 (0.4)	13.4 (1.6) *	11.5 (1.6)	3.0 (0.8) **	23.2 (8.7)	3.8 (0.7) *	13.0 (2.1)	7.6 (2.8) ns
	11.4 (1.3)	12.0 (1.8) ns	6.8 (1.3)	4.7 (0.6) ns	12.7 (4.3)	4.7 (0.9) ns	25.6 (4.2)	13.8 (2.4) *

At a given soil depth, the average relative surface areas (% of total mineral surface area) of plagioclase and of biotite in the 50- to 500-μm fraction and of biotite in the 10- to 50-μm fraction were invariably lower beneath hemlock than beneath sugar maple, although differences were not always significant. Biotite surface areas were markedly lower in the 0- to 10-cm soil layer compared to the 20- to 30-cm soil layer.

Table 1. Average sand, silt and clay fraction and organic matter content (%) of the mineral soils at 0- to 10-cm, 20- to 30-cm, and 50- to 70-cm depth (standard error in parentheses, n = 18).

Soil property	Depth		
	0-10 cm	20-30 cm	50-70 cm
Sand (%)	42.2 (2.4)	45.2 (2.5)	46.9 (2.8)
Silt (%)	48.9 (1.8)	50.7 (1.8)	47.1 (2.2)
Clay (%)	8.9 (0.8)	7.5 (0.5)	6.1 (0.7)
Organic matter (%)	15.6 (12.0)	5.0 (2.4)	2.2 (0.7)

The Ca/Sr ratios of the soil from 0- to 20-cm depth were slightly lower than from 50- to 70-cm depth (Figure 3). The Ca/Sr ratios in stem wood were all higher than the ones measured in the soil and in the soil solution at 20-cm depth, but lower than the atmospheric deposition ratios, except for one hemlock sample. The Ca/Sr ratio in stem wood was significantly higher for hemlock than for the other tree species (Table 3), even though they grew in soils with a similar Ca/Sr ratio. All species displayed large but comparable variability in wood Ca concentration, but stem wood of hemlock was significantly lower in Sr concentration than that of other species (Table 3).

The $^{87}Sr/^{86}Sr$ ratios measured in atmospheric deposition showed no significant temporal variation, ranging between 0.70999 and 0.71073 (Table 4) with a weighted average of 0.71021. The $^{87}Sr/^{86}Sr$ ratio in the stem wood and soil water samples varied from 0.71574 to 0.71995 and 0.71550 to 0.72100 respectively (Table 4). The $^{87}Sr/^{86}Sr$ ratio of the soil water was generally comparable to the ratio of the stem wood sample measured at the same site (difference < 0.2%). At one site, stem wood of six individual beech trees was sampled in an area of approximately 15×15 m. Although these trees differed in age between 40 and 130 years, the $^{87}Sr/^{86}Sr$ ratio measured in the stem wood varied only between 0.71627 and 0.71651 (Table 4). The $^{87}Sr/^{86}Sr$ ratios in the bulk soil at 50- to 70-cm depth varied between 0.72069 and 0.72969 while for the individual minerals it varied between 0.71117 (plagioclase) and 0.76438 (muscovite, Table 4).

The proportion of the Sr in the wood derived from weathering was calculated for each site according to equation (1). We used the $^{87}Sr/^{86}Sr$ ratio measured in the bulk soil at 50- to 70-cm depth at each site as the weathering end member for that site. Between 39 and 63% of the Sr in the biomass of all tree species was derived from soil weathering (Figure 4). With three replicates per tree species no significant differences in the weathering derived Sr were observed among tree species. However, there was a significant positive correlation with the Sr content in the soil (P < 0.005). The Ca weathering rate in the rooting zone at each site was estimated by equation (2), again using the $^{87}Sr/^{86}Sr$ ratio measured in the bulk soil at 50- to 70-cm depth at each site as the weathering end member for that site. Strontium atmospheric deposition was 0.42 mg m^{-2} yr^{-1}.
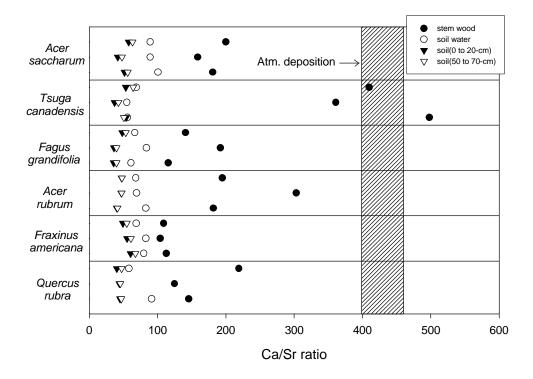
Figure 3. The Ca/Sr ratio in atmospheric deposition, in the soil (0- to 20-cm and 50- to 70-cm depth), soil water and stem wood for each site dominated by one of the six tree species.

Table 3. Average total Ca and Sr content and Ca/Sr ratios measured in stem wood for different tree species (standard error in parentheses, n = 3).

Tree species	Ca ($\mu g\ g^{-1}$)	Sr ($\mu g\ g^{-1}$)	Ca/Sr
Acer saccharum	990 (136) a [a]	5.53 (0.61) a	180 (11.8) a
Tsuga canadensis	943 (73) a	2.25 (0.13) b	423 (40.1) b
Fagus grandifolia	867 (243) a	5.61 (0.61) a	150 (22.3) a
Acer rubrum	1041 (129) a	4.68 (0.33) a	227 (38.3) a
Fraxinus americanum	741 (145) a	6.93 (0.87) a	107 (12.8) a
Quercus rubra	1047 (137) a	5.71 (0.96) a	183 (30.0) a

[a] Different letters indicate significant differences between tree-species ($P < 0.05$) with one-way ANOVA, Post Hoc Tukey test.

We used the Ca/Sr ratio measured in the first 20 cm of the soil as the proportional release of Ca and Sr through weathering (r_{Ca}/r_{Sr}). Because of the old age of the forest stand we expected that there is little net ecosystem production and therefore that the net increment of Sr in the biomass and litter, *B* was small compared to the amount of Sr lost through leaching, *L*.

Table 4. Strontium isotope ratios and Sr concentrations in atmospheric deposition and soil minerals, and ^{87}Sr/^{86}Sr ratios in bulk mineral soil from 50- to 70-cm depth, soil solution from 20-cm depth and stem wood for each site dominated by one of the tree species.

Atmospheric deposition	^{87}Sr/^{86}Sr	Sr (μg l^{-1})	
15 May – 12 Jun 1998	0.70999	0.61	
19Jun – 23 Jul 1998	0.71000	0.28	
21 Aug – 19 Sep 1998	0.71073	0.61	
29 Sep – 17 Oct 1998	0.71033	0.11	
Soil minerals	^{87}Sr/^{86}Sr	Sr (μg g^{-1})	
Quartz	0.72498	1.7	
Alkali-feldspar	0.72999	206.5	
Plagioclase	0.71117	379.4	
Biotite	0.75496	63.8	
Muscovite	0.76438	44.3	
Vermiculite	0.75141	33.7	
Site-species	**Soil**	**Soil solution** ^{87}Sr/^{86}Sr	**Wood**
Acer	0.72680	0.71745	0.71742
saccharum	0.72746	0.71898	0.71995
	0.72564	0.71991	0.71957
Tsuga	0.72816	0.71786	0.71827
canadensis	0.72969	0.71807	0.71867
	0.72963	0.71881	0.71862
Fagus	0.72442	0.71607	0.71574
grandifolia	0.72399	0.71940	0.71789
	0.72150	0.71675	0.71627
			0.71634
			0.71637
			0.71640
			0.71647
			0.71651
Acer	0.72577	0.71691	0.71680
rubrum	0.72491	0.71747	0.71730
	0.72726	0.72100	0.71889
Fraxinus	0.72442	0.71795	0.71840
americana	0.72520	0.71748	0.71667
	0.72069	0.71550	0.71662
Quercus	0.72453	0.71867	0.71870
rubra	0.72713	0.71882	0.71853
	0.72645		0.71797

Furthermore, the ^{87}Sr/[^{87}Sr + ^{86}Sr] ratio in the soil water Sr_L was close to the ratio found in the nearby tree and therefore, according to equation (3), it was possible to substitute Sr_O with Sr_L in equation (2) without creating large errors. We expected that solutions that percolate through these coarse textured soils are well mixed at 20-cm depth and therefore the analyzed ^{87}Sr/^{86}Sr ratio in the soil solution could be used as the ratio for the leaching

water below 20 cm. As with Sr, we did not observe significant differences in the Ca weathering rate in the surface soil among tree species (Figure 5). Rather, the Ca weathering rate significantly increased with total amount of Ca in these soils ($P < 0.001$).
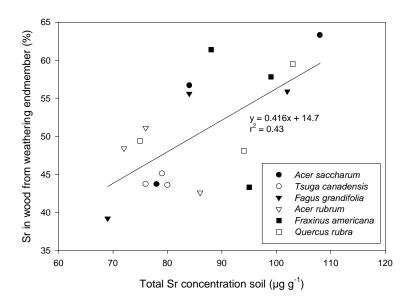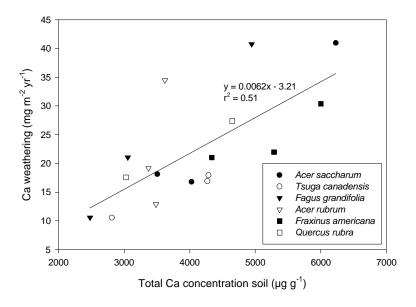

Figure 4. The proportion of Sr in stem wood derived from soil weathering (% of total Sr in wood) as a function of the total Sr concentration in the first 20 cm of the soil for the different tree-species.

Figure 5. The Ca weathering rate in the first 20 cm of the soil as a function of the total Ca concentration in the first 20 cm of the soil for the different tree species.

The sensitivity of the Ca weathering rate (as calculated from equation (2)) to variations in the composition of the weathering end member was evaluated for the sugar maple and hemlock sites. We considered uncertainties about the nature of the composition of the weathering end member (resulting from variable soil mineralogy with depth), and uncertainties about the relative weathering rates of the dominant weatherable minerals. We varied plagioclase:biotite surface area ratios and ratio of Sr weathering rates from plagioclase and from biotite within conceivable limits to obtain different possible weathering end members for each of the sugar maple and hemlock sites. The fact that plagioclase and biotite were quantitatively important weatherable minerals with distinctly different $^{87}Sr/^{86}Sr$ ratios (Table 4), increased the sensitivity of our analysis. Biotite usually weathers faster than plagioclase (Blum *et al*., 1994; Blum and Erel, 1997). First we kept the ratio of plagioclase:biotite Sr weathering rates at 1:3 and varied the overall plagioclase:biotite surface area ratio such that between 80 to 20% of the Sr weathering was with a plagioclase:biotite surface area ratio found in the soil at 0- to 10-cm depth, and the remaining Sr weathering was with a plagioclase:biotite surface area ratio found in the soil at 20- to 30-cm depth. This is labeled as the plagioclase-biotite composition effect (Figure 6A). Next, we calculated the Ca weathering rate when 60% of the Sr weathering was with a plagioclase:biotite surface area ratio found in the 0- to 10-cm surface soil, and 40% with a plagioclase:biotite surface area ratio in the soil at 20- to 30-cm depth, while varying the ratio of plagioclase:biotite Sr weathering rates between 1:1.5 and 1:10. The result is shown as the plagioclase:biotite weathering rate effect in Figure 6B. For all scenarios, the rate of Ca weathering increased on average with the total Ca content in the soil. Dotted lines in Figure 6 show the regression of the average value of Ca weathering at each site with the total Ca concentration in the soil. At all sites the Ca weathering rate decreased as more weathering took place with mineral ratios found at greater depth, and as weathering rates of biotite increased relative to those of plagioclase. The maximum values of Ca weathering that were calculated for sugar maple sites were higher than for hemlock, but not significantly so (P = 0.11 for plagioclase-biotite composition effect and P = 0.13 for weathering rate effect). The minimum values of Ca weathering showed a positive relation with the total Ca concentration in the first 20 cm of the mineral soil (P = 0.10 for plagioclase:biotite composition effect and P = 0.05 for weathering rate effect), but no tree species effect.

Discussion

The heterogeneity of the soil mineral composition between sites and with depth, a common feature of soils formed from glacial deposits, hampered the interpretation of our results. There was a tendency of lower relative surface areas of plagioclase and biotite in soils at 0- to 10-cm and 20- to 30-cm depths beneath hemlock than beneath sugar maple. This pattern could have been caused by the selective force of soil parent material on tree species composition, but could also have been a result of higher soil weathering beneath hemlock. Especially in the first 10 cm of the mineral soil we found indication of more intense weathering beneath hemlock.
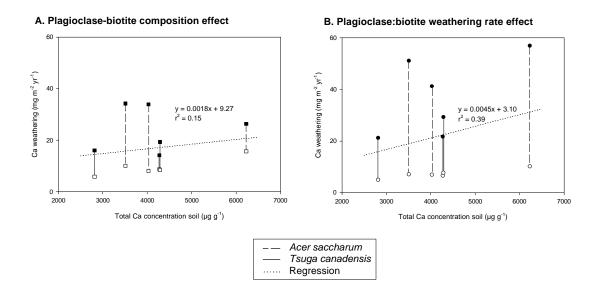
A. Plagioclase-biotite composition effect

y = 0.0018x + 9.27
r² = 0.15

B. Plagioclase:biotite weathering rate effect

y = 0.0045x + 3.10
r² = 0.39

– – *Acer saccharum*
— *Tsuga canadensis*
····· Regression

Figure 6. The relationship between Ca weathering rate and total soil Ca concentration in the first 20 cm of the soil for sugar maple and hemlock sites, calculated by different assumptions about the weathering end member. A. Effects of variations in weathering end member due to different plagioclase-biotite surface area ratios. B. Effects of different ratios of the plagioclase:biotite weathering rates. Vertical lines show the variation on Ca weathering under sugar maple (dashed line) and hemlock (solid line). Open squares: 20% of Sr weathering takes place at 0- to 10-cm depth, and 80% at 20- to 30-cm depth; filled squares: 80% of Sr weathering takes place at 0- to 10-cm depth and 20% at 20- to 30-cm depth. Open circles: plagioclase:biotite weathering rate = 1:10; filled circles: plagioclase:biotite weathering rate = 1:1.5. Dotted lines are the regressions of the average Ca weathering rate at each site with total Ca concentration in the soil. See text for details.

Biotite mineral staining by iron oxide (biotite grains with darker color), as a result of weathering, was more pronounced in the upper 10 cm of the soil beneath hemlock than beneath sugar maple. Optical observations in a 7×7-cm thin section from an undisturbed soil sample beneath hemlock showed complete absence of biotite in the first 3 cm of the mineral soil, and also plagioclase showed more frayed surfaces in the upper centimeters (F.A. Dijkstra, unpublished). Biotite appeared to have higher weathering rates than alkali-feldspar and plagioclase in the upper 10 cm of the soil and may have weathered faster beneath the ectomycorrhizal hemlock than beneath the endomycorrhizal sugar maple. Wallander (2000) showed that tree species associated with ectomycorrhiza stimulated K uptake and biotite weathering. Blum *et al*. (1994) and Blum and Erel (1997) showed that biotite weathered up to eight times faster than plagioclase and up to 21 times faster than alkali-feldspar in young soils (0.4 kyr), but that these differences decreased with soil age. Soils at our sites, developed in Wisconsinian glacial till, are relatively young (younger than 14,000 years, Likens and Davis (1975)) and higher weathering of biotite compared to plagioclase and alkali-feldspar is probable.

   The higher Ca/Sr ratio in stem wood than in soil solution at 20-cm depth beneath all tree species could mean that most of the Ca and Sr is taken up above a depth of 20 cm in soil, where the Ca/Sr ratio in soil solution is probably higher and closer to the Ca/Sr ratio

in atmospheric deposition. The Ca/Sr ratio in stem wood of hemlock, was highest and close to the Ca/Sr ratio in atmospheric deposition. This finding suggests that hemlock utilizes much atmospheric Ca and Sr. Indeed, root length measurements at these sites showed that hemlock had significantly more of its total fine root length in the forest floor and upper 30 cm of the mineral soil than sugar maple (Chapter 6). On the other hand, Poszwa *et al*. (2000) found that spruce (*Picea abies*) preferentially took up Ca over Sr on acid soils in a forest in France. Preferential uptake of Ca over Sr could also explain the relatively high Ca/Sr ratio in stem wood of hemlock.

The weighted average $^{87}Sr/^{86}Sr$ ratio we calculated for the atmospheric end member (0.71021) was slightly higher than the present-day ratio of sea water (0.709198, Hess *et al*., 1986). Our $^{87}Sr/^{86}Sr$ ratios in atmospheric deposition were very similar to those found by others in the northeastern US (Dasch, 1969; Bailey *et al*., 1996; Miller *et al*., 1993). In addition, those earlier studies also showed that the $^{87}Sr/^{86}Sr$ ratio in atmospheric deposition is relatively constant over time. We are therefore confident that the weighted average $^{87}Sr/^{86}Sr$ ratio of 0.71021 is a good approximation of the atmospheric end member.

Similarity between $^{87}Sr/^{86}Sr$ ratios in stem wood samples and in soil solutions implies that the turnover of Sr within the ecosystem was rapid compared to the rate of its addition from either weathering or atmospheric input (Graustein, 1989). The small variation in the $^{87}Sr/^{86}Sr$ ratio of stem wood from closely spaced beech trees, of different age at one of our sites, suggests that there is no significant change in the pool of weathered Sr during the single lifetime of the trees. By contrast, Åberg (1995) concluded that a temporal change in the pool of weathered Sr in the soil was responsible for the variability in the $^{87}Sr/^{86}Sr$ ratio found in different tree rings.

Given the low organic matter content (2.2%) at 50- to 70-cm depth, variation of the $^{87}Sr/^{86}Sr$ ratio in the bulk soil at 50- to 70-cm depth must have been caused by variations in soil mineral concentration. Minerals such as biotite, muscovite (micas) and vermiculite (weathering product of biotite) had much higher $^{87}Sr/^{86}Sr$ ratios than plagioclase.

In assessing the Sr weathering rate according to equation (2), we approached the problem of identifying a weathering end member in two ways. First, in view of the relatively large variation in the Sr isotopic composition of the soils, we used the isotope ratio of total Sr in the soil at 50- to 70-cm depth at each site as the site-specific ratio for the weathering end member. Based on this assumption, between 39 and 63% of the Sr in stem wood of all tree species is derived from soil weathering. Other studies at sites with similar soils gave similar values, between 47 (Miller *et al*., 1993) and 68% (Bailey *et al*., 1996). On soils in Hawaii of different age, between 20 and 90% of wood Sr was attributed to weathering (Chadwick *et al*., 1999). Our Ca weathering rates (between 11 and 41 mg m^{-2} yr^{-1}) are rather low compared to those from other studies in the same region. Bailey *et al*. (1996) estimated a Ca weathering rate of 120 mg m^{-2} yr^{-1} for the Cone Pond Watershed in New Hampshire. The most recent estimate of Ca weathering at the Hubbard Brook Experimental Forest is 228-312 mg m^{-2} yr^{-1} (Likens *et al*., 1998). Lower Ca weathering at our site could be due to different composition and abundance of weatherable minerals in our soils and because our soils are shallower than those at the sites in New Hampshire (S.W. Bailey, personal communication). Further, estimates by Bailey *et al*. (1996) and Likens *et al*. (1998) are based on whole watersheds, where

weathering from deeper unconsolidated material may have contributed to their higher numbers. At current weathering rates, the upper 20 cm of the mineral soil at our sites would be depleted of Ca in 26,000 to 32,000 years.

Both the proportion of Sr in stem wood derived from soil weathering and the Ca weathering rate showed significant positive trends with total Sr and Ca concentration in the soil respectively. The highly significant correlation between total Ca concentration in the first 20 cm of the mineral soil and the plagioclase surface area measured in the first 10 cm of the mineral soil ($r^2 = 0.70$, P < 0.001) suggests that plagioclase is the most important source of Ca weathering in these soils.

Second, because of the large variability in mineralogy with soil depth and likely differences in relative weathering rates among feldspars and biotite, we tested the sensitivity of the calculated weathering rates to the choice of a site-specific weathering end member. Varying the weathering end member based on the measured variability in biotite and plagioclase contents at sugar maple and hemlock sites, and considering different relative weathering rates of these two minerals, we found a relatively large range of Ca weathering rates at each site. However, the maximum calculated Ca weathering rate, 60 mg m^{-2} yr^{-1}, was, relative to other studies, still low. Because a blend of different mineral concentration and relative weathering ratios in the soil would average out the more extreme Ca weathering rates that we calculated here, we believe that the actual Ca weathering rates lie closer to the average than to the extreme values that we calculated. Then again, a positive correlation is observed between Ca weathering rate and the total soil Ca concentration in the first 20 cm of the mineral soil. As regards to species effects on weathering rates, the applied Sr isotope method we used is not sensitive enough to detect significant differences.

Direct mineralogical observations, on the other hand, suggest that under hemlock, biotite has undergone stronger weathering than under sugar maple. If hemlock stimulates biotite over plagioclase weathering more than sugar maple, as suggested from our optical and image analysis (Table 2), then the weathering end member would be at the higher end and the Ca weathering rate at the lower end of our estimates at hemlock sites. This result contradicts our hypothesis that the acidifying hemlock increases Ca weathering in the surface soil. Because of overall slow soil weathering, the stronger weathered character of especially biotite below hemlock may have been the result of more intense biotite weathering over a period of several generations of hemlock trees. The Ca/Sr ratios that we measured in stem wood, atmospheric deposition and soil solution could mean that hemlock utilizes more Ca from atmospheric deposition at the surface of the soil profile than the other tree species. The proportions of Sr in wood derived from atmospheric deposition that we calculated tended to be higher beneath hemlock sites (and would increase if we underestimated the relative weathering of biotite at these sites) than beneath the other tree species, but not significantly.

Conclusions

Optical mineral analysis suggests that biotite weathering in the upper 10 cm of the soil is more intense beneath hemlock than beneath sugar maple. However, with the Sr isotope

study, we were unable to detect significant differences in Ca weathering beneath the six tree species studied here, regardless of a range of assumptions about the weathering end member. Also, regardless of the weathering end member considered, the rate of Ca weathering was low (< 60 mg m^{-2} yr^{-1}) in these acidic soils, and positively related to the total Ca concentration in the surface soil (presumably mainly from plagioclase).

   Organic acid production and increased soil acidity are mechanisms suggested to influence soil weathering. Higher amounts of dissolved organic acids in the soil solution beneath hemlock (Dijkstra *et al.*, 2001) may have caused higher weathering intensities in the upper mineral soil. However, the annual supply of Ca for plant uptake through soil weathering in these acidic soils derived from granitic material, appears to be very low for all tree species. The role of soil organic acids in mineral weathering processes is still controversial. Other studies have also suggested that organic acids have no large effect on the dissolution rates of primary Ca minerals of granitic rocks, but may be more effective on more mafic rock types (Drever and Vance, 1994; Raulund-Rasmussen *et al.*, 1998). Within the sensitivity of our method, this research indicates that the tree species studied here do not have a significant distinct effect on the Ca and Sr weathering rates in acidic surface soils.

Chapter 3

The effect of organic acids on base cation leaching from the forest floor under six North American tree species

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Abstract

Organic acidity and its degree of neutralization in the forest floor can have large consequences for base cation leaching under different tree species. We investigated the effect of organic acids on base cation leaching from the forest floor under six common North American tree species. Forest floor samples were analysed for exchangeable cations and forest floor solutions for cations, anions, simple organic acids and acidic properties. Citric and lactic acid were the most common of the acids under all species. Malonic acid was found mainly under *Tsuga canadensis* (hemlock) and *Fagus grandifolia* (beech). The organic acids were positively correlated with dissolved organic carbon and contributed significantly to the organic acidity of the solution (up to 26%). Forest floor solutions under *Tsuga canadensis* contained the most dissolved C and the most weak acidity among the six tree species. Under *Tsuga canadensis* we also found significant amounts of strong acidity caused by deposition of sulphuric acid from the atmosphere and by strong organic acids. Base cation exchange was the most important mechanism by which acidity was neutralized. Organic acids in solution from *Tsuga canadensis*, *Fagus grandifolia*, *Acer rubrum* (red maple) and *Quercus rubra* (red oak) were hardly neutralized while much more organic acidity was neutralized for *Acer saccharum* (sugar maple) and *Fraxinus americana* (white ash). We conclude that quantity, nature and degree of neutralization of organic acids differ among the different tree species. While the potential for base cation leaching with organic acids from the forest floor is greatest under *Tsuga canadensis*, actual leaching with organic anions is greatest under *Acer saccharum* and *Fraxinus americana* under which the forest floor contains more exchangeable cations than does the strongly acidified forest floor under *Tsuga canadensis*.

Introduction

Soil properties such as pH and the amount of base cations available in the soil may differ greatly under trees of different species. These differences can reflect differences in soil parent material, but can also be caused by differences among tree species (van Breemen *et al.*, 1997).

Trees affect the soil and its formation by producing organic acids in the soil solution. These organic acids are derived from the decomposition of litter and organic matter within the soil and from leaf leaching and leaf washing. Low molecular weight (LMW) organic acids are exuded by soil fungi (Cromack *et al.*, 1979; Malajczuk and Cromack, 1982) and plant roots (see review by Jones, 1998). Organic acidity can be neutralized by exchange with base cations on the cation exchange complex (CEC) and by mineral weathering (e.g. Mulder *et al.*, 1987; Raulund-Rasmussen *et al.*, 1998). In return, the neutralized anions can enhance leaching of base cations from the surface soil (Mollitor and Raynal, 1982; Vance *et al.*, 1986). Evidently those tree species that produce more organic acidity will have a greater potential for base cation leaching. Actual leaching of base cations depends also on the presence of base cations in the surface soil, however.

The organic acidity produced in the forest floor is determined by the concentration and the degree of dissociation and strength of the organic acids. A large fraction of dissolved organic acids in soils are of high molecular weight and are usually referred to as fulvic acids. Little is known about their dissociation properties. Lundström (1993) could describe the organic acids from solutions of a coniferous stand in Sweden as one monoprotic acid. Bergelin *et al*. (2000) identified four groups of organic acids with specific pK_a values from forest soils in Sweden and Finland, and Tipping and co-workers described organic dissociation properties by a combination of intrinsic pK_a values and an electrostatic interaction factor (Tipping *et al*., 1988; Tipping *et al*., 1995). Van Hees *et al*. (2000) showed that the LMW organic acids, although small in concentration, played a significant part in the total acidity of soil solutions. Little is known about the organic acid properties and production in soils for different tree species, though Strobel *et al*. (1999) have found different LMW organic acid concentrations in soil solutions from different vegetation types.

To investigate the role of organic acids, we titrated solutions taken from the forest floor of six tree species and evaluated them by Gran plots (Gran, 1952). Low molecular weight organic acids were determined by the method of van Hees *et al*. (1999). Total dissolved organic carbon (DOC), pH, and ion concentrations were determined. The principal component analysis (PCA) was used to analyse all variables measured in the forest floor solution, together with data of exchangeable cations in the forest floor. In this way we attempted to relate properties of specific organic acids to certain tree species and their importance for base cation leaching.

Materials and Methods

Site description

The 3 000 ha Great Mountain Forest in north-western Connecticut, USA, is on Canaan Mountain, at 300-500 m above sea level. The soils throughout are acidic, well-drained, sandy loams derived from glacial till over mica-schist bedrock. They are poorly developed without a clear eluvial horizon and at most a slightly developed illuvial horizon. Six tree species, namely *Acer saccharum* (sugar maple), *Tsuga canadensis*, Carr. (eastern hemlock), *Fagus grandifolia*, Ehrh. (American beech), *Acer rubrum*, L. (red maple), *Fraxinus americana* (white ash) and *Quercus rubra*, L. (red oak) are common there and we investigated the soil beneath them. The study site is in a second growth stand with a history of logging but no recent history of agriculture. The structure of the forest is simple, with no major shrub or sub canopy tree species. We selected 36 fairly flat sites, six for each species. At each site four to ten mature trees (~80 - 130 years old) of one of the six tree species clustered together were dominating the vegetation.

Sampling and processing

Solutions were sampled from the forest floor. At each site six PVC cylinders (diameter 4.6 cm, height 7 cm) were driven vertically into the forest floor and upper mineral soil.

The cylinders were then removed and capped at top and bottom and brought back immediately to the laboratory where the samples were stored at 4 °C for a maximum of 24 hours. Before centrifuging, any mineral material was removed from the samples which were then centrifuged for 15 minutes at an acceleration of 16 500 × g while maintaining the temperature at 5 °C. Immediately after centrifuging, the samples were filtered through a 0.45-μm filter (Millex-HV, Millipore). The solution was bulked for the six replicates from each site and then divided into two sub-samples. One sub-sample for each site was measured for pH, dissolved organic C, ions and Al speciation as soon as possible. The other sub-sample was deep frozen and analysed later for LMW organic acids and used for titration. Deep freezing of soil solutions appeared to be able to preserve LMW organic acids in soil solutions better than sterile filtration or the use of chloroform (Karlsson *et al.*, 1999).

At 18 sites (three replicates for each tree species) forest floor samples were analysed for exchangeable cations. At each of the 18 sites three PVC cores (diameter 4.5 cm, height 15 cm) were driven into the forest floor and upper mineral soil after removing the fresh litter. In the laboratory the forest floor was separated from the upper mineral soil with a sharp knife and forest floor samples were bulked for each site. Forest floor samples were sieved to pass 8 mm and dried for 48 hours at 105 °C.

Analyses

The pH in the solution was measured with a glass electrode connected to a pH meter (Accumet). Dissolved organic C and inorganic C (HCO_3^-) were determined with a total carbon analyser (Shimadzu TOC 5050). Concentrations of Ca^{2+} and Mg^{2+} in solution were determined with an Inductively Coupled Plasma Emission Spectrometer (Perkin-Elmer) and Na^+ and K^+ with a Graphite Furnace Autosampler (Perkin-Elmer). Total monomeric Al (Al_m) and organic Al (Al_{org}) were determined using the pyrocatechol violet and cation exchange method of McAvoy *et al.* (1992). Inorganic Al (Al_{in}) was calculated as the difference between Al_m and Al_{org}. The concentrations of SO_4^{2-} and Cl^- were determined by ion chromatography (Dionex LC-20) while NH_4^+ and NO_3^- were determined colorimetrically (Alpkem).

The low molecular weight organic acids were determined by HPLC by the method of van Hees *et al.* (1999). Samples were filtered twice through a 1000-D filter (Diaflo YM-1, Amicon), under pressure with N_2 gas at 350 kPa, to remove interfering compounds. Cations were removed by running the sample through a cation exchange column (Bio-Rex 70, 200-400 mesh). A chromatograph (Shimadzu LC-10) with a Supelco C610-H ion exclusion column, with a mobile phase of 2 % H_3PO_4, was used for separation. Oxalic, acetic, fumaric, malonic, formic and propionic acid were determined at 30 °C, while citric, lactic and shikimic acid were determined at 70 °C. These LMW organic acids were considered to be the most common acids in forest soil solutions (van Hees *et al.*, 2000).

For the titration, solutions were first acidified to pH < 2.85 with 1 M HCl and stabilized for 15 minutes at 25 °C. By acidifying the sample, any HCO_3^- present was removed as CO_2. Samples were titrated at 25 °C with 0.01 M NaOH to pH > 10.6. A constant flow of argon was supplied to the sample to remove any atmospheric CO_2 during

the titration. The titrations were performed with an Autoburette system (Metrohm) and a DG 115-SC glass electrode (Mettler Toledo) connected to a HP 34401A Multimeter. The Gran procedure was used to evaluate the amounts of strong and weak acids in the solutions (Molvaersmyr and Lund, 1983). In interpreting the titration results, we assumed that the organically-bound Al recombined with the organic compounds during the titration (Lundström, 1993).

The exchangeable cations from the forest floor samples were measured by extracting 3 g of sample with 30 ml of 0.1 M $BaCl_2$ (Hendershot *et al.*, 1993). Samples were shaken for 2 hours on a shaker table (45 rpm) and then filtered through Whatman Number 41 filter paper. Concentrations of exchangeable Ca^{2+}, Mg^{2+}, K^+, Na^+ and Al^{3+} were measured by Atomic Absorption Spectrometry (Perkin-Elmer). For ten samples exchangeable acidity (exchangeable Al^{3+} and H^+) was measured by titration with 0.01 M NaOH to pH 8.2. After subtraction of exchangeable Al^{3+}, the calculated exchangeable H^+ concentrations were regressed on H^+ concentrations that were calculated from H^+ activities measured in the original $BaCl_2$ extracts with a glass electrode (R^2 = 0.988, P < 0.0001). The exchangeable H^+ of the other samples was then calculated by using this regression on H^+ concentrations calculated from pH measured in the $BaCl_2$ extracts.

To examine differences between tree species, variables were analysed with one-way ANOVA. When there was a significant effect, the post hoc Tukey test was used to compare tree species means. A principal component analysis (PCA) was performed on all the variables measured in solution together with exchangeable pools. To run an ANOVA on the separate variables one at a time could create false impressions. This is because with a limited number of replicates, there is always a risk that a difference is no more than a sampling effect. The chance of judging significance wrongly increases with the number of variables. A better way is to look at all variables simultaneously. To run a PCA, data were first standardized to limit variance. Scores and variable correlations were then computed for the first eight principal components (PCs).

Results

The average concentrations for ions in solution are shown in Figure 1. Sugar maple and white ash had significantly higher pH (one to two units) and larger concentrations of Ca^{2+} and Mg^{2+} (two to three times) than the other tree species (P < 0.05). Calcium and Mg^{2+} were the dominant cations in solution under sugar maple and white ash, while protons were the most important cations in solution under hemlock. Because of the high pH, HCO_3^- was found in most samples of sugar maple and white ash. Bicarbonate was not detected in the other samples. The forest floor under hemlock had significantly more SO_4^{2-} (one and a half to two times) than that under sugar maple, beech, white ash and red oak (P < 0.05). Inorganic Al was significantly more concentrated (two to five times) under hemlock, beech and red maple than under the other species (P < 0.05), while Al_m and Al_{org} were also rich in the forest floor under these species, although not significantly more so than for the other tree species.

Concentrations of NH_4^+ and NO_3^- were small for all tree species. The anion deficit in solution was calculated as the difference between cations and anions where the speciation

of inorganic Al was calculated with the program MINEQL+ (version 2.2, Environmental research software, Edgewater, MD, USA), while organic Al was considered without charge. We expected to attribute the anion deficit to organic anions (Lundström, 1993). The forest floor under all tree species had significant amounts of organic anions (A^-, Figure 1), ranging between 25 and 43% of the total sum of negative charge. Together with SO_4^{2-}, organic anions were the most important anions in solution. Our estimation of organic anions was subject to large errors due to summation of many different components and the uncertainty about the Al speciation.
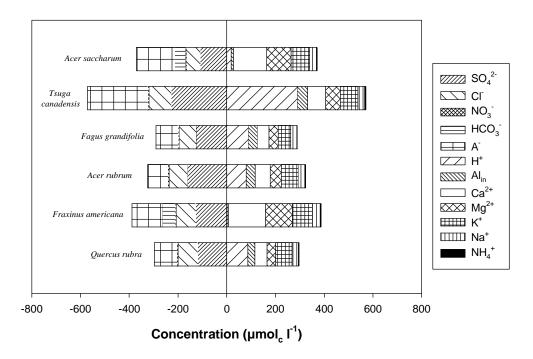

Figure 1. Average ion concentrations of forest floor solutions for the six tree species (A^- stands for organic anions).

The concentrations of LMW organic acids in solution are shown in Table 1. All samples contained citric and lactic acid, which were also the dominant ones. In most samples also oxalic and shikimic acid were detected. Oxalic and shikimic acid can be detected at very small concentrations because of their UV absorbance, which explains why these acids were so often found in solution (van Hees *et al*., 2000). The forest floor under hemlock and beech in particular contained malonic acid in the solution. Propionic acid was not found in any of the samples.

From titration curves of all solutions, the strong acidity (SA, strong acids minus free bases) and weak acidity (WA, sum of weak acids and free bases) were determined using Gran plots (after Molvaersmyr and Lund, 1983). The average strong acidity and weak acidity in the forest floor solutions under the six tree species together with concentrations of dissolved organic C are shown in Table 2.

Table 1. Concentrations of low molecular weight (LMW) organic acids in soil solution for all sites (*bdl* means below detection limit, detection limits for oxalic, citric, shikimic, lactic, acetic, fumaric, malonic and formic acid are 0.1, 2, 0.1, 5, 3.5, 0.1, 1.5 and 3.5 μmol l^{-1} respectively).

Species	Oxalic	Citric	Shikimic	Lactic	Acetic μmol l^{-1}	Fumaric	Malonic	Formic	Sum LMW
Acer	0.1	4.9	0.4	25.3	*bdl*	0.1	*bdl*	*bdl*	30.9
saccharum	0.5	8.4	0.4	13.8	*bdl*	*bdl*	*bdl*	*bdl*	23.1
(Sugar maple)	0.5	11.0	1.1	13.8	*bdl*	0.2	3.2	*bdl*	29.8
	0.4	33.8	2.7	58.8	50.4	0.4	5.2	*bdl*	151.6
	0.1	9.7	0.2	15.1	4.4	*bdl*	*bdl*	*bdl*	29.5
	0.1	8.7	0.3	10.1	4.1	*bdl*	*bdl*	*bdl*	23.4
Tsuga	*bdl*	10.4	3.2	27.2	4.7	0.1	10.9	4.2	60.8
canadensis	0.5	4.7	0.7	19.8	*bdl*	*bdl*	5.2	*bdl*	31.0
(Hemlock)	1.1	8.9	2.6	17.8	12.4	0.2	*bdl*	*bdl*	43.0
	bdl	11.7	18.5	7.0	*bdl*	0.1	39.4	7.2	84.0
	bdl	7.8	2.7	5.9	*bdl*	0.1	7.0	*bdl*	23.5
	1.5	182.1	4.1	57.9	*bdl*	0.1	52.6	9.2	307.5
Fagus	0.3	13.9	0.5	8.4	*bdl*	0.1	2.7	*bdl*	25.9
grandifolia	0.2	10.6	0.2	13.8	*bdl*	0.1	2.9	*bdl*	27.7
(Beech)	0.1	8.2	0.6	14.4	9.8	0.1	9.8	*bdl*	43.1
	0.2	4.7	0.1	5.9	*bdl*	*bdl*	*bdl*	*bdl*	10.9
	0.2	8.7	0.2	17.5	*bdl*	*bdl*	5.0	*bdl*	31.6
	0.5	6.9	0.2	28.7	*bdl*	*bdl*	1.7	*bdl*	38.1
Acer	0.2	3.0	0.5	7.0	*bdl*	*bdl*	*bdl*	*bdl*	10.7
rubrum	0.1	3.5	0.4	12.4	*bdl*	*bdl*	*bdl*	*bdl*	16.4
(Red maple)	0.3	29.8	0.3	7.5	*bdl*	0.1	*bdl*	3.7	41.6
	0.1	10.3	0.4	8.6	*bdl*	*bdl*	*bdl*	*bdl*	19.4
	0.4	6.1	0.3	6.4	*bdl*	*bdl*	*bdl*	*bdl*	13.2
	0.2	5.8	0.3	16.9	*bdl*	0.1	10.1	*bdl*	33.3
Fraxinus	0.2	9.5	0.3	27.3	*bdl*	*bdl*	*bdl*	*bdl*	37.4
americana	0.4	20.4	0.5	35.6	*bdl*	*bdl*	*bdl*	*bdl*	56.9
(White ash)	0.3	9.9	0.4	22.7	*bdl*	*bdl*	*bdl*	*bdl*	33.3
	0.5	2.2	0.1	23.1	*bdl*	*bdl*	*bdl*	*bdl*	25.9
	1.1	2.9	0.1	44.6	*bdl*	*bdl*	*bdl*	*bdl*	48.8
	0.2	4.9	0.1	17.7	*bdl*	*bdl*	*bdl*	*bdl*	22.9
Quercus	0.2	2.9	*bdl*	18.9	*bdl*	*bdl*	*bdl*	*bdl*	22.0
rubra	0.2	3.3	*bdl*	6.1	*bdl*	*bdl*	*bdl*	*bdl*	9.7
(Red oak)	0.1	4.3	*bdl*	11.8	*bdl*	0.1	*bdl*	*bdl*	16.8
	0.2	4.3	0.3	23.4	3.8	0.1	*bdl*	*bdl*	32.1
	0.2	3.5	1.2	12.5	*bdl*	*bdl*	*bdl*	8.8	26.2
	0.1	3.3	0.1	20.0	*bdl*	*bdl*	*bdl*	*bdl*	23.6

Sugar maple, white ash and red oak gave negative values for strong acidity. This indicated that a corresponding amount of free bases (weak acids neutralized by strong base cations) was present in solution. Solutions under sugar maple and white ash contained the most free bases and therefore neutralized the most weak acid. Hemlock was the only tree species with significant amounts of strong acids in solution. Hemlock was also associated with significantly larger concentrations of weak acidity and dissolved organic C than the other species.

Table 2. Averages and standard errors (in brackets, n = 6) of organic and acidic properties of the soil solutions for the different tree species. DOC = dissolved organic carbon, SA = strong acidity, WA = weak acidity and LMW = low molecular weight organic acids. Different letters in each column indicate significant differences between tree species ($P < 0.05$) with one-way ANOVA, post hoc Tukey test.

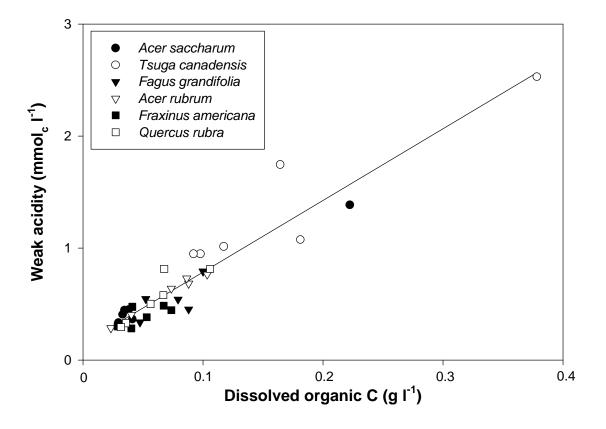| Species	DOC mg l^{-1}	SA µmol$_c$ l^{-1}	WA µmol$_c$ l^{-1}	%LMW of DOC	%LMW of total acidity
Acer saccharum	67 (31) a	-157 (17) a	565 (165) a	3.5 (0.2) bc	12.0 (1.0) ab
Tsuga canadensis	172 (44) b	236 (70) c	1377 (262) b	2.1 (0.5) abc	10.2 (3.6) ab
Fagus grandifolia	71 (9) a	46 (35) bc	531 (61) a	2.0 (0.2) abc	9.4 (0.8) ab
Acer rubrum	69 (13) a	21 (46) ab	585 (79) a	1.7 (0.2) ab	7.0 (1.3) ab
Fraxinus americana	51 (7) a	-174 (52) a	395 (36) a	3.6 (0.8) c	13.7 (2.1) b
Quercus rubra	61 (11) a	-40 (29) ab	555 (93) a	1.6 (0.2) a	5.6 (0.7) a

Figure 2. Weak acidity as a function of dissolved organic C in forest floor solutions for the 36 sites. The regression of weak acidity (*y*) on dissolved organic C (*x*) is shown by the line through the data with equation $y = 6.39x + 0.146$.

A significant correlation was found between weak acidity and total dissolved organic C (Figure 2). The density of weak acid functional groups of the organic C was estimated as the slope of the regression line, being 6.39 mmol$_c$ g^{-1} C, while the intercept of 0.15 mmol$_c$ l^{-1} indicates that some other weak acids were present in solution (e.g. inorganic aluminium). No differences in the density of functional groups of the dissolved organic C were found between tree species. We assumed that the weak acidity contained all the organic acidity in solution, except the first dissociating group of oxalic and citric acid, which were considered as strong acids (van Hees *et al.*, 2000). Total acidity (i.e. mainly organic acidity) was then calculated by adding the oxalic and citric acid concentrations to the weak acidity. The contribution of LMW organic acids to the total dissolved organic C and the total acidity are shown in Table 2. Sugar maple and white ash contained the most LMW organic acids. The contribution of the LMW organic acids to the total acidity was considerably greater than their contribution to dissolved organic C. The largest fraction was under hemlock (26.2%). On average fractions ranged between 5.6% for red oak and 13.7% for white ash.
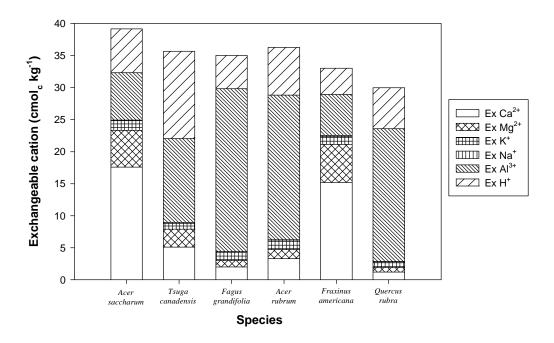

Figure 3. Average exchangeable cation concentrations in the forest floor for the six tree species.

The average concentrations of exchangeable cations from the forest floor are presented in Figure 3. Significant differences were found between tree species for exchangeable Ca^{2+} and Mg^{2+} (P < 0.05) with sugar maple and white ash having the largest concentrations (two to eight times higher than for the other species). This accords with the results of Finzi *et al.* (1998*a*). The forest floor under hemlock had considerable amounts of exchangeable H$^+$ in the forest floor, while that under beech, red maple and

red oak contained the most exchangeable Al^{3+}. We had too few replicates (three) to establish significant differences in exchangeable H^+ and Al^{3+} between tree species.

The principal component analysis was done on all the variables measured in the forest floor. The eigenvalues of the first eight components and their percentage of variance explained are shown in Table 3. The first two components explained most of the variance (37% for the first and 57% with the second). The other components did not improve clustering of samples meaning that the first two components presented the main aspects of differences between sites. The scores and variable correlations of the first two components are shown in Figures 4 and 5 respectively. From Figure 4 it can be seen that the first component divides white ash and most of the sugar maple samples from the other tree species. The second component separates hemlock from beech, red maple and red oak. Concentrations of Ca^{2+}, Mg^{2+}, HCO_3^- and pH and exchangeable Ca^{2+} and Mg^{2+} showed a strong negative correlation and concentrations of dissolved organic C, weak and strong acidity, Al species, SO_4^{2-}, most of the LMW organic acids and exchangeable H^+ showed a strong positive correlation with the first component (Figure 5). Therefore, all these variables had a large influence on the separation of samples by the first component. Exchangeable Al^{3+} showed especially a strong negative correlation with the second component, causing a large influence on the separation of samples by this component.

Table 3. Eigenvalues, percentage of variance explained and their cumulants (in brackets) for the first eight components of the PCA.

Component	Eigenvalues		% of Variance explained	
1	11.1	(11.1)	37.1	(37.1)
2	6.0	(17.1)	19.9	(57.0)
3	2.7	(19.8)	9.0	(66.0)
4	2.0	(21.8)	6.5	(72.5)
5	1.5	(23.2)	4.9	(77.4)
6	1.3	(24.5)	4.4	(81.8)
7	0.7	(25.2)	2.3	(84.1)
8	0.6	(25.9)	2.1	(86.2)

Discussion

Lactic and citric acid were the most common LMW organic acids in all solutions. Both have frequently been detected in solutions and extracts of forest soils (e.g. Fox and Comerford, 1990; Krzyszowska *et al*., 1996; Strobel *et al*., 1999; van Hees *et al*., 2000). Apart from malonic acid, which was specific to hemlock and beech, the organic acids could not be attributed to certain tree species. In general the concentrations of the different LMW organic acids varied much between samples. In the PCA the variable correlation coefficients of the LMW organic acids were all in the same quadrant as the dissolved organic C (Figure 5), suggesting a positive correlation with dissolved organic C. When dissolved organic C was correlated with each individual LMW organic acid, correlations were all significant ($P < 0.05$, Table 4).
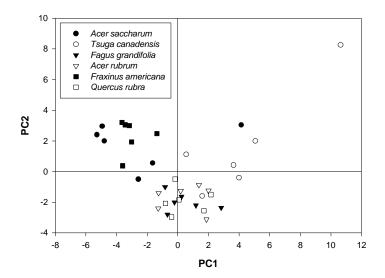
Figure 4. Scores plot of the first two principal components from the PCA of forest floor exchangeable and solution concentration data.
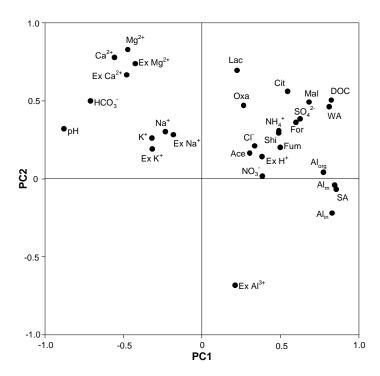

Figure 5. Variable correlation coefficients for the first two principal components from the PCA of forest floor exchangeable and solution concentration data.

Table 4. Pearson correlation coefficients between dissolved organic carbon and low molecular weight organic acids in forest floor solutions for the 36 sites.

LMW organic acid	correlation coefficient	LMW organic acid	correlation coefficient
Oxalic acid	0.44	Acetic acid	0.37
Citric acid	0.81	Fumaric acid	0.53
Shikimic acid	0.49	Malonic acid	0.83
Lactic acid	0.57	Formic acid	0.70

White ash had significantly larger LMW organic acid fractions of the total dissolved organic C and of the total acidity than red oak (Table 2). This could mean that under white ash relatively more LMW organic acids are produced from decomposition than under red oak, but could also indicate that other sources (e.g. root exudation) are responsible for the larger fractions found for white ash. For all samples the LMW organic acid fraction of the total acidity was much larger than the LMW fraction of the dissolved organic C. This is caused by the greater density of carboxyl groups of the LMW organic acids than in the remainder of the dissolved organic C (van Hees *et al*., 2000).

Samples from hemlock contained significant amounts of strong acids in solution. Their presence implies that the forest floor of these samples has little capacity to neutralize incoming acidity. Their presence could also mean that hemlock received more strong acid from the atmosphere than the other species. This accords with the significantly larger amount of SO_4^{2-} that we found under hemlock and with the results of Miller *et al*. (1991) who showed that coniferous tree species capture acidic compounds (e.g. sulphuric acid) from the atmosphere more efficiently than deciduous trees do. However, because there was a considerable amount of organic anions in solution under hemlock (see Figure 1), a substantial part of the strong acidity must be attributed to strong organic acids such as citric and oxalic acid and perhaps other unidentified organic acids. The forest floor under hemlock showed some unidentified peaks in the chromatogram of the HPLC that could possibly be related to aromatic compounds that could not be clearly separated by the method we used. Aromatic compounds were often found in forest litters from coniferous tree species (Vance *et al*., 1986; Pohlman and McColl, 1988). Bergelin *et al*. (2000) found in some soil solutions from coniferous stands in Sweden and Finland strong organic acids with a pK_a value as little as 2.6.

A strong correlation was found between weak acidity and concentration of dissolved organic C (Figure 2). However, no significant differences were found between tree species in the density of functional groups of the dissolved organic C. The average density of 6.39 mmol$_c$ g^{-1} C accords with results of measurements from soil and surface waters by Oliver *et al*. (1983), Cronan and Aiken (1985), Lundström (1993) and Bergelin *et al*. (2000). Henriksen and Seip (1980) concluded that inorganic Al contributed significantly to the weak acid concentrations in lake waters. However, the strong correlation of weak acidity with dissolved organic C that we found suggests that the amount of weak acidity coming from inorganic Al was small compared with the weak acidity from dissolved organic C.

Large amounts of strong and weak acidity under hemlock were not neutralized in the forest floor. Also under beech, red maple and red oak little of the weak acidity was neutralized (positive or slightly negative strong acidity). Low exchangeable base cation concentrations under these tree species (Figure 3) prevented much organic acid neutralization through base cation exchange. The high exchangeable H^+ under hemlock may have been caused by large accumulated inputs of inorganic and strong organic acids in the forest floor.

In the forest floor solutions under sugar maple and white ash the organic anions were mainly compensated with base cations (Figure 1), and solutions contained significant amounts of free bases (high negative strong acidity, Table 2). Most of these bases were considered to be organic anions, because HCO_3^- was removed before the titration started, and $Al(OH)_x$ species were negligible for these samples (according to the MINEQL+ model, data not shown). With large amounts of exchangeable base cations in the forest floor (Figure 3) sugar maple and white ash sites neutralize more organic acidity and consequently leach more base cations from the forest floor than the other sites. Base cations in the forest floor under these species can be re-supplied through uptake from deeper soil layers, followed by mineralization in the forest floor. Unpublished results show that the root density in the sub soil (30-60 cm) is significantly higher under sugar maple than under hemlock, suggesting that the former tree is better able to explore for base cations that are leached into the sub soil.

Conclusions

Organic acids significantly influenced solution chemistry in the forest floor under six common tree species in the Great Mountain Forest of Connecticut. Between 25 and 43% of the negative charge could be attributed to organic anions. For *Acer saccharum* and *Fraxinus americana* these organic anions were balanced mainly by base cations, while for hemlock protons were the most important cation.

The forest floor under *Tsuga canadensis* contained the most dissolved organic C and organic acidity in solution, and organic acids with the greatest strength. Exchange with base cations was most important in neutralizing organic acidity in the forest floor under *A. saccharum* and *F. americana*. The mobility of base cations caused by organic anions to move to deeper soil layers was greater for these two species than for the others. Under *Tsuga canadensis*, *Fagus grandifolia*, *Acer rubrum* and *Quercus rubra* much of the organic acidity remained un-neutralized in the forest floor. Exchangeable bases are also present in small concentrations in the upper mineral soil under these species (Finzi *et al*., 1998*a*), and so other mechanisms such as weathering under release of Al (e.g. Mulder *et al*., 1987), decomposition (Lundström *et al*., 1995) and adsorption and precipitation of organic acids with or without Al (Ugolini *et al*., 1979; Driscoll *et al*., 1985) are probably involved in neutralizing organic acids under these species.

Acknowledgements

Chapter 4

Aluminum solubility and mobility in surface soils affected by different tree species.

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Abstract

The effects of tree species on aluminum solubility and mobility in surface soils were studied by comparing solid and aqueous Al concentrations in soil under each of six tree species: sugar maple (*Acer saccharum*), hemlock (*Tsuga canadensis*, Carr.), American beech (*Fagus grandifolia*, Ehrh.), red maple (*Acer rubrum*, L.), white ash (*Fraxinus americana*) and red oak (*Quercus rubra*, L.). In forest floors, exchangeable Al showed no clear relationship to pH, and was low under sugar maple (pH 4.9) and hemlock (pH 3.9), and high under beech and red maple (pH 4.4). Apparently high supply of dissolved organic acids (under hemlock) and mineralized Ca (under sugar maple) depresses exchangeable Al in forest floors. The DOC under all species appeared to have a similar capacity to bind dissolved Al. However, that capacity was not saturated at high DOC concentrations, as under the forest floors of hemlock and red oak. Particularly under hemlock, low pH and high concentrations of organic acids percolating from the forest floor helped to dissolve Al from soil minerals, and more dissolved organic Al (Al_{org}) moved to deeper soil layers under hemlock than under the hardwood species. Despite pronounced differences in dissolved Al among species, no significant differences were found in the concentrations of pyrophosphate extractable Al pools in mineral soil (Al_{pyr}; presumably solid organically bound Al) among tree species at different depths. The age of the tree stands was probably too young to have caused pronounced effects on Al migration and redistribution in the soil.

Introduction

Tree species have been found to affect Ca availability in surface soils in a temperate forest in northwestern Connecticut, USA (Finzi *et al*., 1998*a*). Calcium and Al concentrations in soils and soil solutions are interrelated through exchange reactions. A mechanism that could affect the Ca availability in the soil is the displacement of Ca on the exchange complex by Al in soil solution (Lawrence *et al*., 1995). The displaced Ca is then prone to leach out of the soil with drainage water. Low Ca concentrations in the soil solution may enhance the phytotoxicity of dissolved Al (e.g. McCormick *et al*., 1978; Schier, 1985; Asp *et al*., 1988; Ulrich, 1989).

The ion Al^{3+} is considered to be most toxic for plants (Asp *et al*., 1988; Parker *et al*., 1988). Complexes of Al with organic compounds (both in solid and dissolved form) suppresses concentrations of Al^{3+} in soil solutions and are believed to reduce Al toxicity (Bartlett and Riego, 1972; Hue *et al*., 1986). Binding to solid organic matter may control dissolved Al^{3+} in surface soils, most notably at high concentrations of organic matter (Bloom *et al*., 1979; Mulder *et al*., 1989*a*; Walker *et al*., 1990; Berggren and Mulder, 1995; Wesselink *et al*., 1996). These strong Al complexes may also be less competitive for cation exchange with Ca^{2+} than Al^{3+} because of their less favorable charge properties. Organic Al bound to DOC that is resistant to (rapid) degradation is able to migrate to deeper soil layers where adsorption of DOC and co-precipitation of Al with DOC may occur (Ugolini and Dahlgren, 1987).

Tree species differ in their effect on soil organic matter pools and DOC concentrations (David and Driscoll, 1984; Binkley, 1996; Finzi *et al*., 1998*b*), and therefore influence the solid and dissolved organic binding of Al. As a consequence, tree species may affect the solubility and mobility of Al in the soil. We are not aware of previous studies investigating the influences of tree species on soil solution chemistry of Al. To identify the effect of tree species on Al solubility and mobility, cation exchangeable pools (BaCl$_2$ extraction) and Al extractable pools (Na pyrophosphate extraction) in the soil and cation concentrations in soil solution were compared among different tree species at different depths. Factors controlling the binding of Al to organic compounds were determined to estimate their importance on Al speciation and mobility for each tree species.

Materials and methods

Study site

The study area was the Camp Pond watershed (~ 25 km^2) at Great Mountain Forest (GMF), a mixed hardwood forest (elevation 300 - 500 m) located in the northwestern part of Connecticut (Canham *et al*., 1994). The study site at GMF is in a second growth (~80 - 130 yr. old) stand with a history of logging but no recent history of agriculture. The most common tree species were sugar maple (*Acer saccharum*), hemlock (*Tsuga canadensis*, Carr.), American beech (*Fagus grandifolia*, Ehrh.), red maple (*Acer rubrum*, L.), white ash (*Fraxinus americana*) and red oak (*Quercus rubra*, L.) which were also the tree species used for this study. The soil in the Camp Pond watershed is an Inceptisol (Dystrochrept) that does not show signs of incipient podzolization. The soils of the sites were similar in texture (sandy loams) and total Al content (F.A. Dijkstra, unpublished data, 1998). We selected six sampling sites dominated by a cluster of 4 to 10 mature trees for each of the six studied tree species, giving a total of 36 study sites.

Sampling

In the summer of 1997 tension lysimeters (Rhizon SMS, Eijkelkamp) were installed at each sampling site at two depths, 0 cm (the boundary between the forest floor and mineral soil) and 20 cm deep. A small pit was dug and at each depth 6 lysimeters were pushed into the sidewall, (minimum distance between two lysimeters was 10 cm) and the pit was backfilled. The lysimeters, 10 cm long with a diameter of 0.5 cm, consisted of a hydrophilic porous polymer sheath fitted around a stainless steel wire and connected to PVC tubing. Soil solutions were obtained by connecting vacuumed bottles (40 kPa) to the PVC tubes. Three lysimeters were connected to one bottle so that solutions were sampled in duplicate at each depth. Soil solution samples were collected during the spring of 1998 and 1999 and stored before analyses at 4 °C in the dark. All materials for solution sampling were cleaned in 50% hydrochloric acid before use. In the summer of 1998 at each sampling site, forest floor and mineral soil from 0- to 5- and 10- to 20-cm depth were sampled at three locations in the vicinity of the lysimeters. At each location,

two cores (length: 15 cm, diam.: 4.5 cm) were pounded into the soil. From the first core the forest floor and the first 5 cm of the mineral soil were sampled, while the second core contained the 10-to 20-cm sample. Forest floor samples were separated from the mineral soil with a sharp knife. The samples from the three sampling locations at each site were then bulked.

Analyses

Soil solutions were analyzed for pH (glass electrode, Orion 610A), Ca, Mg, K and Na (AAS Perkin Elmer AA 300) and DOC (Total Carbon Analyzer, Shimadzu 5050). Total monomeric Al (Al_m) and organic Al (Al_{org}) were measured colorimetrically by a technique utilizing pyrocatechol (McAvoy *et al*., 1992). The Al_{org} was separated from inorganic Al (Al_{in}) by cation exchange chromatography (Driscoll, 1984). Inorganic Al was calculated as the difference between Al_m and Al_{org}. All analyses were completed within 3 weeks after sampling, with pH being measured immediately after sampling. Forest floor and mineral soil samples were dried for 48 h at 105°C and sieved (through 8- and 2-mm mesh respectively) to remove roots and stones. Exchangeable cations were extracted with 0.1 M $BaCl_2$ (Hendershot *et al*., 1993). A 0.5 g subsample of the homogenized forest floor and a 3 g subsample of the mineral soil with 30 ml of 0.1 M $BaCl_2$ was placed on a shaker table at 45 rpm for 2 h. The suspensions were centrifuged at 2000 rpm for 15 minutes, extracts were filtered through Whatman 41 filter paper and Ca, Mg, K, Na and Al were measured by AAS. For Ca and Mg the extracts were diluted 10 times with 1.11% aqueous $LaCl_3$, and for K and Na 10 times with 0.63% aqueous CsCl. Exchangeable acidity was measured for 10 samples by titration with 0.01 M NaOH to pH 7.8 (Buurman *et al*., 1996). Exchangeable H was calculated by subtracting exchangeable Al and these concentrations were regressed with H concentrations that were calculated from H activities measured with a glass electrode ($P < 0.001$, $r^2 = 0.988$). For all other samples exchangeable H was estimated from the pH of the $BaCl_2$ extract using this regression. Pyrophosphate extractable Al (Al_{pyr}) was obtained by shaking 1 g of the forest floor or mineral soil sample overnight with 100 ml of 0.1 M Na pyrophosphate (Buurman *et al*., 1996). In the extracts superfloc was added before centrifuging at 2500 rpm for 15 minutes. Extracts were then filtered through Millipore filters (VSWP, 0.025 μm) before analyses of Al by AAS. Total C of ground samples was measured for the forest floor and mineral soil samples with the Elemental Analyzer (Fisons Instruments, EA 1108).

One-way analysis of variance was performed on soil and solution data for each soil depth separately (SPSS, version 7.5). Tukey's Post-Hoc test was used to separate the means of cation contents in soil and solution among tree species at a 0.05 significance level. For the solution data, the average cation concentrations from the two lysimeters at each site and soil depth were taken. The variance of the solution concentrations from the two lysimeters at a given depth and site did not differ significantly from that between tree species (nested ANOVA with tree species as a fixed factor and lysimeters as a random factor).

Results

Mean pH and concentrations of Ca and DOC differed significantly among tree species at both depths, while mean concentrations of Al_m, Al_{org}, and Al_{in} differed significantly at 20-cm depth (Table 1). Only the results from spring 1999 are presented, as results from spring 1998 showed the same trends. The mean pH was significantly lower for hemlock than for sugar maple and white ash at both depths. At 0-cm depth, the mean Ca concentration for sugar maple was significantly greater than for beech, red maple, and oak. At 20-cm depth, the mean Ca concentration for sugar maple was significantly greater than all other species, except ash; in addition, the mean Ca concentration for ash was significantly greater than for beech. At 20-cm depth, the mean Al_{org} concentration was significantly greater for hemlock than for sugar maple, red maple, and ash, while the mean Al_{in} was significantly greater for hemlock than for sugar maple. At 0-cm depth, the mean DOC concentration for hemlock was significantly greater than for sugar maple, beech, red maple, and ash, while at 20-cm depth, the mean DOC concentration for hemlock was significantly greater than for ash.

Concentrations of exchangeable cations showed similar results as cation solution concentrations (Table 2). Mean exchangeable Ca in the forest floor was significantly greater under sugar maple than under hemlock, beech, red maple, and oak, at 10- to 20-cm depth it was greater under sugar maple than all other species. Exchangeable Al in the forest floor was greater under beech and red maple than sugar maple, while exchangeable Al in the 0- to 5-cm mineral soil was greater under hemlock than sugar maple. In 10- to 20-cm mineral soil, exchangeable Al was greater under hemlock than sugar maple, beech, red maple, and ash. Exchangeable H in the forest floor was greater under hemlock than sugar maple and ash. The effective CEC (CEC_e) in the forest floor was greater under sugar maple than oak; the CEC_e in 10- to 20-cm mineral soil was greater under hemlock and sugar maple than beech. The Al saturation in the forest floor was greater under beech, red maple, and oak than sugar maple, while Al saturation in 0- to 5-cm mineral soil was greater under beech than sugar maple. The Al saturation at 10- to 20-cm mineral soil was lower under sugar maple than all other species while ash was also significantly lower than hemlock. In the forest floor total C was greater under hemlock than sugar maple and ash.

At 20 cm dissolved Al_{org} had a significant linear positive relationship with DOC ($r^2 = 0.914$, P < 0.001, Figure 1). A significant linear positive relationship between Al_{pyr} and total C was evident at 10- to 20-cm depth ($r^2 = 0.667$, P < 0.001, Figure 2). Both in solution and in the solid phase, less Al was organically bound per amount of carbon in the upper layers (Figures 1A, 2A and 2B). At 0 cm dissolved Al_{org} could be better described as a function of DOC, Al_{in} and pH than of DOC alone. The following regression was applied on $-^{10}$log transformed data:

$$pAl_{org} = 2.50 + 0.837pDOC + 0.343pAl_{in} - 0.183pH \qquad r^2 = 0.775, P < 0.001 \qquad (1)$$

with Al_{org} and Al_{in} expressed in mol l^{-1} and DOC in g l^{-1}. Although pH contributed significantly to the regression (P = 0.007) the r^2 improved only slightly from 0.737 to 0.775.

. The average pH, Ca, monomeric Al (Al_m), organic Al (Al_{org}), inorganic Al (Al_{in}) and DOC concentration in solutions from 0- and 20-cm depth, sampled in Tukey test.

pH	Ca	Al_m	Al_{org}	Al_{in}	DOC
		µmol l^{-1}			mmol l^{-1}
4.88 (0.20) b	41.9 (10.4) b	10.2 (2.5)	6.6 (2.1)	3.6 (0.9)	0.92 (0.27) a
3.89 (0.21) a	19.9 (5.2)ab	28.2 (7.3)	15.3 (2.9)	12.9 (5.5)	3.63 (0.96) b
4.46 (0.12)ab	11.9 (2.8) a	23.1 (3.0)	11.4 (3.0)	11.7 (3.0)	1.10 (0.33) a
4.38 (0.22)ab	12.8 (5.4) a	20.4 (3.6)	8.8 (2.8)	11.6 (6.4)	1.15 (0.50) a
4.77 (0.08) b	23.5 (5.3)ab	21.6 (4.1)	11.3 (2.1)	10.3 (2.1)	0.86 (0.10) a
4.31 (0.17)ab	11.7 (3.4) a	23.3 (3.4)	9.0 (1.6)	14.9 (3.8)	1.43 (0.53)ab
5.22 (0.21) b	31.2 (6.4) c	10.1 (4.6) a	2.2 (0.9) a	7.9 (3.9) a	0.33 (0.08)ab
4.41 (0.14) a	9.0 (1.0)ab	40.0 (5.7) b	8.4 (1.8) b	31.6 (6.8) b	0.52 (0.07) b
4.69 (0.07)ab	7.1 (2.5) a	28.2 (3.3) b	3.7 (0.6)ab	24.5 (3.7)ab	0.30 (0.05)ab
4.76 (0.03)ab	9.5 (1.5)ab	28.9 (5.6)ab	2.6 (0.5) a	26.3 (5.3)ab	0.24 (0.03)ab
4.96 (0.10) b	23.4 (5.1)bc	17.5 (3.6)ab	2.3 (0.2) a	15.2 (3.5)ab	0.22 (0.01) a
4.70 (0.06)ab	7.9 (1.9)ab	28.3 (1.1) b	4.2 (1.4)ab	24.1 (2.0)ab	0.34 (0.10)ab

. Average exchangeable Ca, Al and H, CEC_e, extractable Al (Al_{pyr}), Al saturation (Exch. Al/CEC_e), and total C in the forest floor and mineral soil Tukey test.

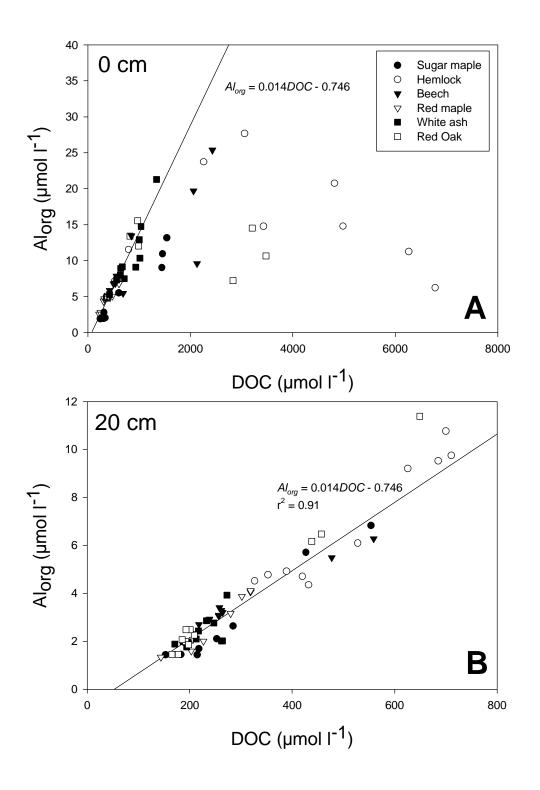| Exch. Ca	Exch. Al	Exch. H	CEC_e	Al_{pyr}	Exch. Al /CEC_e	Total C
cmol$_c$ kg^{-1}				mol kg^{-1}	%	mol kg^{-1}
24.4 (7.6) b	6.1 (1.9) a	7.1 (2.3) a	46.6 (7.6) b	0.17 (0.06)	15 (4) a	37.4 (1.5) a
5.4 (1.1) a	8.8 (4.5)ab	18.7 (3.2) b	37.1 (0.8)ab	0.17 (0.13)	24 (12)ab	43.6 (0.7) b
1.6 (0.4) a	20.5 (3.7) b	8.7 (2.6)ab	33.5 (1.4)ab	0.32 (0.10)	60 (10) b	41.2 (0.5)ab
2.9 (1.2) a	22.2 (3.2) b	8.7 (2.1)ab	36.5 (2.0)ab	0.41 (0.15)	62 (10) b	39.9 (1.5)ab
12.7 (2.9)ab	11.5 (2.8)ab	4.3 (0.8) a	34.3 (2.2)ab	0.38 (0.09)	34 (9)ab	37.5 (2.0) a
1.5 (0.4) a	17.3 (2.8)ab	8.9 (2.8)ab	29.5 (2.9) a	0.36 (0.16)	61 (10) b	39.2 (1.1)ab
7.0 (4.6)	4.6 (1.1) a	1.2 (0.4)	15.4 (5.1)	0.30 (0.08)	44 (11) a	12.9 (2.3)
0.9 (0.2)	10.9 (1.7) b	3.7 (0.9)	16.6 (2.0)	0.34 (0.14)	65 (6)ab	21.7 (4.3)
0.2 (0.04)	7.0 (0.5)ab	1.7 (0.5)	9.4 (0.6)	0.24 (0.06)	76 (5) b	12.5 (0.8)
1.0 (0.8)	7.6 (0.8)ab	2.1 (0.8)	11.6 (1.5)	0.36 (0.12)	70 (9)ab	18.1 (3.3)
2.1 (0.6)	7.8 (1.1)ab	1.0 (0.3)	12.0 (1.9)	0.50 (0.16)	66 (2)ab	17.3 (2.7)
0.3 (0.1)	5.8 (0.5)ab	2.3 (0.8)	9.0 (1.1)	0.28 (0.11)	68 (7)ab	17.1 (5.2)
3.2 (0.7)b	2.9 (0.3) a	0.5 (0.2)	7.7 (1.0) b	0.36 (0.07)	40 (6) a	7.2 (0.8)
0.1 (0.04)a	6.5 (1.2) b	0.9 (0.2)	7.7 (1.4) b	0.20 (0.03)	85 (2) c	4.7 (0.3)
0.1 (0.02)a	3.1 (0.4) a	0.5 (0.03)	3.7 (0.4) a	0.40 (0.05)	83 (1)bc	5.2 (0.5)
0.1 (0.05)a	3.5 (0.7) a	0.6 (0.1)	4.2 (0.8)ab	0.30 (0.07)	83 (2)bc	4.7 (1.0)
0.6 (0.3)a	2.7 (0.3) a	0.4 (0.03)	4.0 (0.4)ab	0.45 (0.09)	69 (6) b	6.8 (1.2)
0.1 (0.04)a	4.2 (0.7)ab	0.8 (0.3)	5.3 (1.0)ab	0.30 (0.11)	82 (2)bc	4.9 (1.1)

Figure 1. Organic Al in solution (Al$_{org}$) as a function of dissolved organic carbon (DOC) for six different tree species at two depths. A: 0 cm; B: 20 cm.
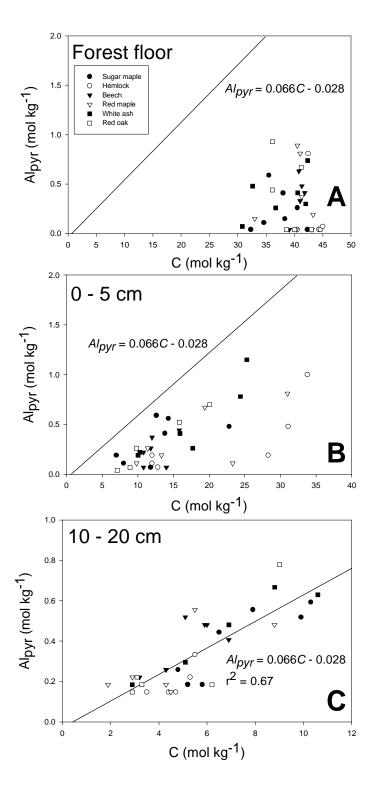
Figure 2. Sodium pyrophosphate extractable Al (Al$_{pyr}$) as a function of the carbon content (C) in the soil for six different tree species at three depths. A: Forest floor; B: 0-5 cm; C: 10-20 cm.

Discussion

The fairly narrow linear relationship between Al_{org} and DOC at 20 cm for all sites, suggests that DOC was saturated with Al at this depth and had the same complexation capacity for Al under all species. At 0 cm Al_{org}/DOC ratios had an upper limit similar to those at 20-cm depth, but tended to decrease with increasing DOC concentrations, most notably under red oak and hemlock. At 0 cm, especially DOC and Al_{in} seemed to control the formation of Al_{org} (Eq. (1)). The pH had only a slight influence. Lazerte (1989) also found only a slight pH effect on Al_{org} at high DOC concentrations. The lower Al_{org}/DOC ratios at relatively high DOC values just below the forest floor might reflect a lack of available Al present to bind with DOC. When moving downward through the soil profile more Al becomes available to bind with DOC. In these young soils, relatively high in weatherable minerals, this Al is presumably released from (aluminum silicate) minerals.

Because DOC concentrations were much lower at 20 cm than at 0 cm, DOC must be precipitated, be adsorbed, or be decomposed during downward migration. The Al_{org} associated with such DOC will precipitate as secondary solid Al phases (organic or inorganic), remain in solution as inorganic Al, or enter the adsorption complex. The higher DOC and Al_{org} concentrations suggest that migration of dissolved Al_{org} from the surface soil to deeper soil layers is more enhanced under hemlock than under the other tree species.

The Al extracted with Na pyrophosphate (Al_{pyr}) was used to compare the distribution of organic Al in the soil affected by tree species. We assumed that the Na pyrophosphate extracted Al solid organically bound Al with only small amounts of amorphous Al hydroxides (McKeague, 1967). The Al_{pyr} showed a large variation without significant differences among tree species in the different soil layers. Other studies used Al_{pyr} and other extraction methods to compare the effect of coniferous and deciduous tree species on the podzolisation process and the distribution of organic Al complexes in the soil (De Kimpe and Martel, 1976; Herbauts and De Buyl, 1981). Organic Al in the spodic B horizon in soils in southeastern Quebec and Maine was higher under the coniferous forest (fir and spruce) than under sugar maple and beech (De Kimpe and Martel, 1976). Herbauts and De Buyl (1981) observed incipient podzolization under an 80-year old spruce and not under much older beech forest in the Belgian Ardennes, but without differences in Al_{pyr}. The period of time that the spruce stand could have influenced the distribution of organic Al in the soil was probably too short to observe significant differences. Also at our study sites trees were not older than 130 years and the identity of previous tree species grown on the sites are unknown. Therefore, the large variation in Al_{pyr} found at our sites may partly be related to differences in the vegetation history of each site and partly to mechanical disturbances, such as windthrows, and bioturbation by soil fauna.

The maximum yearly migration of Al by DOC between 0- and 20-cm depth was estimated by multiplying the decrease in DOC concentration between solutions from 0- and 20-cm depth with the maximum Al complexation capacity of the DOC (regression line in Figure 1C), and with water fluxes that were calculated with a hydrologic model (Brook90; Federer, 1995). The Al migration was then calculated as 5.7 and 6.3 mmol m^{-2} yr^{-1} under sugar maple and white ash respectively while this was 21 mmol m^{-2} yr^{-1} under hemlock. The average pool of Al_{pyr} in the first 20 cm of the mineral soil ranged between

35 and 62 mol m^{-2}. These calculations suggest that even if all the migrated Al was transformed to Al$_{pyr}$ in the soil, formation of Al$_{pyr}$ in the first 20 cm of the soil must have taken several thousands of years.

Significant differences were found among tree species in the exchangeable Al pools in the different soil layers. Hemlock showed increased amounts of exchangeable Al at 0 to 5 and 10 to 20 cm in the mineral soil. Increased levels of exchangeable Al in the mineral soil may have originated from Al release after DOC decomposition, but also from increased Al dissolution induced by a low soil pH (Mulder *et al.*, 1987, 1989*b*; Dahlgren *et al.*, 1990; Van Grinsven *et al.*, 1992). Hemlock had the lowest pH in soil solution at 20-cm depth (Table 1). Exchangeable Al at 10-20 cm decreased with increasing solution pH at 20-cm depth (P = 0.001, Figure 3). In the forest floor exchangeable Al showed no relationship with pH. Exchangeable Al was especially high for beech, red maple and red oak. This contrasts with other studies where Al pools in the forest floor under coniferous stands were higher than under hardwood stands (Messenger *et al.*, 1978; David and Driscoll, 1984). High Al pools in the forest floor are ascribed to Al biocycling via plants and via ectomycorrhiza, capillary rise of dissolved Al, and incorporation of mineral grains by various processes (Messenger *et al.*, 1978; David and Driscoll, 1984; Lawrence *et al.*, 1995; Rustad and Cronan, 1995; Giesler *et al*, 2000; Van Breemen *et al* 2000). In our study protons occupied most of the CEC$_e$ of the forest floor under hemlock (Table 2). The source of exchangeable H is probably from organic acids that are constantly produced in the forest floor under hemlock (Dijkstra *et al.*, 2001). In the absence of Al dissolution in the forest floor protons were then able to occupy most of the exchange sites.
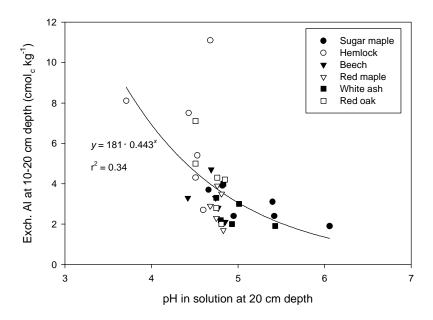

Figure 3. Exchangeable Al at 10-20 cm depth as a function of pH in soil solution at 20-cm depth for all sites.

Conclusions

The capacity of DOC to bind dissolved Al was similar under the six tree species and DOC became more saturated with Al while moving deeper in the soil. Concentrations of DOC and Al_{org} were higher for hemlock than for the other tree species, causing higher Al migration to deeper soil layers for this tree species. However, no differences in the pyrophosphate extractable Al pools were detected between tree species. Compared to other processes such as bioturbation and mechanical disturbances, Al migration with DOC appeared to be too slow of a process to show significant tree species effects. Because of limited supply of Al and high acid production in the forest floor, protons occupied a significant portion of the CEC_e under hemlock. Exchangeable Al was especially high in the forest floor under beech, red maple and red oak while Ca was an important cation on the CEC_e of sugar maple and white ash. In the mineral soil low pH may have caused increased mineral Al dissolution resulting in high exchangeable Al pools for hemlock.

Acknowledgments

Chapter 5

Calcium mineralization in the forest floor and surface soil beneath different tree species

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Submitted to *Plant and Soil*

Abstract

The immediate availability of calcium (Ca) in forest ecosystems is largely dependent on mineralization of Ca in organic form, which may differ significantly among tree species. I estimated *in situ* net Ca mineralization in the forest floor and upper 15 cm of mineral soil beneath six tree species in Great Mountain Forest, a mixed-species forest in northwestern Connecticut using the buried bag method. Net Ca mineralization in the forest floor was significantly correlated with mass loss of the decomposing forest floor litter. Higher mass loss fractions during the summer and in forest floors beneath sugar maple (*Acer saccharum*) and white ash (*Fraxinus americana*) coincided with higher net Ca mineralization rates. More Ca was released per unit mass loss of forest floor beneath sugar maple and white ash than beneath red maple (*Acer rubrum*), American beech (*Fagus grandifolia*), red oak (*Quercus rubra*) and hemlock (*Tsuga canadensis*). This pattern was attributed to differences in Ca content of the incoming litter. The more recalcitrant litters of red maple, beech, red oak, and hemlock may have formed binding sites that immobilize Ca during decomposition, further reducing the net Ca mineralizaton per amount of decomposed forest floor. Due to the high forest floor mass beneath red maple, beech, red oak, and hemlock, net Ca mineralization in the forest floor (mmol m^2) beneath these tree species did not differ from sugar maple and white ash. Net Ca mineralization in the mineral soil was substantial beneath sugar maple and white ash and significantly higher than beneath the other tree species. These results show the importance of measuring Ca mineralization over the entire forest floor and upper mineral soil.

Introduction

The importance of Ca as a nutrient in temperate forests of the northeastern United States has been well demonstrated by several studies that reported decreased primary production, and increased canopy dieback because of Ca deficiencies (Likens *et al*., 1996, 1998; Wilmot *et al*., 1995, 1996). Net Ca mineralization from decomposing litter is one of the highest Ca fluxes within temperate forest ecosystems and determines to a large extent the immediate Ca availability for plant uptake in these systems. A few studies have attempted to quantify net Ca mineralization rates of fresh litter by using litter bags and measuring concentrations and absolute amounts of Ca in decomposing litter. While some studies showed a net release of Ca closely related to weight loss (Attiwill, 1968; Gosz *et al*., 1973) indicating that Ca is a structural litter component, others found Ca immobilization during the first years of litter decomposition (Bockheim *et al*., 1991; Van Wesemael, 1993). Calcium immobilization can occur through strong binding of Ca on sites that are created in litter during decomposition (Staaf and Berg, 1982; Van Wesemael, 1993). Different parts of litter have different rates of decomposition and of net Ca mineralization. Thomas (1969) showed that Ca and weight loss of decomposing leaves, fruits, and twigs of dogwood trees (*Cornus florida* L.) proceeded at considerably different rates, influencing the overall net Ca mineralization in magnitude and time. No

studies have been done to estimate net Ca mineralization from the combined organic matter accumulated in forest floor and surface soil.

Rates of weight loss of litter vary widely between northeastern US tree species (e.g. Aber *et al*., 1990; Melillo *et al*., 1982). Species with slow rates of litter decomposition accumulate significantly thicker forest floors beneath their crowns (Finzi *et al*., 1998*b*), and it is unclear whether total net Ca mineralization from the forest floor and upper mineral soil organic matter will vary significantly beneath different tree species. I estimated *in situ* net Ca mineralization beneath five temperate hardwood and one coniferous tree species by measuring changes in exchangeable Ca from forest floor and surface soil samples incubated in plastic bags that were buried in the field. In this manner I was able to estimate for each tree species the actual amount of Ca that becomes available for plant uptake during litter decomposition.

Methods

Study site

This study was done at Great Mountain Forest (GMF) in northwestern Connecticut. It is a second growth forest stand (~80 - 130 yr. old) that has experienced some logging activities but no recent history of agriculture. Soils are acidic, well-drained, sandy loams derived from glacial till over mica-schist bedrock. Net Ca mineralization was investigated beneath the six most common tree species at this site: sugar maple (*Acer saccharum*), hemlock (*Tsuga canadensis*, Carr.), American beech (*Fagus grandifolia*, Ehrh.), red maple (*Acer rubrum*, L.), white ash (*Fraxinus americana*) and red oak (*Quercus rubra*, L.). A sparse and scattered understory vegetation is present consisting primarily of hayscented fern (*Dennstaedtia punctilobula*). Within GMF 36 sites were selected among three locations (Camp Pond, Wangum and Trail 4, see Figure 1). Four to ten mature trees of one of the six tree species dominated each site. The area of each site had a diameter of approximately 25 m. Three sites of each tree species were selected at Camp Pond, two at Wangum and one site of each tree species at Trail 4.

Sampling

Net Ca mineralization in the field was estimated by the buried polyethylene bag technique that previously has been used for N mineralization (Eno, 1960; Pastor *et al*., 1984; Vitousek and Matson, 1985). This method accounts for the effects of daily and seasonal temperature fluctuations on decomposition. However, moisture conditions do not change in the bags during the incubation. The incubation periods need to be long enough to establish significant changes in exchangeable Ca concentrations. Because the mineralization/available pool ratio in the forest floor and mineral soil was expected to be much smaller for Ca than for N, the incubation period required to observe significant changes in exchangeable Ca is longer than is commonly used for N mineralization studies. Samples therefore were incubated during one year divided in two periods.
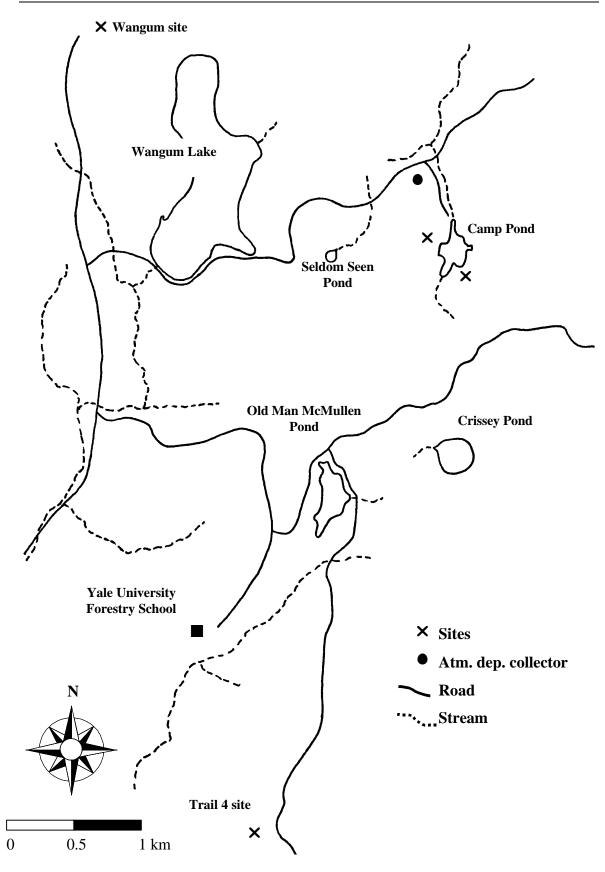
Figure 1. Site locations at Great Mountain Forest.

The first was from 18 June 1999 until 3 November 1999 (summer incubation). The second started at 3 November, where freshly fallen leaf litter was included in the forest floor samples, and lasted until 18 June 2000 (winter incubation).

Forest floor was sampled by cutting around the edges of an acrylic square (20×20 cm) that was randomly placed on top of the forest floor within each site. Forest floor was removed gently by cutting forest floor from the mineral soil beneath. Depth of the forest floor was measured. Where the forest floor was removed, two soil cores (diameter 4.5 cm) were taken to a depth of 15 cm, and the two cores were bulked. In the laboratory samples of forest floor and mineral soil were thoroughly homogenized. A sub sample (initial sample) was taken for water content, organic matter content (mineral soil only), exchangeable Ca, and pH measurement. The remainder of the forest floor and mineral soil samples were divided into four equal portions. Each portion was weighed and put in a polyethylene bag that was closed with a knot. The bags were placed back in the field at the same spot where samples came from and were covered with forest litter and a piece of poultry wire to protect bags from shifting. After the field incubation, the bags were returned to the laboratory where intact bags with forest floor and mineral soil were bulked for each site (final samples). Burst bags were discarded.

Analyses

Initial and final samples were dried (70°C, 72 h), weighed, sieved (8 mm mesh) and subsampled for moisture content (105°C, 48 h). Calculated weight loss during the incubation was based on oven dried (105°C) samples. The organic matter content of the mineral soil samples was estimated by loss on ignition. Approximately ten grams of oven dried soil was combusted in a muffle furnace at 450°C for five hours. Initial and final samples were measured for pH in 10:1 slurries of deionized water with forest floor and 2:1 slurries with mineral soil (glass electrode, Accumet). All samples were stirred once initially and after 15 minutes and then allowed to settle for 0.5 h before pH was measured. Exchangeable Ca was measured according to a slightly modified method by Hendershot et al. (1993). Five grams of forest floor and ten grams of mineral soil were extracted with 100 ml of 0.1 M $BaCl_2$. Samples were shaken for two hours on a shaker table and then filtered through Whatman Number 41 filter paper. Calcium concentrations were determined with an Inductively Coupled Plasma Emission Spectrometer (Perkin-Elmer). Changes in exchangeable Ca concentrations between initial and final forest floor samples were corrected for weight loss. The mineral soil samples did not show a measurable change in weight during the incubation.

Significant differences between initial and final pH and exchangeable Ca were tested with a paired t-test. Analyses of covariance (ANCOVA) were done on net Ca mineralization per unit mass (mmol kg^{-1} d^{-1}) and per unit area (mmol m^{-2} yr^{-1}) with initial exchangeable Ca concentration/content as covariate, and species identity as fixed factor. Another ANCOVA was done on net Ca mineralization in the forest floor per unit mass with forest floor mass loss as covariate and species identity as fixed factor. When there was a significant species × covariate interaction term, I did a series of species-specific linear regressions. All statistical analyses were done in SPSS (version 7.5).

Results

The forest floor pH was for both incubations higher in the final sample than in the initial sample (Table 1). In the mineral soil pH also increased during the winter incubation, but decreased during the summer incubation. Differences were more pronounced for the winter incubation where the incubation period was longer (seven and a half months).

Tabel 1. Mean pH with standard error in brackets (n = 6), in the forest floor and first 15 cm of the mineral soil during summer and winter incubation beneath the different tree species. Significant differences between initial and final sample are indicated as: ns: not significant, *: $P < 0.1$, **: $P < 0.01$.

Species	pH Summer		Winter	
	Initial	Final	Initial	Final
Forest floor				
Acer saccharum	4.57 (0.15)	4.73 (0.17) ns	4.47 (0.16)	5.27 (0.30) **
Fraxinus americana	4.76 (0.27)	4.76 (0.38) ns	4.30 (0.22)	5.03 (0.28) **
Fagus grandifolia	4.21 (0.16)	4.30 (0.10) ns	4.16 (0.27)	4.75 (0.30) *
Acer rubrum	3.89 (0.08)	3.92 (0.06) ns	3.72 (0.12)	4.16 (0.16) **
Quercus rubra	4.06 (0.14)	4.19 (0.13) *	3.79 (0.13)	4.40 (0.16) **
Tsuga canadensis	3.71 (0.07)	3.79 (0.07) ns	3.51 (0.14)	3.84 (0.11) **
Mineral soil				
Acer saccharum	4.48 (0.18)	4.18 (0.12) *	4.69 (0.32)	5.03 (0.29) **
Fraxinus americana	4.66 (0.14)	4.41 (0.23) *	4.16 (0.17)	4.48 (0.17) **
Fagus grandifolia	4.34 (0.10)	4.14 (0.05) *	4.02 (0.09)	4.49 (0.13) **
Acer rubrum	3.93 (0.16)	3.91 (0.15) ns	3.88 (0.15)	4.19 (0.17) **
Quercus rubra	4.23 (0.09)	4.13 (0.08) **	3.86 (0.16)	4.13 (0.18) **
Tsuga canadensis	3.74 (0.14)	3.64 (0.12) *	3.83 (0.17)	4.14 (0.14) **

Initial exchangeable Ca concentrations in the forest floor and mineral soil were highest beneath sugar maple and white ash and lowest beneath red maple, red oak and hemlock (Figure 2). Initial Ca concentrations were sometimes lower and sometimes higher at the start of the winter incubation than at the start of the summer incubation, but mostly not significantly. Daily net Ca mineralization per unit mass (mmol kg^{-1} d^{-1}) in the forest floor and mineral soil during both incubations was highest beneath sugar maple and white ash (Figure 3). Net Ca mineralization per unit mass was lower during the winter than during the summer and it was much lower in the mineral soil than in the forest floor. The ANCOVA showed that there was a tree species effect on net Ca mineralization per unit mass in the forest floor during winter incubation and in the mineral soil during summer incubation (Table 2). Further, net Ca mineralization per unit mass showed a significant correlation with the initial exchangeable Ca concentration in the forest floor for the winter incubation. No interaction effects were observed.

Yearly net Ca mineralization per unit area (mmol m^{-2} yr^{-1}) in the forest floor did not show significant differences between tree species (Figure 4 and Table 2). Instead, net Ca mineralization per unit area in the forest floor showed a significant correlation with the initial exchangeable Ca content.
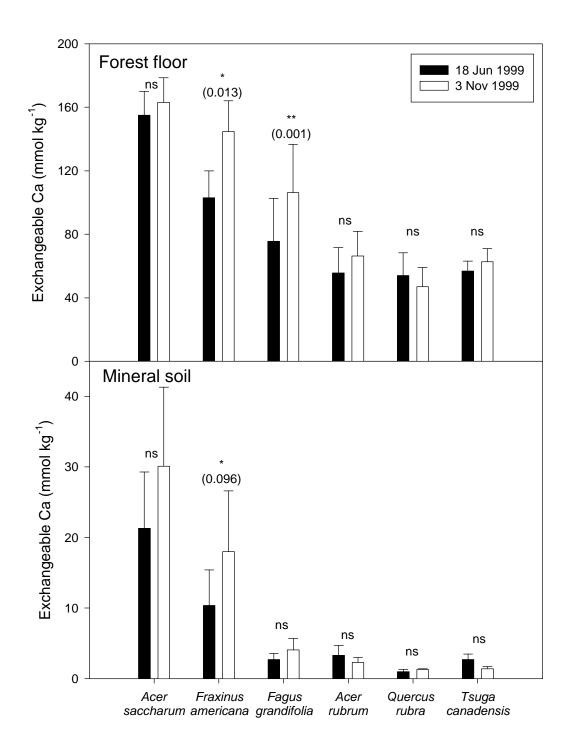
Figure 2. Mean exchangeable Ca concentrations (± SE) in the forest floor and mineral soil at the start of each incubation beneath the different tree species. Significant differences between concentrations from 18 June and 3 November 1999 are indicated as: ns: not significant, *: $P < 0.1$, **: $P < 0.01$.
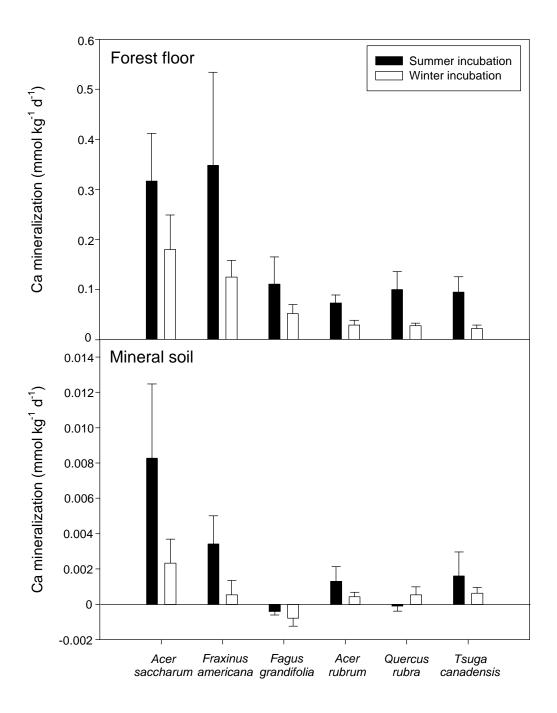
Figure 3. Mean changes in exchangeable Ca concentrations (± SE) in the forest floor and mineral soil during summer and winter incubation beneath the different tree species.

. The effects of tree species (fixed factor), exchangeable Ca (covariate) and their interaction term from the ANCOVA on Ca mineralization expressed mmol kg⁻¹ d⁻¹) in the forest floor and mineral soil during the summer and winter incubation and Ca mineralization expressed per unit area mmol m⁻² yr⁻¹) in the forest floor, mineral soil and total soil profile. Significant differences are indicated as: ns: not significant, *: $P < 0.05$, **: $P < 0.01$,

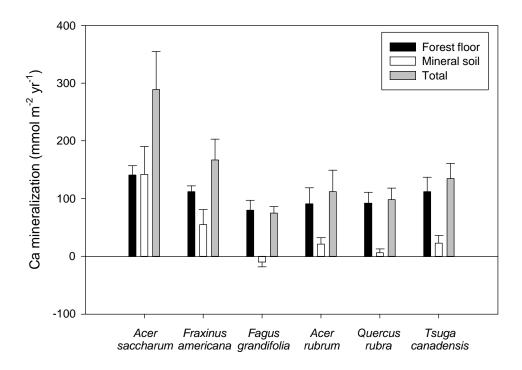| | Ca mineralization (mmol kg⁻¹ d⁻¹) | | | | Ca mineralization (mmol m⁻² yr⁻¹) | | |
| | Forest floor | | Mineral soil | | Forest floor | Mineral soil | Total |
	Summer	Winter	Summer	Winter			
	ns	*	*	ns	ns	***	**
	ns	**	ns	ns	*	ns	ns
×Exch. Ca	ns	ns	ns	ns	ns	ns	ns

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Figure 4. Mean calcium mineralization in the forest floor, mineral soil and total soil profile beneath the different tree species.

Significant differences were found among tree species in the net Ca mineralization per unit area in the mineral soil and in the total soil profile (Table 2, Figure 4). Net Ca mineralization per unit area in the mineral soil was much higher under sugar maple and white ash than under the other tree species.

Hemlock had a significantly greater forest floor mass than sugar maple and white ash (Table 3). The forest floor mass loss during incubation was higher during the summer than during the winter incubation. The forest floor mass loss fraction (g kg^{-1} d^{-1}) during incubation was highest for sugar maple and white ash (Table 3). Expressed on an area basis (g m^{-2} d^{-1}), however, forest floor mass loss was similar among the six tree species. The ANCOVA where the change in exchangeable Ca concentration in the forest floor during incubation was modeled as a function of mass loss fraction (covariate) and species identity (fixed factor) resulted in a significant species $\times$ covariate interaction term (P < 0.001), violating the assumption of homogeneity of slope among species. Therefore tree-specific linear regressions were done. The slope for each species, representing the average amount of Ca that becomes available per amount of decomposed litter (in mmol kg^{-1}) is shown in Table 4. Litter of sugar maple and white ash had the highest and red maple the lowest amount of net Ca mineralization per amount of decomposed litter.

. Forest floor mass (kg m⁻²) and its loss (g kg⁻¹ d⁻¹ and g m⁻² d⁻¹) during summer and winter incubation. Values are the mean followed by the standard

| | Forest floor mass | | Forest floor mass loss | | | |
| | Summer | Winter | Summer | Winter | Summer | Winter |
	kg m⁻²		g kg⁻¹ d⁻¹		g m⁻² d⁻¹	
saccharum	2.4 (0.8) a	2.5 (0.6) a	1.00 (0.17) b	0.49 (0.08) b	1.8 (0.2)	1.0 (0.1)
americana	2.2 (0.6) a	2.6 (0.6) a	0.85 (0.14) ab	0.49 (0.10) b	1.6 (0.4)	1.0 (0.2)
grandifolia	4.0 (1.3) ab	3.8 (0.8) ab	0.62 (0.12) ab	0.36 (0.03) ab	2.2 (0.8)	1.3 (0.3)
rubrum	5.5 (0.6) ab	5.4 (0.8) ab	0.51 (0.08) a	0.22 (0.04) a	2.9 (0.6)	1.1 (0.2)
rubra	4.8 (0.4) ab	5.4 (0.5) ab	0.64 (0.13) ab	0.25 (0.04) ab	2.9 (0.4)	1.3 (0.1)
canadensis	7.0 (0.8) b	6.5 (0.8) b	0.48 (0.06) a	0.14 (0.01) a	3.3 (0.4)	0.9 (0.1)

Table 4. The slope with standard error (SE) and P-values calculated from linear regressions between change in exchangeable Ca and forest floor mass loss during incubation for each tree species, representing the amount of Ca that becomes available per amount of decomposed litter (mmol kg^{-1}) in the forest floor.

species	slope (mmol kg^{-1})	SE	P-value
Acer saccharum	362	49	< 0.001
Fraxinus americana	390	78	< 0.001
Fagus grandifolia	183	32	0.004
Acer rubrum	133	23	0.095
Quercus rubra	147	22	0.021
Tsuga canadensis	190	37	0.047

Discussion and conclusions

Mineralization of base cations in the forest floor and mineral soil samples during incubation will cause an increase in pH, while nitrification will lead to a decrease in pH. The overall increase in pH during incubation of the forest floor, suggests that the effect of base cation mineralization on pH may have been stronger than that of nitrification. Nitrification was apparently more important in the mineral soil during the summer incubation.

Samples from the summer incubation showed a larger average net Ca mineralization per unit mass than from the winter incubation for all tree species (except the mineral soil under red oak). Forest floor mass loss fractions were also higher during the summer than during the winter incubation and were significantly related to the change in exchangeable Ca concentration during incubation. Higher temperatures during the first incubation may have resulted in increased decomposition and net Ca mineralization during the summer incubation.

Net Ca mineralization rates in the forest floor per amount of decomposed litter was significantly higher for sugar maple and white ash litter than for the other tree species. Low total Ca concentrations of the incoming litter may have caused lower net Ca mineralization rates per amount of decomposed litter beneath red maple, beech, red oak and hemlock. Leaf litter fall that was collected at the same sites during autumn of 1999 showed highest Ca concentrations from sugar maple and white ash sites (G.M. Lovett, unpublished data). Vesterdal (1999) found increased net Ca release from decomposing foliage litter of beech and Norway spruce with higher initial Ca concentration. Calcium immobilization may also have been responsible for the low net Ca mineralization per amount of decomposed litter beneath red maple, beech, red oak, and hemlock. Litters beneath these tree species had the smallest mass loss fractions during incubation. The remaining more recalcitrant litter from these tree species can form more sites during decomposition that bind strongly with Ca (Staaf and Berg, 1982; Van Wesemael, 1993), immobilizing mineralized Ca.

The higher forest floor mass beneath beech, red maple, red oak, and hemlock helped increase the net Ca mineralization per unit area in the forest floor to the same level as under sugar maple and white ash, where the mineralization per unit mass (mmol kg^{-1} d^{-1}) was higher but where forest floors were thinner. Differences between tree species

therefore decreased and were non-significant. Net Ca mineralization per unit area did correlate significantly with the initial exchangeable Ca content in the forest floor. Calcium mineralization may have been stimulated with higher initial exchangeable Ca content and higher pH. However, more likely is that high net Ca mineralization is causing a high exchangeable Ca content in the forest floor instead of being the effect. Because tree species affect exchangeable Ca content in the surface soil (see Finzi *et al.*, 1998*a*), exchangeable Ca content is not an ideal covariate to separate soil effects from tree species effects on net Ca mineralization.

Net Ca mineralization in the first 15 cm of the mineral soil showed significant tree species effects. Especially beneath sugar maple and white ash net Ca mineralization in the mineral soil was appreciable, especially at sites where much earthworm activity was observed. It is plausible that earthworms move organic matter from the forest floor to the upper mineral soil where the organic matter can still release substantial amounts of Ca through decomposition. It must be noted however that increases in Ca concentration during incubation were relatively small, but involved an appreciable mass of Ca. Small increases in Ca concentration during incubation could have been caused by disturbance of the soil accelerating Ca release through organic mineralization or mineral weathering.

To extrapolate net Ca mineralization measured in buried bags to actual net Ca mineralization in the field, a number of potential errors are introduced. First, the activity of earthworms within the bag is limited and is therefore probably much lower inside than outside the bag. As a result, decomposition and net Ca mineralization will be underestimated. This error may have been large for sugar maple and white ash forest floors where at some sites many earthworms have been observed in the field. Second, samples were disturbed and moisture conditions remained constant in the bags during incubation. Disturbance markedly affects N mineralization in the mineral soil (e.g. Raison *et al.*, 1987). The effect of disturbance on Ca mineralization in the forest floor is unclear. Third, the long incubation periods that were used may have induced decomposition of fresh fine roots that were killed during sampling and were incorporated within the bags, and may have overestimated net Ca mineralization. Based on fine root mass that was measured in forest floor and mineral soil of hemlock and sugar maple sites at GMF (Chapter 6) and Ca root concentrations reported by Fahey *et al.* (1988), maximum release of Ca due to decomposition of fresh fine roots during each incubation could not have been more than 10 mmol m^{-2}. Further, Fahey *et al.* (1988) showed that there was little release of Ca during the first years of fine root decomposition. Therefore, errors due to freshly cut root decomposition in net Ca mineralization estimates were probably small. However, annual fine root turnover may return substantial amounts of Ca to the soil. Likens *et al.* (1998) estimated for the Hubbard Brook Experimental Forest an annual Ca return from fine root turnover of 27 mmol m^{-2} yr^{-1}, with 19 mmol m^{-2} yr^{-1} contributed to the forest floor and 8 mmol m^{-2} y^{-1} to the mineral soil. Compared to the net Ca mineralization rates that I estimated, fine root turnover could contribute up to 30% of the net Ca mineralization in forest floor and mineral soil.

In spite of uncertainties about translating measured values to actual rates of net Ca mineralization in the field, it is evident that net Ca mineralization in the forest floor and mineral soil is an important source of Ca for immediate plant uptake for all tree species. Other inputs of Ca input at GMF are much smaller than net Ca mineralization in the forest floor (4 mmol m^{-2} yr^{-1} for atmospheric deposition and 2 mmol m^{-2} yr^{-1} for mineral

weathering, Chapter 2). No studies have been encountered in the literature where net Ca mineralization in the entire forest floor and upper mineral soil was measured. Gosz *et al.* (1973) estimated Ca release from fresh litter (both leaves and branches) of 17,260 g ha^{-1} yr^{-1} (43 mmol m^{-2} yr^{-1}) during the first 12 months in the Hubbard Brook Experimental Forest, New Hampshire, or 42% of the Ca content of the yearly litter fall. This number is lower than the lowest net Ca mineralization rate observed under beech at GMF. They stated however that their number underestimated the yearly release from the entire forest floor since release of Ca from tissues of previous litter fall was not taken into account. My results show that large amounts of net Ca mineralization occur in the entire forest floor and for sugar maple and white ash also in the upper mineral soil. To estimate the amount of Ca that becomes available through organic mineralization in temperate forests, all soil litter that has been accumulated over time has to be considered.

Acknowledgements

Chapter 6

Tree species effects on calcium cycling:
the role of calcium uptake in deep soils

Feike A. Dijkstra and Mark Smits
Submitted to *Ecosystems*

Abstract

Soil acidity and Ca availability in the surface soil differ substantially beneath sugar maple (*Acer saccharum*) and eastern hemlock (*Tsuga canadensis*) trees that are growing in a mixed forest in northwestern Connecticut. We determined the effect of pumping of Ca from deep soil (rooting zone below 20-cm mineral soil) to explain the higher available Ca content in the surface soil beneath sugar maple. We compared Ca inputs from atmospheric deposition, soil weathering and release through decomposition in the surface soil (rooting zone above 20-cm mineral soil) with Ca leaching below the surface soil beneath sugar maple and hemlock stands. We also measured root length distribution with depth beneath both tree species. Calcium leaching from the surface soil was much higher beneath sugar maple than hemlock and was positively related with the amount of Ca available in the surface soil. Calcium leaching from the surface soil beneath sugar maple was higher than Ca inputs from atmospheric deposition and soil weathering. Without Ca uptake in the deep soil, surface soils are being depleted in Ca, especially beneath sugar maple. More organically bound Ca was mineralized beneath sugar maple than beneath hemlock. A relatively small part of this Ca release was leached below the surface soil, suggesting that, beneath both tree species, most of the Ca cycling is occurring in the surface soil. Sugar maple had more fine roots in the deep soil than hemlock and a greater potential to absorb Ca in the deep soil. We illustrated the effect of Ca uptake from deep soil on Ca availability in the surface soil with a simple model, which showed that a relatively small amount of Ca uptake in the deep soil beneath sugar maple is able to sustain high amounts of available Ca in the surface soil.

Introduction

It is well known that individual trees alter soil acidity and available Ca content in surface soils (e.g. Zinke, 1962; Boettcher and Kalisz, 1990; Nordén, 1994; Bockheim, 1997; Finzi *et al*., 1998*a*; Amiotti *et al*., 2000). In a mixed forest, therefore, temporal and spatial alterations of soil acidity and available Ca content may develop, which subsequently may affect the distribution of the forest vegetation. In addition, trees growing in soils of different base cation availability may react differently to human induced stresses such as acid rain. Different mechanisms may help trees to alter soil acidity and available Ca content in the surface soil, but their relative importance remains unclear.

Biotic control over Ca availability in the surface soil can establish through different pathways (Figure 1). Several studies have shown that Ca uptake and allocation to biomass pools are the main cause for changes in Ca content in the surface soil (Alban, 1982; Johnson and Todd, 1987, 1990; Eriksson and Rosen, 1994). Bockheim (1997) found lower contents of Ca in the surface soil beneath hardwood stands dominated by sugar maple compared to hemlock stands and attributed this to higher Ca biomass fixation in sugar maple trees. However, Finzi *et al*. (1998*a*) found at sites similar to ours, higher Ca contents in the surface soil beneath sugar maple than hemlock of similar age.
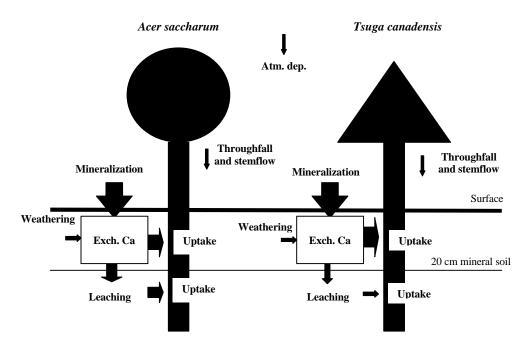
Figure 1. The Ca pools and fluxes influenced by *Acer saccharum* and *Tsuga canadensis*. The width of the arrows corresponds to the hypothesized size of the Ca flux.

Their results therefore can not be explained by higher Ca biomass fixation in sugar maple.

A potential mechanism by which trees may affect the exchangeable Ca content in surface soils is through the influence of trees on chemical weathering in the soil. Several authors have reported apparent differences in soil weathering caused by different tree species (Spyridakis *et al*., 1967; Bouabid *et al*., 1995; Quideau *et al*., 1996; Tice *et al*., 1996). Strontium isotope studies by Dijkstra *et al*. (Chapter 2), however, observed no detectable differences in Ca weathering in surface soils among tree species associated with different contents of exchangeable Ca in the soil. The Ca weathering rate did increase however, with the content of Ca weathering minerals in the soil.

The production of organic acids from decomposing litter and root/mycorrhizal exudation lowers soil pH and increases solubility of aluminum and iron that compete with base cations for binding sites on the exchange complex (e.g. Johnson *et al*., 1994; Lawrence *et al*., 1995; Dijkstra and Fitzhugh, Chapter 4). The exchanged base cations are then likely to leach with drainage water to deeper soil layers. Dijkstra *et al*. (2001) showed that organic acid production was much higher in forest floors beneath hemlock than sugar maple, but that actual leaching of Ca with organic anions was greatest beneath sugar maple where the forest floor contained more exchangeable base cations.

How, then, in spite of greater Ca leaching rates, do sugar maple trees enhance the pool of available surface soil Ca? The flux in Figure 1 that can maintain a high available Ca content in the surface soil, is to recapture appreciable amounts of Ca leached from the surface soil via deep roots. We postulate, therefore, that sugar maple takes up appreciable larger quantities of Ca from the deeper soil than hemlock. Even when enough Ca is released by mineral weathering to potentially increase the available pool of

Ca in the surface soil under hemlock, this pool will remain low because hemlock does not have a root system that is able to retain Ca lost from the surface soil.

To test our hypothesis we compared Ca inputs from atmospheric deposition, soil weathering and release through organic matter decomposition with Ca leaching below 20 cm in the mineral soil beneath sugar maple and hemlock stands. We measured the presence of roots at depth in the soil, and developed a simple model to calculate and compare plant uptake from surface and deep soil, and to illustrate the effect of plant uptake from deep soil on Ca availability in the surface soil.

Methods

Study site

This research was done on the Canaan Mountain Plateau at elevations of 300 – 500 m in northwestern Connecticut. Sites were located near Camp Pond, Wangum Reservoir, and near Trail 4 (Figure 2). Soils at these fairly flat sites are acidic, well-drained sandy loams derived from glacial till over mica-schist bedrock. The dense glacial till at all sites starts approximately at 60-cm depth. The sites have not been cleared for agriculture while some selective logging has occurred. Forest structure is relatively simple, with no major shrub or sub canopy tree species present.

We selected sites that were either dominated by mature sugar maple (*Acer saccharum* Marsh.) or hemlock (*Tsuga canadensis* Carr.) trees (~80-130 years old): six sugar maple and six hemlock sites at Camp Pond, two sugar maple and two hemlock sites at Wangum, and one sugar maple and one hemlock site at Trail 4. At Camp Pond all trees with a diameter at breast height (DBH) $\geq$ 5 cm were identified and their DBH measured within a circle of 10-m radius at each site (on average 22 trees at each site). Total basal area density and the proportion of the dominant tree (sugar maple or hemlock) was calculated for each site. The total aboveground biomass was calculated according to biomass equations found for each tree species in the literature (Ter-Mikaelian and Korzukhin 1997). The average total basal area density for hemlock sites was significantly higher than for sugar maple sites (Table 1). Also the average total biomass was higher, but not significantly.

Total and exchangeable calcium in the soil

At all 12 sites at Camp Pond the first 20 cm of the mineral soil was sampled in the spring of 1997 for determination of total mineral Ca concentration. At each site three cores (diam. 4.5 cm) were randomly pounded into the soil and bulked for each layer. At these same sites forest floor and mineral soil from 0- to 5- and 10- to 20-cm depth were sampled in the same way in the summer of 1998 for exchangeable Ca determination. Forest floor and mineral soil samples were dried for 48 h at 105 °C and sieved (through 8- and 2-mm mesh respectively) to remove roots and stones. Samples were weighed for bulk density determination.

Table 1. Average aboveground biomass measurements at sugar maple and hemlock sites at Camp Pond (standard error, n = 6).

Site	Total basal area density cm^2 m^{-2}	Basal area dominant tree %	Total aboveground biomass[a] kg m^{-2}
Acer saccharum	30.1 (4.3)	72.9 (8.7)	22.7 (3.1)
Tsuga canadensis	49.3 (4.1)	70.8 (5.3)	28.5 (1.8)
Significance[b]	**	n.s.	n.s.

[a] Biomass equations for *Acer rubrum*, *Acer saccharum*, *Betula alleghaniensis*, *Fagus grandifolia*, and *Tsuga canandensis* are from Young and others (1980), for *Fraxinus americana* and *Quercus rubra* are from Perala and Alban (1994), and for *Prunus serotina* from Wiant and others (1979), all cited in Ter-Mikaelian and Korzukhin (1997).
[b] Independent samples t-test. ** Significance at P < 0.05, n.s. not significant.

Total mineral Ca concentration of the samples from 0- to 20-cm depth was analyzed with X-ray fluorescence after Buurman *et al*. (1996). Exchangeable Ca was extracted with 0.1 M BaCl$_2$ (Hendershot *et al*., 1993) and concentrations of Ca were measured by AAS (see Dijkstra and Fitzhugh, Chapter 4). We calculated for each layer the exchangeable Ca content (mol m^{-2}). To calculate total exchangeable Ca content in the forest floor and first 20 cm of the mineral soil, the content of each layer was totaled. We assumed that the exchangeable Ca concentration in the 5- to 10-cm layer was equal to the concentration in the 10- to 20-cm layer. Judging from field observations we estimated that 30% of the volume in the first 20 cm of the mineral soil was taken by large rocks, stones, and roots. Although this is a very rough estimate, it did not have large effects on the significant differences that were found in exchangeable Ca content in the forest floor plus first 20-cm mineral soil. We will refer to the forest floor and first 20 cm of the mineral soil as surface soil, while the rooting zone below 20-cm mineral soil will be called the deep soil.

Calcium from bulk atmospheric deposition

Bulk atmospheric deposition was collected in two collectors, 1 m above the ground, at a clearing close to Camp Pond (Figure 2). Collectors were made of a polyethylene funnel (diam: 20 cm) connected to a polyethylene bottle. Bulk atmospheric deposition was collected weekly from May until October in 1997, 1998, and 1999, and stored in the dark at 4 °C prior to analysis. All materials for solution sampling were cleaned in 50% hydrochloric acid and rinsed with nanopure water before use. Solutions were analyzed for Ca by Inductively Coupled Plasma Emission Spetrometer (ICP). Average annual bulk atmospheric deposition of Ca was calculated from volume-adjusted Ca concentrations and from precipitation data that were collected at a weather station within 10 kilometers from our site in Norfolk, Connecticut. Although canopy trees affect acid deposition (Bergkvist and Folkeson, 1995), there is no clear evidence that they have a significant influence on the deposition of Ca in northeastern forests of the US. According to Lindberg *et al*. (1986) most of the dry deposition in Temperate forests of the northeastern US is in particles >2 μm in diameter and occurs under the influence of gravity.
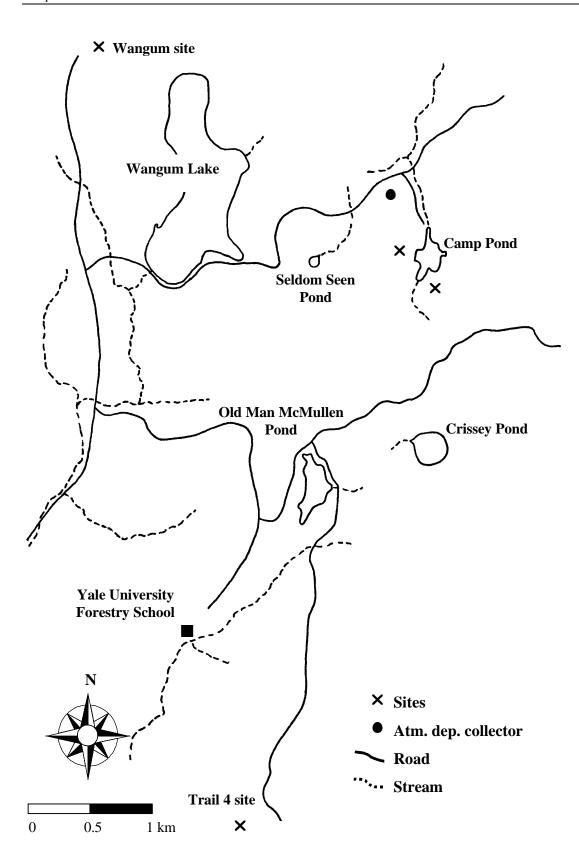
Figure 2. Site locations at Great Mountain Forest.

Calcium leaching

At the same sites where exchangeable calcium was determined, tension lysimeters (Rhizon SMS, Eijkelkamp) were installed at 20-cm depth in the mineral soil in the summer of 1997 (see Dijkstra and Fitzhugh, Chapter 4). Soil solution samples were collected during autumn 1997, spring and autumn 1998, and spring 1999, and stored before analyses at 4 °C in the dark. Soil solutions were analyzed for Ca by AAS. We estimated Ca leaching below 20-cm mineral soil by multiplying Ca concentrations with water fluxes at 20-cm mineral soil that were calculated with a hydrologic model (BROOK90, Federer, 1995; Lawrence *et al*., 1995).

Calcium weathering

The similar geochemical behavior of Ca and Sr (Graustein, 1989) has led us to the use of strontium isotopes to estimate Ca weathering rates in the first 20 cm of the mineral soil. At three sugar maple and three hemlock sites at Camp Pond, stem wood, soil, and soil solution samples were taken during the summers of 1997 and 1998. Together with bulk atmospheric deposition, these samples were analyzed for $^{87}Sr/^{86}Sr$ by mass spectrometry. Using a linear mixing equation, with atmospheric deposition and weathering end members, the proportion of Sr fixed in stemwood that was originally derived from soil weathering was calculated. With $^{87}Sr/^{86}Sr$ ratios measured in soil solution and Ca/Sr ratios measured in the surface soil, the Ca weathering rate in the surface soil was calculated for each site. For a detailed description of the methods used see Dijkstra *et al*. (Chapter 2).

Calcium release through organic matter decomposition

At the three sugar maple and hemlock sites where Ca weathering was estimated, net Ca release through organic matter decomposition in the forest floor and first 15 cm of the mineral soil was estimated by incubating samples in polyethylene bags in the field. From June 1998 until June 1999 samples were incubated in two subsequent incubation periods. Net Ca release through organic matter decomposition was calculated as the difference between initial and final exchangeable Ca that was measured by ICP and corrected for weight loss during incubation, Ca weathering in the mineral soil, and volume taken by rocks and roots in the mineral soil (see Dijkstra, Chapter 5).

Root density characterization

One mature tree was selected at four sugar maple and four hemlock sites to measure the root density at different soil depths during the summer of 2000. Around each tree within a circle of 1-m radius eight cores (diam. 5 cm) were taken to a depth of 60 cm. Each core was subdivided into the forest floor, 0- to 5-cm, 5- to 15-cm, 15- to 30-cm, 30- to 45-cm, and 45- to 60-cm samples and each individual sample was analyzed separately. Power

analysis showed that eight cores were enough to characterize the root density for each layer accurately (se < 10%, M. Smits, unpublished data). Tree roots were collected by sieving and gently rinsing samples with water, and were then divided into fine (diam. < 2 mm) and coarse roots. Fine and coarse root length was measured by counting intersections of roots laid on a grid (Newman, 1966). Root density (cm cm^{-3}) of each layer was calculated by dividing root length with the volume of each layer for each core. For each site the mean root density per layer was then calculated taking the average of the eight cores.

Statistical analyses

Analyses of covariance (ANCOVA) were done on exchangeable Ca content (mmol m^{-2}) and Ca leaching (mmol m^{-2} yr^{-1}) in the surface soil with total mineral Ca concentration in the surface soil (mg g^{-1}) as covariate and species identity as fixed factor. Significant differences were accepted at P < 0.05. The mean root density of each layer was compared between sugar maple and hemlock trees with t-tests. We used a Bonferroni adjustment and considered significant differences between tree species at P < 0.05/6 = 0.0083. All statistical analyses were done in SPSS (version 7.5).

Model

A simple model was developed to illustrate the effect of Ca uptake from surface and deep soil on the exchangeable Ca content in the surface soil. The exchangeable Ca content (mmol m^{-2}) in the surface soil at time step t ($E_{s,t}$) can be calculated as:

$$E_{s,t} = E_{s,t-1} + A + W_s + R_s - U_s - L_{s,t} \qquad (1)$$

where $E_{s,t-1}$ is the exchangeable Ca content in the surface soil at time step t-1 (mmol m^{-2}), A is Ca atmospheric deposition, W_s is Ca weathering in the surface soil, R_s is Ca release through organic matter decomposition in the surface soil, U_s is Ca uptake in the surface soil, and $L_{s,t}$ is the Ca leaching below the surface soil at time step t (mmol m^{-2} yr^{-1}) where t is in years. Calcium leaching below the surface soil at time step t is modeled as a fixed proportion of the exchangeable Ca content α in the surface soil at time step t-1:

$$L_{s,t} = \alpha\, E_{s,t-1} \qquad (2)$$

For the sake of simplicity we ignored the flux of Ca throughfall and stemflow and considered this flux as part of Ca release through organic matter decomposition (see results and discussion below). When the exchangeable Ca content in the surface soil is in steady state, Ca uptake in the surface soil can be calculated as:

$$U_s = A + W_s + R_s - L_{s,t = \text{steady state}} \qquad (3)$$

Using the values of A, W_s, R_s, and $L_{s,t}$ that we measured at sugar maple and hemlock sites at Camp Pond as steady state values, we then calculated Ca uptake in the surface soil at these sites. To illustrate the effect of Ca uptake from deep soil on exchangeable Ca in the surface soil we further set Ca release through organic matter decomposition equal to total Ca uptake by the tree. We then could calculate Ca uptake in the deep soil (U_d) by sugar maple and hemlock with:

$$U_d = R_s - U_s \qquad\qquad (4)$$

and equation (1) becomes:

$$E_{s,t} = E_{s,t-1} + A + W_s + U_d - \alpha\, E_{s,t-1} \qquad\qquad (5)$$

With this equation we could model the exchangeable Ca content in the surface soil over time beneath different sugar maple and hemlock sites assuming that Ca uptake from the deep soil is unlimited and constant over time, but tree species dependent. The model is now independent of Ca release through decomposition, because of the linkage of Ca release with Ca uptake in the surface soil. Even though our sites are probably not in steady state as defined here, the model is useful to illustrate divergent effects of differences in Ca uptake from surface versus deep soil on available Ca content in the surface soil beneath sugar maple and hemlock.

Results and discussion

Ca pools and fluxes

Exchangeable Ca contents and rates of Ca leaching in the surface soil were significantly higher beneath sugar maple than beneath hemlock ($P = 0.003$ for exchangeable Ca and $P = 0.010$ for Ca leaching, Figure 3). The covariate (total mineral Ca concentration in the top 20 cm of the mineral soil) and species×covariate interaction terms were non-significant in the ANCOVA. A study by Finzi *et al*. (1998*a)*, in the same study area, found a significantly higher slope for sugar maple than for hemlock when the exchangeable Ca concentration was plotted against the mineral Ca concentration in the top 7.5 cm of the soil. Although non-significant, exchangeable Ca content and Ca leaching generally increased with total mineral Ca concentration beneath sugar maple, while for the hemlock sites exchangeable Ca content and Ca leaching remained low over a range of total mineral Ca concentration (Figure 4A and B). There was also a positive trend between exchangeable Ca content in the surface soil and Ca leaching for the sugar maple sites, while the range of exchangeable Ca content was too small beneath hemlock sites for a significant relationship (Figure 4C). These results suggest that Ca leaching below the surface soil is highly controlled by the amount of Ca that is available in the surface soil for leaching. The significant regression through all data points in Figure 4C ($R^2 = 0.64$, $P = 0.002$) shows that Ca leaching can roughly be estimated from the exchangeable Ca content.
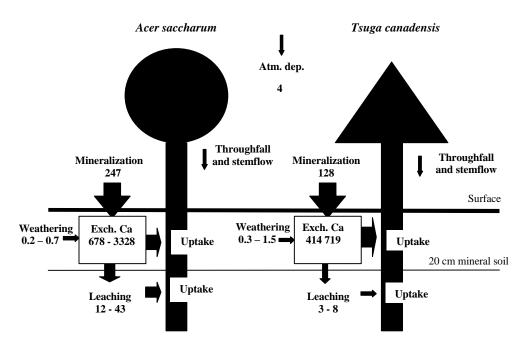
Figure 3. The Ca content in the surface soil (mmol m^{-2}) and the Ca fluxes (mmol m^{-2} yr^{-1}) at *Acer saccharum* and *Tsuga canadensis* sites at Camp Pond.

Dijkstra *et al*. (Chapter 2) showed that Ca weathering in the surface soil was in general very low at Camp Pond sites and no significant differences could be detected among tree species. They concluded that the parent material of the soil had a greater effect than tree species on Ca weathering. Since both sugar maple and hemlock are found on similar soils at Great Mountain Forest (Van Breemen *et al*., 1997), Ca weathering in the surface soil was of the same magnitude for these tree species (Figure 3).

Net Ca release through organic matter decomposition in the surface soil was significantly lower for hemlock than for sugar maple (Chapter 5, Figure 3). The net Ca release in the surface soil was not related to the initial exchangeable Ca content or the total mineral Ca concentration in the surface soil. Throughfall and stemflow are other Ca sources to the surface soil. Likens *et al*. (1998) estimated an annual Ca flux in throughfall and stemflow of 11 mmol m^{-2} yr^{-1} at the Hubbard Brook Experimental Forest in New Hampshire. Compared to our sites, the Ca flux in throughfall and stemflow would be 4 and 9% of net Ca release through organic matter decomposition for sugar maple and hemlock respectively. Other studies did not find significant differences of the Ca flux in throughfall among tree species (Lovett *et al*., 1985; Johnson and Todd, 1987, 1990). The annual internal cycling of Ca via Ca release through organic matter decomposition greatly exceeds the fluxes into and out of the system for sugar maple and hemlock sites (Figure 3), implying a tight Ca cycling for both tree species.

Although the above ground biomass is slightly but not significantly higher for the hemlock sites (Table 1), a higher above ground biomass for hemlock sites can not explain the large difference in exchangeable Ca content in the surface soil between sugar maple and hemlock. Calcium concentrations in stem wood of the six most common tree species at GMF were similar and around 1 g kg^{-1} dry weight (Chapter 2).
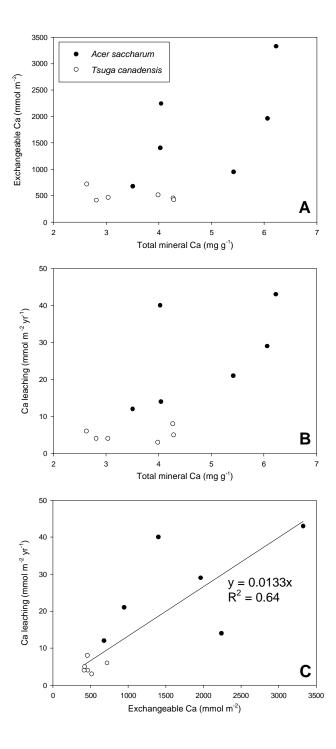
Figure 4. Exchangeable Ca (mmol m^{-2}) and Ca leaching (mmol m^{-2} yr^{-1}) below the surface soil beneath *Acer saccharum* and *Tsuga canadensis* sites at Camp Pond. A. Exchangeable Ca as a function of total mineral Ca concentration in the soil (mg g^{-1}), B. Ca leaching as a function of total mineral Ca concentration in the soil, and C. as a function of exchangeable Ca content.

On average an extra 5.8 g m^{-2} or 145 mmol m^{-2} of Ca would be stored in aboveground biomass at the hemlock sites compared to the sugar maple sites.

By taking the boundary of the tree-soil system at 20-cm mineral soil, we compared the fluxes into and out of the system for sugar maple and hemlock sites. Calcium inputs from atmospheric deposition and weathering are almost the same as Ca leaching below 20-cm mineral soil at hemlock sites. At all sugar maple sites however, Ca leaching exceeds inputs from atmospheric deposition and soil weathering (Figure 3). To maintain appreciable amounts of exchangeable Ca in the surface soil, sugar maple needs to take up Ca below 20-cm mineral soil (deep soil). This Ca is then transferred in litter fall to the surface soil where it is mineralized and enhances the Ca content in the surface soil beneath sugar maple. Storage of Ca because of an increment in net biomass and forest floor in the tree-soil system would require further Ca uptake in the deep soil, both for sugar maple and hemlock. At present, we do not have data on annual net Ca storage at our sites. Likens *et al*. (1998) estimated an average net Ca uptake in above and below ground biomass of 5.4 mmol m^{-2} yr^{-1}, based on the difference in biomass storage between 1982 and 1992 at the Hubbard Brook Experimental Forest (Watershed 6).

Without Ca uptake in the deep soil, surface soils beneath sugar maple sites lose Ca at rates between 8 and 37 mmol m^{-2} yr^{-1}. Without Ca uptake in the deep soil, surface soils beneath hemlock would undergo little or no Ca depletion. Calcium depletion would be higher if there is a net increment in biomass and forest floor at sugar maple and hemlock sites. There is substantial evidence that Ca is depleted in northeastern forests of the US under the influence of acid atmospheric deposition (Lawrence *et al*., 1995; Likens *et al*., 1996, 1998). Likens *et al*. (1998) estimated that the total amount of Ca lost from the complete soil profile between 1965 and 1992 at the Hubbard Brook Experimental Forest was 9.9-11.5 kmol ha^{-1} or on average between 37 and 43 mmol m^{-2} yr^{-1}. However, Yanai *et al*. (1999) concluded that during the last 20 years there was no Ca depletion in the forest floor at the Hubbard Brook Experimental Forest. Considering the large influence of trees on Ca cycling at our sites, a possible explanation for the above discrepancy is that most of the Ca depletion occurs mainly at greater soil depths.

Root density

For a mobile cation such as Ca, mass flow of soil solution is thought to be an important mechanism in the supply of Ca to the root surface (Rengel, 1993; Yanai, 1994). Higher fine root densities would therefore increase the potential for Ca uptake by the tree. To test the difference in potential Ca uptake in the deep soil under sugar maple and hemlock, we measured fine root density at different depths beneath these two species. Fine root density beneath sugar maple was higher than beneath hemlock in each layer (Figure 5A) but this difference was insignificant after applying the Bonferroni adjustment. Because the forest floor beneath hemlock was much thicker than beneath sugar maple (on average 6.9 cm for hemlock and 1.3 cm for sugar maple), the fine root length per area forest floor was significantly higher beneath hemlock (43.6 cm cm^{-2} for hemlock and 16.2 cm cm^{-2} for sugar maple).
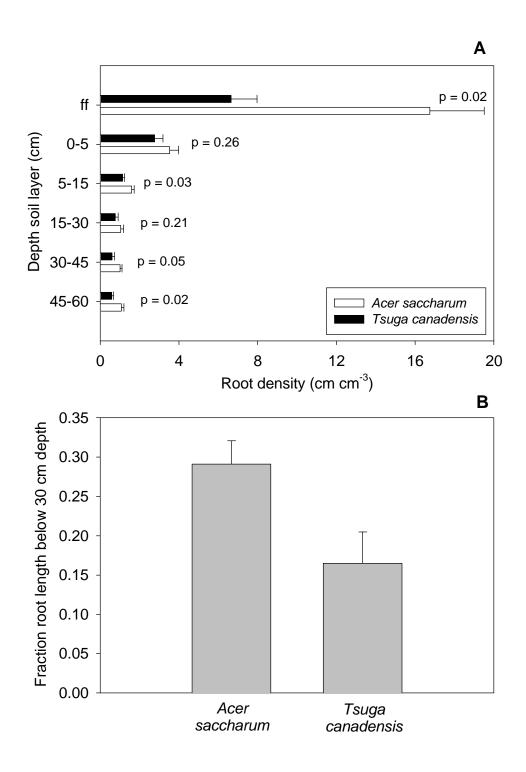
A

B

Figure 5. Average fine root density in different soil layers (A) and average fine root length below 30-cm depth as a fraction of total root length (B) for *Acer saccharum* and *Tsuga canadensis*.We compared the fine root length measured below a depth of 30 cm as a fraction of root length in the total profile between sugar maple and hemlock.

While no differences in total fine root length were found, the fraction of fine root length below 30 cm was significantly higher under sugar maple (Figure 5B). Many fine roots of hemlock were infected with ectomycorrhiza, especially in the upper soil layers (M. Smits, unpublished). These results indicate that sugar maple has a higher potential for Ca uptake in the deep soil than hemlock. Higher fine root densities, extended with mycorrhizal mycelium, in the surface soil beneath hemlock suggest a higher potential by this tree to explore and absorb Ca in the surface soil.

High Ca uptake rates in the surface soil that are close to release rates of Ca through organic matter decomposition could keep the available Ca pool low in the surface soil beneath hemlock. As soon as Ca is released through organic matter decomposition, the tree may take it up before any buildup of Ca can occur in the surface soil. Beneath sugar maple Ca uptake rates in the surface soil may not be as high as Ca release rates through organic matter decomposition, and therefore the available Ca pool in the surface soil could increase, which would stimulate Ca leaching to deeper soil layers. Having more fine roots in the deep soil, part of the leached Ca in the deep soil could then be taken up by sugar maple.

Model

We used our model to test the possibility that difference in deep uptake of Ca could explain the differences in contents of exchangeable Ca in the surface soil that were observed beneath sugar maple and hemlock. First, we used equations (3) and (4) to calculate Ca uptake in the surface and deep soil respectively, assuming steady state Ca levels under sugar maple and hemlock sites, for the lowest and for the highest total mineral Ca concentration in the soil observed beneath each species (Table 2).

Table 2. Calcium uptake (mmol m^{-2} yr^{-1}) for sugar maple and hemlock sites at Camp Pond in steady state (percentage of total)

	Acer saccharum Total mineral Ca conc.		*Tsuga canadensis* Total mineral Ca conc.	
	Low	High	Low	High
Ca uptake (mmol m^{-2} yr^{-1})				
Surface soil	239 (97)	209 (85)	128 (100)	125 (98)
Deep soil	8 (3)	38 (15)	0 (0)	3 (2)

We emphasize that with this calculation we ignored Ca input from throughfall and stemflow, annual net Ca storage in the biomass, and change in exchangeable Ca content in the surface soil. Addition of Ca coming in through throughfall and stemflow, would increase Ca uptake rate in the surface soil under steady state conditions, while annual net Ca storage in biomass (net Ca uptake) at our sites would result in higher total Ca uptake rates, both in the surface and deep soil, than calculated here in steady state. Likens *et al*. (1998) reported a relatively small net Ca uptake rate at the Hubbard Brook Experimental Forest (5.4 mmol m^{-2} yr^{-1}) and we also expect that our sites are at an age where net Ca uptake rates, especially in the deep soil, will not be very large. Our calculations suggest

that Ca uptake from the surface soil is much higher than from the deep soil for both tree species, because of the high input of Ca release through organic matter decomposition at the surface. Fluxes of Ca release through uptake, litter fall and mineralization should indeed be high because Ca is not retranslocated within the tree before leaf abscission (Kramer and Kozlowski, 1979). Under steady state conditions, Ca uptake from the deep soil is slightly higher beneath sugar maple than beneath hemlock, and Ca uptake from the deep soil becomes only substantial at the high total mineral Ca site beneath sugar maple. These results indicate that Ca uptake in the deep soil not only depends on tree species, but also on the parent material of the soil.

We modeled the exchangeable Ca content in the surface soil over time for sites with low and high total mineral Ca concentration in the soil for sugar maple and hemlock ('low' and 'high' sites), using equation (5). We evaluated the effect of each of the two tree species on the Ca availability in a surface soil that at the start had the exchangeable Ca content typical of the other species. Thus, we started our model at $t = 0$ with an exchangeable Ca content of 414 and 719 mmol m^{-2} in the surface soil for 'low' and 'high' sugar maple sites and of 678 and 3328 mmol m^{-2} for 'low' and 'high' hemlock sites. These values correspond with exchangeable Ca contents measured at hemlock and sugar maple sites respectively (Figure 3). We further used parameters that were measured (A, W_s, Figure 3) and calculated (α, U_d, Table 2) at these sites. Note that in this model we do not need to parameterize Ca uptake in the surface soil. We assumed α to be the same for all sites by taking the slope of the regression through all points in Figure 4C ($\alpha = 0.0133$). Our model suggests that small differences in Ca uptake from the deep soil had a large effect on the exchangeable Ca content in the surface soil over few centuries, i.e. the life time of old-growth canopy dominants (Figure 6). The exchangeable Ca content in the surface soil beneath the 'high' sugar maple site increased much faster over time than the 'low' sugar maple site. This is caused by the higher Ca uptake from the deep soil at the sugar maple site with a high total mineral Ca content (Table 2). While the exchangeable Ca content in the surface soil increases with time beneath sugar maple, so does Ca leaching below the surface soil until it equals Ca uptake from the deep soil plus the Ca inputs from atmospheric deposition and weathering and steady state is reached. Because of a lack of sufficient Ca uptake from the deep soil beneath hemlock, the exchangeable Ca contents in the surface soil drop until Ca leaching has decreased sufficiently.

These results suggest that Ca uptake in the deep soil has the effect of bringing the exchangeable Ca content in the surface soil from parent material ranging from low to high in Ca beneath sugar maple into a fairly wide range. The lack of Ca uptake in the deep soil beneath hemlock results in a convergence of exchangeable Ca, no matter what the parent material Ca concentration is. The divergent relationships between exchangeable and total mineral Ca under these two tree species are in agreement with observations at the Canaan Mountain plateau by Finzi *et al*. (1998*a*), van Breemen *et al*. (1997), and ourselves. Our model shows that a change in tree composition can alter the exchangeable Ca content in the surface soil significantly within the life span of the tree.
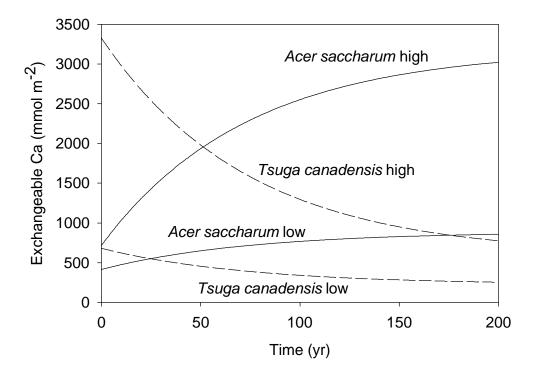
Figure 6. Exchangeable Ca in the surface soil modeled with time for *Acer saccharum* and *Tsuga canadensis* sites with low and high total mineral Ca concentrations in the soil.

Conclusions

Calcium leaching to soil depths below 20 cm was much higher beneath sugar maple than beneath hemlock. Beneath sugar maple Ca leaching was positively correlated with the total mineral Ca concentration in the soil and was always higher than the sum of Ca input from atmospheric deposition and weathering in the surface soil. Also the release of Ca through organic matter decomposition was significantly higher beneath sugar maple than beneath hemlock. These results support two possible explanations: 1) Ca depletion from the surface soil (forest floor + upper 20 cm of the mineral soil) occurs at our sites much faster beneath sugar maple than beneath hemlock, and 2) appreciable Ca uptake in the deep soil helps to maintain high exchangeable Ca contents in the surface soil beneath sugar maple. A higher Ca uptake in the deep soil beneath sugar maple was supported by higher fine root densities in the deep soil beneath sugar maple than beneath hemlock. The high flux of Ca release through organic matter decomposition compared to the low Ca leaching below the surface soil indicates however that for both tree species most of the Ca released through decomposition is taken up again in the surface soil (>85%). Beneath hemlock more fine roots were present in the forest floor, where possibly, with

the aid of ectomycorrhizal mycelium, Ca uptake by the tree was potentially larger, while the organic matter decomposition rate was slower. This may have kept exchangeable Ca contents in the surface soil small beneath hemlock resulting in small Ca leaching losses to deeper soil layers. With a simple model we illustrated that even a slightly higher Ca uptake from the deep soil can substantially increase Ca availability in the surface soil within the life span of these trees.

Acknowledgements

Chapter 7

General Conclusions

One of the key mechanisms by which tree species can alter soil acidity and Ca availability in the soil is through their production of organic acids. Organic acids and the associated decrease in soil pH can enhance mineral weathering. At the same time Al released by weathering can compete for Ca on exchange sites, and consequently enhance leaching of Ca and organic anions to deeper soil layers. Of the six tree species studied in this thesis, hemlock produced most organic acidity (both low molecular weight organic acids and fulvic acids), especially in the forest floor. Micromorphological data suggest that soil weathering in the upper 10 cm of the mineral soil is more intense, with stronger weathering of biotite grains, below hemlock than below sugar maple, presumably due to a lower soil pH and higher production of strong organic acids. From a strontium isotope study however, I could not detect differences in Ca weathering rates in the upper 20 cm of the mineral soil among the six tree species. Calcium weathering rates appeared to be small (less than 2 mmol m^{-2} yr^{-1}, compared to 4 mmol m^{-2} yr^{-1} from atmospheric deposition) and therefore, the impact of organic acids on Ca weathering in acidic soils derived from granitic material is probably small. The Ca weathering rates were significantly positively correlated with total Ca concentrations in the upper 20 cm of the mineral soil, where plagioclase was the most important Ca weatherable mineral.

Organic acidity in the forest floor is mainly neutralized through cation exchange. Because of low exchangeable base cation concentrations in the forest floor beneath hemlock, little of the organic acidity was neutralized in the forest floor. Higher exchangeable Al concentrations in the mineral soil beneath hemlock suggest that the organic acidity beneath hemlock may be neutralized by Al that is released through mineral weathering. Base cation concentrations were much higher in the forest floor beneath sugar maple and white ash than beneath the other species, and consequently much more of the organic acidity was neutralized in sugar maple and white ash forest floors. Also leaching of Ca (and other base cations) below 20 cm of the mineral soil was higher beneath sugar maple and white ash than beneath the other tree species. Leaching of Al bound to DOC was significantly higher in the mineral soil beneath hemlock. Much of this Al precipitates deeper in the soil profile, e.g. as organic solid Al phases, which is a characteristic feature of the formation of podzols (e.g. Ugolini and Dahlgren, 1987). However, I found no evidence of a higher organically bound Al pool (pyrophosphate extractable Al) in the mineral soil beneath hemlock than beneath the other tree species.

Another important mechanism by which tree species can alter Ca availability in the soil is through their effect on Ca storage (in biomass and litter), release and uptake. Net Ca mineralization from decomposing litter is one of the highest Ca fluxes within the tree-soil system and determines to a large extent the immediate Ca availability for plant uptake in this system. More Ca was released per unit mass loss of forest floor beneath sugar maple and white ash than beneath the other tree species, which was attributed to higher Ca content of the incoming litter. Litters of red maple, beech, red oak, and hemlock were more recalcitrant, and contributed to a higher forest floor mass beneath these tree species than beneath sugar maple and white ash. Differences in total net Ca mineralization in the forest floor per unit area were insignificant among tree species. However, in the mineral soils beneath sugar maple and white ash, net Ca mineralization was substantial and significantly higher than beneath the other tree species. The annual internal cycling of Ca via Ca release through organic matter decomposition greatly

exceeded the fluxes into and out of the system (atmospheric deposition, soil weathering and leaching) beneath all tree species.

For sugar maple and hemlock sites I compared Ca fluxes into and out of the system by taking the boundary of the system at 20-cm soil depth. At sugar maple sites much more Ca was leached from this layer than entered the layer through soil weathering and atmospheric deposition. By contrast, at 0- to 20-cm depth beneath hemlock, inputs from weathering and atmospheric deposition were similar to leaching of Ca. Without extra Ca inputs into the surface soil (forest floor + upper 20 cm of the mineral soil), sugar maple sites should lose substantial amounts of Ca each year. Sugar maple could sustain high levels of available Ca in the surface soil by taking up appreciable amounts of Ca in deeper soil layers, and returning that Ca in aboveground litter. A higher Ca uptake in the deep soil beneath sugar maple was supported by higher fine root densities in the deep soil beneath sugar maple than beneath hemlock. With a simple model I illustrated that even a slightly higher Ca uptake from the deep soil can substantially increase Ca availability in the surface soil within the life span of these trees.

Calcium fluxes of organic mineralization and uptake are very large compared to fluxes of Ca into (atmospheric deposition and soil weathering) and out (leaching) of the system. When organic mineralization rates are higher than uptake rates of Ca in the surface soil, the amount of available Ca in the surface soil can increase. It is through this balance of organic mineralization and uptake rates, and leaching of accessory Ca (with organic anions) in the surface soil that tree species can significantly alter Ca availability in the surface soil (and other properties, such as pH and Al solubility) within the life time of the tree. In this way, a single tree generation can create soil conditions that will influence the fitness of future tree generations. On the other hand, tree species effects on soil weathering and soil formation (such as podzolization) are much slower and significant differences between tree species may only establish after several tree generations. The results of this thesis plead for an incorporation of tree-soil feedbacks into dynamic forest ecosystem models for a better understanding of long-term forest dynamics.

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Summary

Large differences in soil pH and available Ca in the surface soil exist among tree species growing in a mixed hardwood forest in northwestern Connecticut. The observed association between tree species and specific soil chemical properties within mixed-species stands implies that changes in the distribution and abundance of tree species alter the spatial and temporal pattern of soil acidity and Ca cycling in this forest. With continuing stress of acid atmospheric deposition, these alterations could have large effects on forest community and ecosystem dynamics. The objectives of this thesis were 1) to identify and quantify specific biogeochemical processes that are responsible for the differences in Ca availability in the surface soil (forest floor and upper 20 cm of the mineral soil) and other related soil properties under different tree species and 2) to separate tree species effects from soil effects on soil properties in the surface soil. Mineral weathering, leaching, organic mineralization, and uptake of Ca were studied beneath sugar maple (*Acer saccharum*), hemlock (*Tsuga canadensis*, Carr.), American beech (*Fagus grandifolia*, Ehrh.), red maple (*Acer rubrum*, L.), white ash (*Fraxinus americana*) and red oak (*Quercus rubra*, L.).

Tree species can modify soil weathering by changing soil pH and by producing organic acids that form metal complexes. I used soil mineral data and stable strontium isotopes as a marker for Ca to investigate tree species effects on Ca weathering in the soil (Chapter 2). I also determined the quantity, nature and degree of neutralization of organic acids that are produced in the forest floor under different tree species and examined the role of organic acids on base cation leaching (Chapter 3). I found no significant tree species effect on Ca weathering, which was attributed to the low Ca content of the soil parent material. Organic acids had a significant effect on base cation leaching from forest floors, with higher leaching from forest floors that contained more exchangeable base cations.

Organic acids forming metal complexes influence the distribution and mobilization of aluminum and iron in the soil and enhance the podzolization process. Aluminum affects the Ca availability in the soil by displacing Ca on the exchange complex. I compared concentrations of exchangeable and organic-bound solid Al and of aqueous Al species at different soil depths to study the effect of tree species on the Al solubility and mobility in the soil (Chapter 4). In spite of pronounced differences in dissolved organic Al between tree species, no significant differences were found in the concentrations of organic-bound solid Al between tree species at different depths. The intensity and duration that tree species exert on Al migration was probably too small to have caused pronounced differences in Al redistribution in the soil.

Litter quality and quantity affects the quantity and timing of calcium release in the forest floor. As a result it can influence the availability of Ca in the soil profile. I estimated organic Ca mineralization rates in the forest floor and upper 15 cm of the mineral soil by field incubations (Chapter 5). Per unit area no significant differences in net Ca mineralization rates were observed in the forest floor among tree species. However, net Ca mineralization rates in the mineral soil were substantial beneath sugar maple and white ash and significantly higher than beneath the other tree species.

By comparing Ca weathering, mineralization, and leaching rates between sugar maple and hemlock, I inferred that sugar maple trees could sustain high amounts of

available Ca in the surface soil by taking up appreciable amounts of Ca from deeper soil layers (Chapter 6). Beneath hemlock more fine roots were present in the forest floor than beneath sugar maple, increasing potential Ca uptake in the forest floor. Calcium mineralization rates that are similar to Ca uptake rates in the surface soil may have kept exchangeable Ca contents in the surface soil small beneath hemlock resulting in small Ca leaching losses to deeper soil layers. With a simple model I illustrated that even a slightly higher Ca uptake from the deep soil can substantially increase Ca availability in the surface soil within the life span of these trees.

Samenvatting

Er bestaan grote verschillen in bodem pH en beschikbaar Ca in de bovengrond tussen boomsoorten in een gemengd bos in het noordwesten van Connecticut, de Verenigde Staten. Het waargenomen verband tussen boomsoort en bepaalde bodem chemische eigenschap in een gemengd bos, betekent dat door veranderingen in de distributie en aanwezigheid van bepaalde boomsoorten, de ruimtelijke en tijdelijke patronen van bodem verzuring en Ca beschikbaarheid zullen veranderen in dit bos. Met de aanhoudende stress van zure regen, kunnen deze veranderingen grote gevolgen hebben voor de dynamiek van het bos ecosysteem. De doelstellingen van dit proefschrift waren 1) het identificeren en kwantificeren van specifieke biogeochemische processen die verantwoordelijk zijn voor de verschillen in Ca beschikbaarheid in de bovengrond (strooisellaag en bovenste 20 cm van de minerale bodem) en andere gerelateerde bodem eigenschappen, onder verschillende boomsoorten, en 2) het onderscheiden van effecten van verschillende boomsoorten van effecten van verschillen in moedermateriaal op bodem eigenschappen in de bovengrond. Ik onderzocht minerale verwering, uitspoeling, organische mineralisatie en opname van Ca onder suiker esdoorn (*Acer saccharum*), hemlock (*Tsuga canadensis*, Carr.), amerikaanse beuk (*Fagus grandifolia*, Ehrh.), rode esdoorn (*Acer rubrum*, L.), es (*Fraxinus americana*) en rode eik (*Quercus rubra*, L.).

Boomsoorten kunnen minerale verwering beïnvloeden door de bodem pH te veranderen en door organische zuren te produceren die metaal complexen kunnen vormen. Om de effecten van boomsoorten op de Ca verwering in de bodem te bestuderen, gebruikte ik bodem mineralogische gegevens en stabiele strontium isotopen waarmee de twee Ca bronnen in het boom-bodem systeem te traceren zijn (Hoofdstuk 2). Ook bepaalde ik de hoeveelheid, karakter en mate van neutralisering van de organische zuren die geproduceerd worden in de strooisellaag onder verschillende boomsoorten, en onderzocht ik de rol van organische zuren op uitspoeling van basische kationen (Hoofdstuk 3). Er bestond geen significant boomsoort effect gevonden op de Ca verwering, waarschijnlijk als gevolg van de lage Ca gehaltes van het bodem moeder materiaal. Organische zuren hadden een significant effect op de uitspoeling van basische kationen uit de strooisellaag, met grotere uitspoeling uit strooisellagen die meer uitwisselbare basische kationen bevatten.

Organische zuren, die metaal complexen vormen, beïnvloeden de distributie en mobiliteit van aluminium en ijzer in de bodem en vergroten het podzolisatie proces. Aluminium beïnvloedt de Ca beschikbaarheid in de bodem door Ca van het uitwisselingscomplex te verdringen. Ik vergeleek concentraties van uitwisselbaar en vast organisch gebonden Al en van Al bestanddelen in bodemoplossing op verschillende dieptes in de bodem tussen boomsoorten om hun effect op Al oplosbaarheid en mobiliteit in de bodem te bepalen (Hoofdstuk 4). Ondanks duidelijke verschillen in opgelost organisch Al tussen boomsoorten, vond ik geen significante verschillen in concentraties van vast organisch gebonden Al. De intensiteit en duur die de boomsoorten uitoefenen op Al migratie was waarschijnlijk te klein en te kort om duidelijke verschillen te veroorzaken in Al distributie in de bodem.

De kwaliteit en kwantiteit van het strooisel beïnvloedt het vrijkomen van Ca in de strooisellaag, en daarmee de beschikbaarheid van Ca in het bodemprofiel. De snelheid van mineralisatie van organisch Ca werd geschat in de strooisellaag en in de bovenste 15

cm van de minerale bodem door middel van veld incubaties (Hoofdstuk 5). Per oppervlakte was de netto Ca mineralisatie snelheid in de strooisellaag niet significant verschillend tussen boomsoorten, maar in de minerale bodem verliep de netto Ca mineralisatie significant sneller onder suiker esdoorn en es, dan onder de andere boomsoorten.

Uit vergelijking van Ca verwering, mineralisatie en uitspoelings snelheden onder suiker esdoorn en hemlock, bleek dat suiker esdoorn bomen grote hoeveelheden van beschikbaar Ca in de bovengrond kan handhaven door hogere opname van Ca uit diepere bodemlagen (Hoofdstuk 6). Onder hemlock waren meer fijne wortels aanwezig in de strooisellaag dan onder suiker esdoorn, en was de potentiele Ca opname het hoogst in de strooisellaag. Door ongeveer gelijke snelheden van Ca mineralisatie en van Ca opname in de bovengrond, blijven onder hemlock de uitwisselbare hoeveelheid Ca in de bovengrond laag, en de uitspoeling van Ca naar diepere bodemlagen gering. Met een simpel model werd aangetoond dat slechts een geringe toename in Ca opname uit de diepe bodem onder suiker esddoorn al beduidend hogere beschikbare Ca gehaltes in de bovengrond kan bewerkstelligen binnen de levensduur van deze bomen.

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Appendix
Derivation of weathering equation

The fraction of the atmospheric Sr in a Sr mixture of both atmospheric and weathering sources ($X_{mix,D}$) is given by (after Graustein, 1989):

$$X_{mix,D} = \frac{Sr_W - Sr_{mix}}{Sr_W - Sr_D} \tag{1}$$

where Sr_W is the Sr isotope ratio $^{87}Sr/[^{87}Sr + {}^{86}Sr]$ of the weathering end member, Sr_{mix} is the isotope ratio of the mixture and Sr_D is the isotope ratio of the atmospheric end member. A simple Sr budget for a tree site during a tree's life span is given by (see also Figure 1):

$$\Delta E_{Sr} = D_{Sr} + W_{Sr} - O_{Sr} \tag{2}$$

where ΔE_{Sr} is the net change in the exchangeable pool in the soil, D_{Sr} is the atmospheric deposition of Sr, W_{Sr} is the mineral weathering of Sr and O_{Sr} is the total loss of Sr from the soil (i.e., leaching below the rooting zone L_{Sr} and net biomass increment and fixation of Sr in litter B_{Sr}).
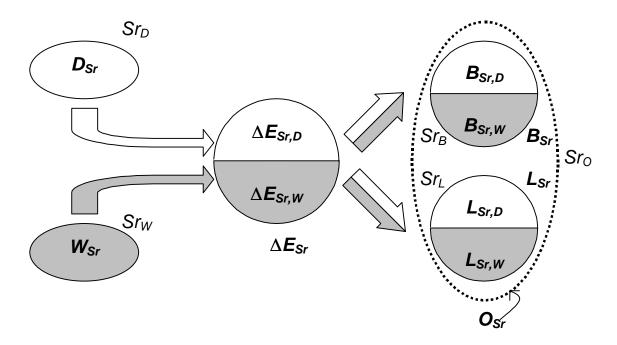

Figure 1. The flow of atmospheric (white) and weathered (gray) strontium through a forest ecosystem. D_{Sr} = atmospheric deposition, W_{Sr} = mineral weathering, ΔE_{Sr} = the net change in the exchangeable soil pool, B_{Sr} = net biomass storage, L_{Sr} = leaching, O_{Sr} = Sr lost from the soil. Sr_x = the Sr isotope ratio in flow X.

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All fluxes are given in mg m^{-2} yr^{-1}. The change in atmospheric Sr in the exchangeable pool in the soil $\Delta E_{Sr,D}$ can be written as:

$$\Delta E_{Sr,D} = D_{Sr} - O_{Sr,D} \tag{3}$$

where $O_{Sr,D}$ is the flux of atmospheric Sr lost from the soil. With:

$$O_{Sr,D} = X_{O,D} O_{Sr} \tag{4}$$

equation (3) can be written as:

$$\Delta E_{Sr,D} = D_{Sr} - X_{O,D} O_{Sr} \tag{5}$$

where $X_{O,D}$ is the fraction of atmospheric Sr lost from the soil. The total net change of Sr in the exchangeable pool can be written as:

$$\Delta E_{Sr} = \Delta E_{Sr,D} + \Delta E_{Sr,W} \tag{6}$$

where $\Delta E_{Sr,W}$ is the change in the amount of weathered Sr in the exchangeable pool in the soil. The fraction of atmospheric Sr in the net change of Sr in the exchangeable pool will be equal to the fraction of atmospheric Sr lost from the soil:

$$\frac{\Delta E_{Sr,D}}{\Delta E_{Sr,D} + \Delta E_{Sr,W}} = X_{O,D} \tag{7}$$

Substituting $\Delta E_{Sr,D}$ of equation (5) into equation (7), $\Delta E_{Sr,W}$ can be expressed as:

$$\Delta E_{Sr,W} = \frac{(1 - X_{O,D})(D_{Sr} - X_{O,D} O_{Sr})}{X_{O,D}} \tag{8}$$

Similar to equation (3) the change in the weathered Sr in the exchangeable pool can also be written as:

$$\Delta E_{Sr,W} = W_{Sr} - (1 - X_{O,D}) O_{Sr} \tag{9}$$

Using equation (8) and (9), eliminating the terms $\Delta E_{Sr,W}$ and O_{Sr}, the mineral weathering of Sr can be expressed as:

$$W_{Sr} = \frac{(1 - X_{O,D})D_{Sr}}{X_{O,D}} \tag{10}$$

and with equation (1):

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$$W_{Sr} = \frac{Sr_O - Sr_D}{Sr_W - Sr_O} D_{Sr} \tag{11}$$

where Sr_O is the isotope ratio of the Sr lost from the soil. The Ca weathering rate W_{Ca} can be calculated by multiplying the Sr weathering rate with the Ca to Sr weathering ratio r_{Ca}/r_{Sr}:

$$W_{Ca} = \frac{Sr_O - Sr_D}{Sr_W - Sr_O} D_{Sr} \frac{r_{Ca}}{r_{Sr}} \tag{12}$$

Curriculum Vitae

Feike Auke Dijkstra werd geboren op 8 februari, 1967 te Castro, Brazilië. In 1985 behaalde hij het VWO diploma aan de scholengemeenschap Jan van Arkel te Hardenberg. Van 1985 tot 1990 studeerde hij Tropische Landbouw met als afstudeerrichting Tropische Bodemkunde en Waterbeheer aan de Internationale Agrarische Hogeschool Larenstein te Deventer. Zijn praktijktijd bracht hij door op een ontwikkelingsproject van de FAO (VN) in het noordoosten van Thailand, waar hij de effecten op de bodem bestudeerde van nieuwe teelt systemen (agroforestry). Na 14 maanden militaire dienstplicht en 15 maanden rondzwerven in Australië en Nieuw Zeeland, begon hij in 1993 aan de studie Bodem, Water en Atmosfeer aan de Landbouwuniversiteit Wageningen (tegenwoordig Wageningen Universiteit). Voor zijn eerste doctoraalonderzoek modelleerde hij het gedrag van Polycyclische Aromatische Koolwaterstoffen (PAK's) in de bodem. Voor zijn tweede doctoraalonderzoek hield hij zich bezig met het modelleren van de koolstof dynamiek in een bosecosysteem in Italië onder invloed van verhoogde atmosferische CO_2 concentraties. In 1996 studeerde hij (met lof) af met als hoofdvakken Bodemhygiëne en –verontreiniging en Bodemvorming. Van 1997 tot 2001 werd hij via de Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO) aangesteld als Onderzoeker In Opleiding (OIO) bij het Laboratorium voor Bodemkunde en Geologie aan de Wageningen Universiteit. Voor zijn promotie onderzoek verbleef hij geruime tijd op het Institute of Ecosystem Studies in Millbrook, New York, de Verenigde Staten. Het onderzoek verricht tijdens deze periode staat beschreven in dit proefschrift.

Feike Auke Dijkstra was born on February 8, 1967 in Castro, Brazil. In 1985 he received the VWO (high school for preparatory scientific education) certificate at Jan van Arkel in Hardenberg, the Netherlands. For his B.S. he studied from 1985 until 1990 at the International Agricultural College Larenstein in Deventer, the Netherlands majoring in Tropical Soil Science and Water Management. His practical training was spent at a development project of the FAO (UN) in the northeast of Thailand, where he studied the effects on soils of agroforestry cropping systems. After 14 months of military service and 15 months of traveling in Australia and New Zealand, he started in 1993 with his M.S. study Soil, Water and Atmosphere at the Wageningen Agricultural University (now Wageningen University), the Netherlands. For his first M.S. thesis he modeled the behavior of Polycyclic Aromatic Carbohydrates (PACs) in soils. For his second M.S. thesis he modeled carbon dynamics in a forest ecosystem in Italy affected by elevated atmospheric CO_2 concentrations. He graduated (*cum laude*) in 1996 specializing in Soil Hygiene and Pollution and Soil Formation. From 1997 until 2001 he was employed by the Netherlands Organization for Scientific Research (NWO) as Researcher in Training (OIO) at the Laboratory of Soil Science and Geology, Wageningen University, the Netherlands. For his Ph.D. research he spent considerable time at the Institute of Ecosystem Studies in Millbrook, New York, USA. The research that has been done during this period is described in this Ph.D. thesis.