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FOLIAR AND SOIL NUTRIENT RELATIONSHIPS IN RED OAK AND WHITE PINE FORESTS

BY

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M.S., University of New Hampshire (1991)

DISSERTATION

Submitted to the University of New Hampshire
in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy
in
Natural Resources

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DEDICATION

To my family and friends who gave their love, support and encouragement.

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ABSTRACT

FOLIAR AND SOIL NUTRIENT RELATIONSHIPS IN RED OAK AND WHITE PINE FORESTS

by

Richard A. Hallett

University of New Hampshire, May, 1996

Red oak (*Quercus rubra* L.) and white pine (*Pinus strobus* L.) forests on sandy soils of the northeastern U.S. may have been depleted of nutrient cations by acid precipitation and intensive land use. Foliar Ca in oak was 5257 mg Ca kg⁻¹ dry matter, or over 3 times the amount of Ca in white pine foliage. Red oak also has more Mg, K, and N than white pine. Foliar Al concentration for white pine, 132 mg Al kg⁻¹ dry matter, is twice that of red oak foliage. Foliar Ca and N are correlated with basal area increment. Foliar Ca:Al ratios and Mg levels in pine foliage suggest a risk to tree health. In the organic horizons of both oak and pine forests, bases occupied 80% of the exchange sites. However, in the mineral horizons, Al occupied 96% of the exchange sites. These data indicate that both forest types are susceptible to nutrient imbalances and deficiencies that result from atmospheric deposition and harvest.

A microwave oven was used to digest standard reference materials for foliage and organic and mineral soils. We achieved recovery rates for total Al, Ca, Fe, K, Mg, Mn,

and P from mineral soils of 87% to 114% with CV's of less than 10%. Recovery rates greater than 90% were achieved for Ca, K, Mg, Mn, and P for Pine foliage. Total nitrogen recovery was 99.3% (CV 9.2%) for B horizon soils. Hyperspectral analysis techniques have proven useful for determining cellulose, lignin, and nitrogen in foliar material. These same techniques may be able to predict other foliar element concentrations thereby reducing the need for acid digestion of foliar material. Near infrared reflectance spectroscopy (NIRS) was evaluated for its effectiveness at predicting Al, Ca, Fe, K, Mg, Mn and P concentrations in white pine (*Pinus strobus* L.) and red oak (*Quercus rubra* L.) foliage. A near infrared spectrophotometer was used to scan dried, ground foliage samples. Predictions were satisfactory for Al, Ca, K, and Mg, producing CVs ranging from 14 (Mg) to 28% (Al) and explained variance ranging from 78% for Mg to 97% for Ca.

INTRODUCTION

The impacts of air pollution on forests have been studied in Europe and the United States for several decades. Research has progressed from investigations into the localized effects of air pollutants from discrete and stationary sources to the regional impacts of air pollutants from all sources. The atmospheric transformation of sulfur dioxide and nitrogen oxides to sulfuric and nitric acids and the resulting deposition of these acids onto forests is cause for major concern. This study focuses on the hypothesis that acid deposition and forest harvest contribute to the degradation of soil nutrient status through aluminum mobilization and loss of calcium, magnesium, and potassium from forest soils.

Precipitation in the New England region has a lower average annual pH than any other region in the United States (Smith 1990). Therefore a large potential exists for base cation loss from the soil due to acid deposition. Another contributing factor to nutrient loss is intensive forest harvesting that has occurred throughout New England's history (Federer et al. 1989; Hornbeck et al. 1990b; Pierce et al. 1993). In combination, these factors could result in nutrient depletion of New England's commercial forest ecosystems (Federer et al. 1989), which will in turn negatively impact forest health and productivity (Shortle and Smith 1988).

Red oak and white pine are two economically important species in New England which have been subjected to intensive harvesting since colonial times. Furthermore, these species will continue to play an important role in the timber economy of the region

(Lancaster and Leak 1978; Sampson et al. 1983). In addition, red oak and white pine occupy infertile sites that are susceptible to nutrient depletion.

The regional scope of the study required that a large number of samples be collected and processed. Efficient methods for soil and foliage digestion had to be developed to process the samples in a timely fashion. Standard methods for the complete digestion of soils involving concentrated acid mixtures and open vessel digestions are time consuming and hazardous (Rechcigl and Payne 1990; Warren et al. 1990). Microwave digestion systems offer the capability of safer, more controlled digestions and have been developed to completely dissolve a wide variety of materials prior to total element analysis. Development of a microwave digestion technique for soils collected in this study was a critical step. Total dissolution of mineral soils is especially important for determining total soil nutrient capitals.

Standard methods for foliar digestion are less hazardous than methods for mineral soil digestion; however, concentrated acids and open vessel digestions are still used. Near infrared reflectance spectroscopy (NIRS) is an environmentally friendly technique, capable of rapid, non-destructive, chemical analysis of vegetative material. NIRS has proven useful for measuring foliar cellulose, lignin, and nitrogen for forest tree species (Wessman et al. 1988; McLellan et al. 1991a; Bolster et al. 1995). Recently, NIRS has been used to determine concentrations of P, Ca, K, B, Mg, Na, Mn, Fe, Cu, and Zn in forage, grain, and grasses (Shenk et al. 1979; Clark et al. 1987, 1989; Garcia-Ciudad et al. 1993; Vazquez de Aldana et al. 1995). Development of this capability for forest tree

species can at least provide a replacement for open vessel acid digestion techniques and has implications for remote sensing applications.

The primary goal of this research is to assess the nutrient status of low elevation red oak (*Quercus rubra* L.) and white pine (*Pinus strobus* L.) forests in New England. The results of this assessment provide new information for these commercially valuable forest types and allow us to suggest indices that may help determine site susceptibility to cation depletion. We are able to suggest management strategies that will help preserve nutrients on susceptible sites. During the course of this study, highly efficient methods were developed for determining total elements in soils and foliage.

The format of this thesis is structured such that the introduction and literature review chapters are followed by three independent papers addressing the following topics:

1. Foliar and soil nutrient relationships in red oak and white pine forests.
2. Microwave digestion of forest soils and foliage.
3. Predicting elements in white pine and red oak foliage with near infrared reflectance spectroscopy.

CHAPTER 1

BACKGROUND AND LITERATURE REVIEW

Historical Perspective of Acid Rain Research

Acid rain, a phenomenon brought about by chemicals introduced into the atmosphere from both industrial and non-industrial sources, is a complex mixture of acids and salts. The most common strong acids in acid precipitation are sulfuric and nitric (Galloway et al. 1976). High levels of these acids in precipitation raise concerns as to the effects of acid rain on both terrestrial and aquatic environments.

Effects of pollution on rainwater chemistry were recognized almost 150 years ago when Robert Smith determined that sulfuric acid dominated rain chemistry in London (Binkley et al. 1989). In 1955, Eville Gorham concluded that the acids in rain were derived from industrial sources and that lakes, streams, and soils could be acidified by these acids (Binkley and Hart 1989). In the early 1960's, Svante Odén in Sweden, concluded that acid precipitation was leading to the acidification of aquatic ecosystems. Odén also stated that due to the transport of air pollutants across international boundaries, acid rain was a global problem. Odén (1976) reported that the concentration of H^+ , SO_4^- , and Ca^{2+} had been increasing in the rivers of Sweden since 1916. He concluded that the Ca^{2+} was steadily leached from the soil by acid rain.

In the early 1970's, a disease known as "fir dieback" was noticed in Bavaria. In 1980, similar symptoms were observed in the spruce of the Black Forest. During this same time period, Douglas fir and some deciduous species became increasingly affected

both in Bavaria and the Black Forest (Prinz et al. 1985). This increase in forest damage beginning in the early 1970's and continuing into the 1980's became known as "neuartige Waldschäden" or novel forest decline. Waldschäden differed from the classical form of smoke damage which was caused mainly by sulfur dioxide (Prinz et al. 1985) because the "novel forest decline" was focused mainly in areas that were previously considered to be clean air regions. One conclusion that came from the review of several studies is that novel forest decline is related to soil nutrient supply (Prinz et al. 1985). Subsequent studies in Europe showed that cation depletion is not only limiting to tree growth, but also detrimental to tree health (Matzner and Ulrich 1985; Zoetl and Huettl 1986; Huettl and Wisniewski 1987). To ameliorate some of the affects of cation deficiency, the German government instituted a 5 year forest fertilization plan costing \$80 million U.S. (Tomlinson 1990).

In North America widespread declines of forests have not been documented. However, high elevation spruce-fir forests in New England seem to be affected by acid deposition (McNulty et al. 1991; Eagar and Adams 1992). Shortle and Bondietti (1992) indicate that acid rain has had a negative impact on cation availability in some New England spruce stands for the past 20 to 40 years. Nutrient deficiencies in relation to acid deposition are also being studied in Quebec sugar maple stands (Bernier and Brazeau 1988a, b; Pare and Bernier 1989a, b; Ouimet and Fortin 1991).

Net losses of cations from soils are occurring in several ecosystems in the United States (Johnson et al. 1982a, b; Johnson and Todd 1990; Johnson et al. 1991a, b; Nowak et al. 1991; Joslin et al. 1992). In order for such cation depletion to occur, the losses from

the system must be greater than inputs. Possible inputs include cations in wet and dry atmospheric deposition, cations that are weathered from soil parent material, and root zone deepening. A New England study looking at low elevation northern hardwood and coniferous forests hypothesized that cations gained from these sources are not sufficient to balance losses (Federer et al. 1989).

Acid Deposition and Intensive Harvesting Trends and Processes

Acid Deposition

Human beings have been polluting the atmosphere for thousands of years. However, with the onset of the industrial age, anthropogenic atmospheric pollutants have increased logarithmically. In the United States, increased public concern relating to environmental quality prompted the adoption of the Clean Air Act (1970), which directed the Environmental Protection Agency to establish air quality standards for particulates, sulfur dioxide, nitrogen dioxide, carbon monoxide, hydrocarbons, and ozone (Smith 1990).

A temporal study of stream water chemistry at the Hubbard Brook Experimental Forest (HBEF) (Driscoll et al. 1989) indicates that sulfate and base cation concentrations in bulk precipitation have been declining since 1970. Driscoll et al. (1989) also reported a marked decline for sulfate and base cations in stream water during the same time period. Air quality monitoring data in the northeastern United States shows declining trends in ambient air concentrations of sulfur dioxide and nitrogen dioxide from 1978 to 1988 (Mohnen 1992). Other studies show that N deposition is not declining and in some cases, has increased during the last decade (Likens 1989; Ollinger et al. 1995).

The effects of acid deposition on forest soil chemistry are complex and varied. The processes covered here will relate to soils with a pH of < 4.5 and low base saturation. With the deposition of sulfuric and nitric acids, soil solution pH will decrease. Consequently, ionic aluminum concentrations will increase due to the dissolution of aluminum-containing minerals or remobilization of aluminum precipitated in the soil and held on exchange sites (Ulrich et al. 1980). The Al^{3+} released into solution is more strongly adsorbed onto soil particles than lower valence base cations, resulting in increased availability to plants or in leaching losses. The combination of additional nitrogen in the form of nitric acid and increased base cation availability can result in a "fertilizer effect" (Shortle and Bondietti 1992). As acid deposition continues, the majority of soil exchange sites can become dominated by Al. At this point, base cations have either been incorporated into biomass or leached, causing the soil solution to become dominated by Al^{3+} . Reuss (1983) examined three common ion exchange equilibrium equations and found that as long as base saturation is above 20%, the cation in solution is almost entirely Ca^{2+} . A reduction in base saturation to 10% results in a marked increase in solution Al.

Soil solutions dominated by Al can inhibit the uptake of Ca^{2+} and Mg^{2+} and in high enough concentrations even become toxic to root tissue (Cronan and Grigal 1995). Shortle and Smith (1988) found declining growth patterns in red spruce located in New England and indicated that a possible cause for this decline was the high (>1) Al:Ca ratio in fine roots. This high ratio could limit Ca supply to spruce trees. Schlegel et al. (1992) studied red spruce on Whiteface Mountain in New York and found an accumulation of Al in mycorrhizae and the root cortex. It has been shown that the root cortex cells can

become blocked with Al^{3+} , thus inhibiting the uptake of Ca^{2+} and Mg^{2+} . Lawrence et al. (1995) hypothesized that Al mobilized in the mineral soil by acid deposition is transported into the forest floor where it accumulates in a reactive, mostly organically complexed, form. This is supported by Rustad and Cronan (1995) who found that Al is accumulating in O horizons of spruce-fir forests. Mobilization of Al in mineral soils has significantly contributed to the documented decrease of root-available Ca in the forest floor (Lawrence et al. 1995).

In New England, impacts of acid deposition have been most intensively studied in high elevation spruce-fir forests where symptoms of forest decline are evident. These forests are most susceptible because of high deposition rates, harsh conditions, and shallow soils. Low elevation commercial forests have not been studied as intensively, however there is evidence that for oak-hickory forests in Ohio growing on sandy loam soils, acid deposition has led to soil changes causing growth decline during the 1970's and 1980's (Armentano et al. 1991). Another study on Al effects on northern red oak seedling growth indicated that present soil Al levels and acidic deposition rates appear to pose no threat to red oak in the southern portion of its range, whereas the possibility of Al toxicity in northeastern spodosols deserves further study (Joslin and Wolfe 1989).

Land Use

New England has been subjected to intensive land use since colonial times; in fact, a scarcity of timber began to be felt in some of the colonies by the end of the 1600's (Harper 1918). By 1875, agricultural land use had peaked (Harper 1918), leaving 20% of New England's land area forested (Foster 1992). Today over 80% of New England is

forested (Lathrop and Bognar 1994). This cycle of timber harvesting, farming, abandonment, reforestation, and continued timber harvesting has undoubtedly had a negative impact on soil nutrient capitals (Hornbeck 1990).

In the future, we can expect to see increased pressure on timber resources in New England. The relatively recent development of equipment capable of removing the total above-ground portion of the tree has changed the way forests are managed. This new technology has resulted in increased utilization of the forest biomass including trees that were previously undesirable (Pierce et al. 1993).

Whole tree harvesting has been shown to more than double the export of N, P, K, and Ca in biomass over that removed by a sawlog harvest (Johnson et al. 1982b). Another effect induced by harvesting is post harvest loss of nutrients by leaching. Within a few months after harvest, nitrification rates begin to increase resulting in higher H^+ (Pierce et al. 1993). The H^+ will displace cations from soil exchange sites. The cations are subsequently leached from the system along with nitrate.

Federer et al. (1989) reviewed data from several eastern forests and determined that harvest removal and harvest induced leaching losses account for less than 3% of the total pool (above ground, roots, forest floor, and mineral soil) of K and Mg while Ca losses ranged between 2 and 19% of the total pool (Federer et al., 1989).

Given that the highest acid deposition rates exist at higher elevations, nutrient losses due to acid deposition on low elevation commercial forests can be expected to be less than that of high elevation spruce-fir forests. However, this could be offset by the effects of past land use and continued intensive harvesting. In fact, Ca losses induced by

acid deposition in combination with losses due to intensive harvesting could remove approximately 50% of biomass and soil Ca in only 120 years (Federer et al. 1989). The nutrients Mg and K are subject to harvest removal and leaching losses to a lesser degree.

An examination of soil and foliar nutrient pools in oak and pine forests will allow us to better understand the susceptibility of these forests to nutrient imbalances caused by Al mobility and expected nutrient loss due to disturbance. Information about nutrient capitals of low elevation commercial forests will provide us with the knowledge necessary to manage our forest resources while protecting soil nutrient capitals.

Critical Element Ratios

Concentration ratios of certain elements within the plant-soil system can provide valuable information as to the relative health of the system. Currently most of the available information on critical element ratios involves high elevation spruce-fir forests or seedlings grown in greenhouse studies. Ratios that are important in relation to cation depletion are: Al:Ca in soils and roots (Shortle and Smith 1988; Bondietti et al. 1990; Shortle and Bondietti 1992; Cronan and Grigal 1995); Al:Mg in soils and roots (Tomlinson 1990); and Mg:N in foliage (McNulty et al. 1991).

Low foliar Mg:N ratios in spruce foliage have been linked to nutrient imbalances brought about by increased N availability and low soil Mg in European forests (Oren and Schulze 1989). Also, in European spruce forests nitrogen deposition can promote growth and soil acidification which in turn leads to low Mg:Al ratios in soil solution, inhibition of Mg uptake, and Mg deficiencies (Ulrich 1994). In a study of high elevation spruce-fir forests across an N deposition gradient in northern New England, McNulty et al. (1991)

found a definite trend toward lower Mg:N ratios with increasing N deposition. Needle discoloration and growth reductions have been associated with low Mg or Mg:N ratios in spruce, white pine, and red pine (Stone 1953; Oren and Schulze 1989).

The inhibitory effects of aluminum on divalent cation uptake which were discussed previously suggest that ratios of Ca and Al may be useful indicators of tree health. Cronan and Grigal found that soil solution Ca:Al ratios used in conjunction with foliar Ca:Al ratios could act as indicators of tree health. Another study showed decreased light-saturated photosynthesis and increased dark respiration with lower foliar Ca:Al ratios in Scots pine (*Pinus sylvestris* L.) on polluted sites in Poland (Reich et al. 1994) possibly resulting in lower growth rates.

Oak, pine, and birch growing in the UK in an area of high deposition rates show no signs of visible damage due to high soil Al, low pH and Ca (Skeffington 1983). However, high Al appeared to inhibit uptake of Ca and Mg by red oak seedlings growing in a variety of forest soil media (Joslin and Wolfe 1989). The documented tolerance of oak and pine (Skeffington 1983) coupled with known effects of mobile Al on nutrient uptake suggests that if nutrient imbalances are evident in these species at low elevations, forest productivity could be declining due to acid deposition and nutrient depletion.

CHAPTER 2

FOLIAR AND SOIL NUTRIENT RELATIONSHIPS IN RED OAK AND WHITE PINE FORESTS

Introduction

Increasing evidence of forest decline in Europe and North America over the last 3-4 decades has stimulated public and scientific interest about causes and possible future effects of this phenomenon (Krahl-Urban et al. 1988; International Air Quality Advisory Board 1989; Kubelka et al. 1993; Rodhe et al. 1995). The European Forest Damage Survey conducted in 1988 indicated that forest damage, expressed as a loss of needles or leaves, has been observed in 25 European countries (Global Environment Monitoring System 1990). Forest decline symptoms have been documented in North America for several forest types (Bernier and Brazeau 1988b; Binkley et al. 1989; Eagar and Adams 1992; Johnson and Lindberg 1992a).

The onset of the recent forest decline symptoms are coincident with increasing industrial inputs into the atmosphere and subsequent transport of pollutants over large geographical regions (Schulze et al. 1989; Blank et al. 1992; Cook and Zedaker 1992; Johnson and Lindberg 1992a). That is not to say that all documented incidences of forest decline are caused by increased acid precipitation and air pollution (Pitelka and Raynal 1989). Forest ecosystems are characterized by variability and continually change in time and space (Smith 1990). Efforts to assess forest decline and its causes and effects have been hampered by the inherent complexity of forested ecosystems which are long-lived

and may respond slowly and inconsistently to stressors (Pitelka and Raynal 1989; Smith 1990; and 1992b).

Many hypotheses put forth by the scientific community to explain forest decline cite changes in nutrient cycling as a central theme among contributing factors to the widespread symptoms of damaged forests. These changes include (i) nutrient deficiencies caused by acidic deposition (Krahl-Urban et al. 1988; Knoepp and Swank 1994) and intensive harvesting (Federer et al. 1989; Hornbeck et al. 1990a); (ii) impacts of increased ionic Al, including toxicity, nutrient imbalances, and interferences with cell level processes (Shortle and Smith 1988; Cronan and Grigal 1995; Rustad and Cronan 1995); (iii) antagonism between elements inhibiting uptake (Tomlinson 1990); and (iv) imbalances caused by increased N availability (McNulty et al. 1991; Aber 1992).

The forested lands of New England have undergone phases of intensive land use in the form of farming and intensive harvesting (Foster 1994). Also, precipitation in the New England region has a higher content of strong mineral acids and a lower average annual pH than any other region in the United States (Smith 1990). In northern New England, high mortality has been noted in the upper elevation spruce-fir forests where harsh environmental conditions and fragile soils exist along with high rates of acid deposition (Cook and Zedaker 1992). Widespread symptoms of forest decline have not been noted at lower elevations among the more commercially valuable tree species. However, evidence of nutrient depletion due to intensive harvesting and the cumulative effects of acid rain has been documented for commercial spruce-fir and northern and

central hardwood forests (Hornbeck and Kropelin 1982; Smith, C.T. et al. 1986; Tritton et al. 1987; Federer et al. 1989).

This evidence has led us to assess the nutrient status of low fertility white pine (*Pinus strobus*) and red oak (*Quercus rubra*) forests in northern New England and New York. This paper (i) provides information on the nutrient status of these sites in relation to cation depletion issues; (ii) compares this information with declining sites in Europe and intensively harvested sites in the United States; (iii) determines if these sites are depleted of cations or are susceptible to cation depletion. We make management recommendations that will ameliorate the depletion of nutrients due to intensive harvesting activities.

Experimental Methods

Study Areas

To address worst-case scenarios regarding cation depletion, plot selection was limited to stands with deep sandy soils (Typic Quartzipsamments) that had been previously farmed, cleared, or harvested and are now dominated by either mature red oak or white pine.

Three 20 by 20 m plots, from pure stands of each species, were selected in each of 5 northeastern states (Fig. 2.1). The soil series on the selected plots were either Adams or Windsor (Table 2.1). These soils were typically greater than 1 m deep, loamy sand texture, well-drained, and have average horizon thicknesses of 2.4 cm for O and 6.6 cm for A. Plots were located on an east to west gradient from western Maine to northern New York. Location, elevation, selected climatological variables, and soil series for each study area are listed in Table 2.1.

Fig. 2.1. Location of study sites.

Table 2.1. Location, elevation, precipitation and deposition data and soil series for each study area.

	State				
	NY	VT	MA	NH	ME
Latitude	44.83° N	44.47° N	42.52° N	43.13° N	43.42° N
Longitude	74.78° W	73.00° W	72.20° W	71.35° W	70.71° W
Elevation (m)	85	152	213	167	75
Precipitation ^a (cm yr ⁻¹)	75	92	119	114	107
N deposition ^a (kg ha yr ⁻¹)	6	6	8	7	6
S deposition ^a (kg ha yr ⁻¹)	9	9	12	10	9
Soil Series	Adams ls	Adams ls	Adams ls	Windsor ls	Windsor ls

^aEstimated from methods used in Ollinger et al. (1995).

Sample Collection and Analysis

SOILS

Soils were classified based on a complete soil pit description that was made for each set of plots (species and state). Each plot was divided into quadrants. For each of three horizons, four subsamples of equal volume were collected and composited from each quadrant and from plot center for a total of 5 composited samples. The horizons sampled consisted of (i) a combination of the Oe and Oa horizons (O); (ii) the A horizon (A); and (iii) the upper B horizon (B). The soils were sieved (mineral 2 mm, organic 5.6 mm), air dried, and stored at room temperature prior to analysis. Extractable nutrients were determined for subsamples of the sieved and air dried soils. Another subsample of each sieved, air dried sample was processed for 1 minute in a shatterbox laboratory mill (Spex Industries Inc., Edison NJ) to powder the sample prior to digestion and total element analyses. All soil samples were analyzed by the methods listed in Table 2.2. Element concentrations (mg kg⁻¹ soil) were expanded to kg ha⁻¹ using bulk density (g soil cm⁻³) and average horizon thickness for each plot to a total depth of 60 cm.

FOLIAGE

Leaves and needles from 5 dominant or co-dominant trees were sampled in each plot by shooting off small branches with a 12 gauge shotgun (#4 steel shot). Two samples were collected from each tree, one from the top of the crown (sun leaves) and one from mid-canopy. All samples were collected between August 1 and August 20, 1993. The element concentrations from the upper and middle samples were averaged for each tree. Foliage samples were separated from the branch and petiole, oven dried at 70^o C, and ground in a Wiley mill to pass a 1 mm mesh screen. Foliage samples were analyzed by methods listed in Table 2.2.

STAND DIMENSIONS

A stand survey was completed for each plot by recording species, diameters, and heights for all trees greater than 10 cm diameter at breast height. Basal area (m²) was calculated for each tree, summed and converted to basal area (m² ha⁻¹) for each plot. Three of the 5 trees sampled for foliage were cored with a 12 mm increment borer. The cores were air dried, mounted, and sanded in preparation for ring width measurements (Krusic et al. 1987). Core measurement and calculation of basal area increment (BAI) was accomplished using the methods of Smith et al. (1990). Average BAI (cm² yr⁻¹) for 1984-1993 was calculated for all cores and used to test for correlations between growth and foliar nutrient concentrations.

Table 2.2. Analytical methods for soils and foliage.

Parameter	Method	Reference
<i>Soils</i>		
pH	0.01 M CaCl ₂	(Kalra and Maynard 1991)
Total Al, Ca, Mg, K	Microwave digestion with HNO ₃ , HCL, HBF ₄ ^a	(Hallett et al. 1996)
Total N	Block digestion (H ₂ SO ₄ , H ₂ O ₂ w/ selenous acid) ^a	(Isaac and Johnson 1976)
Extractable Al, Ca, Mg, K	Extracted with 0.05 N HCl, 0.025 N H ₂ SO ₄ ^a	(Taylor, R.W. 1987)
Organic Matter (%)	Loss on ignition (LOI)	(Kalra and Maynard 1991)
<i>Foliage</i>		
Total Al, Ca, Mg, K, N	Block digestion (H ₂ SO ₄ , H ₂ O ₂ w/ selenous acid) ^a	(Isaac and Johnson 1976)
<i>Calculations</i>		
CEC ^b (meq kg soil ⁻¹)	Sum Extractable (Al, Ca, Mg, K) + [H+]	
Base Saturation (%)	Sum Extractable (Ca, Mg, K)/CEC	
Bulk Density (g soil cm ⁻³)	Derived from LOI	(Federer et al. 1993)

^a Analysis of the digestate for Al, Ca, Mg, and K was by direct current plasma spectrometer. Analysis for N was by a TRAACS 800 autoanalyzer.

^b Cation exchange capacity.

Statistical analyses

Significant differences between states were investigated using analysis of variance followed by the Scheffe method for means separation (Neter et al. 1985). Correlation analysis was used to test for significant relationships between foliar elements and extractable elements in the soil, foliar elements and BAI, and between different foliar elements (Neter et al. 1985). A two-tailed t test was used to test for differences in variables between species (Neter et al. 1985). All statistical tests were performed using the 0.05 level of significance.

Results

Above ground vegetation

The average age of the stands in this study ranged from 59 to 109 years for red oak and 37 to 94 years for white pine (Table 2.3). Average stand diameter ranged from 22 to 32 cm for red oak and 26 to 37 cm for white pine (Table 2.3). Average stand height ranged from 12 to 20 m for both species (Table 2.3). Average 10-year growth rates (1984-1993) ranged from 8 to 20 cm² yr⁻¹ for red oak and 19 to 54 cm² yr⁻¹ for white pine (Table 2.3) confirming that red oak may not be as well suited as white pine to infertile sandy soils (Pritchett 1979). The Vermont site had the highest growth rates for both red oak (20 cm² yr⁻¹) and white pine (54 cm² yr⁻¹).

FOLIAR ELEMENT CONCENTRATIONS

Foliar element concentrations occurred in the following order N>K>Ca>Mg>>Al for both species (Table 2.4). Aluminum occurs in such small amounts because it is a non-essential plant element which is actively excluded from plant uptake (Taylor, G. 1987). There are large, significant differences between species in foliar levels of Al, Ca, Mg, K and N averaged across all sites ($\alpha < 0.05$). Foliar Ca in red oak averaged 5260 mg Ca kg⁻¹ dry matter, or over 3 times the amount of Ca contained in white pine foliage. Red oak also has more Mg, K, and N than white pine. White pine contains 132 mg Al kg⁻¹ dry matter, twice the aluminum content of red oak foliage.

Red oak exhibits highest foliar Ca concentrations in Vermont (Table 2.4) possibly due to the common occurrence of calcareous soil parent material in the Lake Champlain valley. There is a decreasing trend in foliar K levels from east to west, ranging from 8280 mg K kg⁻¹ dry matter in Maine to 7090 mg K kg⁻¹ dry matter in New York (Table 2.4).

There are no significant differences between states for foliar Al, Mg, and N. Foliar N concentrations have been shown to be highly correlated with net primary productivity ($\text{kg ha}^{-1} \text{ yr}^{-1}$) in N limited systems (Field and Mooney 1986). However, on the sites in this study, foliar N concentration was not significantly correlated with BAI (Fig. 2.2). On the other hand, foliar Ca is correlated with 10-year (1984-93) mean BAI ($\text{cm}^2 \text{ yr}^{-1}$) (Fig. 2.2).

Geographically, white pine foliage shows increasing levels of Al, Mg, and N from east to west (Table 2.4). Vermont again has the highest foliar Ca and N levels (Table 2.4). There is no significant difference across the region for foliar K levels (Table 2.4). As with red oak, foliar concentrations of Ca in white pines are correlated with average BAI ($\text{cm}^2 \text{ yr}^{-1}$) for 1984 - 93 ($\alpha < 0.05$) (Fig. 2.2). Foliar concentrations of N are slightly less correlated with average BAI.

Table 2.3. Average stand age, basal area, BAI, DBH and height for each study site by state and species. Standard deviation in parentheses.

State	Age (yrs)	BAI ^a (cm ² yr ⁻¹)	Basal Area ^c (m ² ha ⁻¹)	DBH ^{bc} (cm)	Height ^c (m)
Red Oak					
NY	59 (3)	17 (1)	14 (5)	22 (3)	16 (2)
VT	69 (2)	20 (5)	15 (3)	32 (2)	19 (1)
MA	97 (2)	11 (3)	23 (15)	32 (3)	19 (1)
NH	110 (1)	8 (3)	11 (3)	27 (4)	12 (1)
ME	70 (18)	18 (7)	21 (5)	22 (1)	12 (1)
White Pine					
NY	38 (2)	35 (4)	13 (4)	26 (2)	20 (<1)
VT	95 (16)	54 (5)	24 (1)	31 (8)	17 (4)
MA	70 (17)	20 (1)	33 (3)	31 (5)	17 (3)
NH	82 (10)	19 (2)	23 (5)	30 (3)	12 (<1)
ME	78 (9)	20 (3)	41 (9)	37 (8)	18 (6)

^a BAI averaged over 10 years (1984-1993).

^b Diameter at breast height.

^c Trees > 10 cm DBH.

Table 2.4. Foliar element concentrations by species and state (mg kg⁻¹ dry matter). Standard deviation given in parentheses. Means with different lower case letters are significantly different between states ($\alpha < 0.05$).

State	Al	Ca	Mg	K	N
Red Oak Foliage					
NY	63(59)	ab 5320(1790)	1390(184)	b 7090(410)	19000(3280)
VT	88(4)	b 7360(282)	1510(224)	b 7440(382)	19700(600)
MA	53(4)	a 4130(493)	1480(48)	ab 8060(335)	17200(2480)
NH	65(4)	a 4430(571)	1630(137)	a 9440(850)	15530(67)
ME	59(10)	ab 5050(151)	1770(46)	ab 8280(65)	15800(491)
White Pine Foliage					
NY	b 168(21)	a 1620(87)	c 1170(10)	5190(365)	bc 13500(117)
VT	b 172(12)	b 2370(262)	c 1220(32)	5430(1080)	c 13900(222)
MA	a 123(9)	a 1420(22)	b 875(43)	5520(643)	bc 12300(611)
NH	a 102(11)	a 1260(146)	ab 920(7)	6790(291)	b 11100(323)
ME	a 92(10)	a 1170(299)	a 1000(43)	6670(710)	a 11500(1030)

Fig. 2.2. Red oak and white pine foliar Ca and N (mg kg^{-1}) plotted against 10-year (1984-93) average BAI ($\text{cm}^2 \text{yr}^{-1}$). Best fit line displayed on each graph.

FOLIAR ELEMENT RATIOS

Foliar Mg:N ratios have been shown to decrease with increasing N deposition, suggesting a possible nutrient imbalance brought about by higher N availability and a net loss of available Mg (Oren and Schulze 1989). Foliar Mg:N ratios show an increasing trend from west to east in red oak foliage (Fig. 2.3). This is the same trend that McNulty et al. (1991) found for spruce-fir across a nitrogen deposition gradient in northern New England. White pine foliage does not exhibit a clear trend in foliar Mg:N ratios.

Foliar Ca:Al ratios have been shown to be related to forest decline symptoms (Shortle and Smith 1988; Cronan and Grigal 1995; McNulty et al. 1996). In this study, foliar Ca:Al ratios do not exhibit a regional trend for either species, however white pine foliage has significantly lower values than red oak. ($\alpha < 0.05$)(Fig. 2.4).

Fig. 2.3. Foliar Mg:N ratios for white pine and red oak. Bars marked with different letter combinations are significantly different ($\alpha < 0.05$) between states. Error bars are 1 standard deviation.

Fig. 2.4. Foliar Ca:Al ratios for white pine and red oak. Error bars are 1 standard deviation. The 50% risk line indicates possible nutrient imbalances in white pine.

Soils

All plots evidenced a plow layer indicating that the sites had been farmed. The rooting depth at all sites extended to 40 cm, however 75% (visual estimate) of the roots were found in the O and A horizons (upper 10 cm of the profile). Organic matter content for each horizon can be found in Table 2.5. There were no clear regional trends in any of the soil variables collected and no significant differences between soil pH on the red oak plots versus white pine plots ($\alpha < 0.05$) (Table 2.5, Table 2.6). Normally the lower base content of conifer foliage results in soils supporting conifers having lower pHs than soils supporting hardwoods (Pritchett 1979).

Table 2.5. Cation exchange capacity (CEC), base saturation (%), and organic matter (%) by species, state and horizon. Standard deviation in parentheses. Means with different lower case letters are significantly different between states ($\alpha < 0.05$).

State	Red Oak				White Pine			
	pH (CaCl ₂)	CEC (meq kg ⁻¹ soil)	Base Saturation (%)	OM (% LOI)	pH (CaCl ₂)	CEC (meq kg ⁻¹ soil)	Base Saturation (%)	OM (% LOI)
<i>O horizon</i>								
NY	a 3.9 (<1)	a 383 (17)	a 92 (1)	71 (9)	ab 3.5 (0.1)	313 (48)	88 (2)	88 (1)
VT	a 4.3 (0.2)	b 476 (79)	a 92 (3)	70 (7)	a 4.0 (0.3)	313 (28)	88 (1)	74 (5)
MA	b 3.0 (0.1)	c 231 (10)	b 70 (8)	92 (1)	ab 3.2 (0.3)	224 (65)	64 (13)	87 (1)
NH	a 3.6 (0.2)	ac 306 (22)	ab 84 (2)	97 (3)	ab 3.5 (0.1)	213 (15)	81 (2)	86 (3)
ME	a 4.0 (0.1)	ab 423 (21)	ab 86 (12)	86 (4)	b 3.0 (0.1)	294 (94)	75 (15)	84 (6)
<i>A horizon</i>								
NY	ab 3.6 (0.1)	c 41 (16)	a 8 (3)	2 (<1)	ab 3.7 (0.1)	130 (98)	6 (1)	3 (<1)
VT	b 3.7 (<1)	ac 85 (10)	ab 6 (2)	5 (<1)	b 3.8 (0.1)	60 (10)	8 (3)	4 (<1)
MA	ab 3.7 (0.1)	b 177 (27)	ab 3 (<1)	11 (1)	bc 3.9 (0.2)	136 (57)	2 (1)	10 (3)
NH	a 3.4 (0.1)	ac 93 (23)	ab 2 (<1)	7 (1)	ad 3.3 (<1)	51 (3)	13 (3)	8 (<1)
ME	b 3.9 (<1)	ab 147 (30)	b 2 (<1)	6 (1)	d 3.2 (0.2)	115 (11)	10 (8)	19 (1)
<i>B horizon</i>								
NY	4.5 (0.1)	ab 190 (38)	a 0	2 (<1)	a 4.0 (0.1)	a 124 (46)	2 (<1)	2 (<1)
VT	4.7 (0.1)	a 109 (8)	b 2 (<1)	1 (<1)	b 4.6 (0.1)	a 105 (5)	2 (1)	2 (<1)
MA	4.6 (0.1)	b 286 (33)	a 1 (<1)	5 (1)	b 4.8 (0.1)	b 238 (6)	1 (1)	4 (<1)
NH	4.6 (0.1)	ab 198 (34)	a 0	4 (<1)	b 4.6 (0.1)	a 145 (19)	1 (<1)	3 (<1)
ME	4.6 (0.1)	ab 199 (58)	a 0	3 (<1)	b 4.5 (0.1)	ab 168 (22)	1 (<1)	4 (<1)

Table 2.6. Extractable and total soil elements (mg kg⁻¹ soil) by species, state and horizon. Standard deviation in parentheses. Means with different lower case letters are significantly different between states ($\alpha < 0.05$).

STATE	Al		Ca		Mg		K		N	
	Extractable	Total	Extractable	Total	Extractable	Total	Extractable	Total	Extractable	Total
Red Oak										
<i>O horizon</i>										
NY	a 243(21)	4020(1200)	a 5880(887)	a 7800(786)	a 465(11)	ac 1000(229)	ab 886(100)	a 3430(789)	a 15500(1020)	
VT	b 326(88)	17200(3870)	a 6090(1461)	b 14000(1840)	a 533(173)	b 2420(275)	a 1130(175)	a 3500(219)	a 16300(274)	
MA	a 508(131)	4750(482)	b 2280(439)	c 3930(568)	a 353(53)	ac 682(84)	b 766(89)	b 1670(172)	ac 17200(1100)	
NH	a 408(39)	6060(1417)	ab 4010(459)	ac 4700(527)	a 400(45)	a 635(48)	ab 914(107)	ab 2760(311)	bc 21000(821)	
ME	a 510(473)	2300(636)	a 5330(627)	a 8000(1390)	b 861(119)	c 1330(226)	ab 1100(52)	ab 2760(632)	c 19500(1400)	
<i>A horizon</i>										
NY	a 333(134)	a 15700(980)	ab 33(12)	a 2480(272)	13(12)	a 762(121)	a 20(7)	a 9870(378)	a 445(45)	
VT	ac 715(99)	ab 31700(1400)	b 74(22)	b 4780(191)	12(2)	b 2900(153)	a 22(3)	b 7010(555)	ab 869(155)	
MA	bc 1550(240)	ab 41500(506)	ab 37(18)	c 9860(360)	16(1)	b 2500(49)	b 52(5)	c 12100(628)	b 2170(137)	
NH	ac 813(205)	ab 28800(818)	a 12(2)	ad 3170(99)	9(2)	a 748(63)	a 34(3)	d 15700(334)	ab 1400(143)	
ME	c 1290(267)	b 54800(21700)	a 17(4)	d 4600(1000)	9(1)	a 1060(412)	ab 37(9)	d 16900(1130)	b 2110(1170)	
<i>B horizon</i>										
NY	ab 1560(460)	a 21200(3430)	abc 12(3)	a 2940(690)	a 2(<1)	a 1050(249)	5(1)	a 10400(1240)	ab 450(50)	
VT	a 961(75)	b 35900(541)	a 33(12)	b 4900(165)	a 2(<1)	b 3680(144)	7(3)	a 8300(114)	a 251(40)	
MA	b 2560(300)	c 63600(5790)	ab 31(13)	c 12100(585)	b 4(1)	b 3960(323)	11(1)	b 15300(372)	b 748(251)	
NH	ab 1770(302)	c 54700(4310)	c 5(1)	b 4540(175)	a 2(1)	a 1500(142)	8(<1)	c 18400(730)	ab 586(30)	
ME	ab 1790(523)	bc 46200(5140)	bc 8(3)	b 4440(368)	a 2(<1)	a 1190(318)	8(3)	c 19100(1460)	b 687(169)	
White Pine										
<i>O horizon</i>										
NY	283(16)	1730(287)	4490(954)	ab 5290(151)	450(48)	629(37)	595(66)	1260(91)	16500(887)	
VT	329(61)	11500(9300)	4600(348)	b 7260(1720)	366(57)	1480(740)	585(109)	2440(915)	13900(2834)	
MA	589(127)	3850(1180)	2280(1250)	a 3720(1750)	255(96)	697(354)	503(49)	1430(609)	15100(680)	
NH	310(47)	5850(894)	2790(214)	a 3570(316)	281(28)	570(36)	451(24)	2480(368)	15800(384)	
ME	456(298)	2530(989)	3400(1710)	a 3570(211)	528(295)	806(211)	615(395)	2810(1000)	16000(1279)	
<i>A horizon</i>										
NY	1090(826)	a 10100(308)	113(85)	a 1550(507)	24(24)	a 492(316)	21(7)	a 6600(371)	a 515(109)	
VT	497(82)	b 28340(1434)	70(47)	bd 5320(763)	9(2)	ab 2330(383)	16(1)	a 5500(495)	a 878(62)	
MA	1191(497)	b 40800(10500)	35(29)	c 10600(1380)	11(7)	b 2670(1000)	34(17)	ab 10400(3890)	a 2020(1154)	
NH	393(15)	ab 25200(2050)	93(31)	ab 3310(84)	15(3)	a 634(16)	31(<1)	ab 10800(562)	a 1330(74)	
ME	912(91)	c 75200(7860)	155(129)	d 6030(881)	34(22)	ab 2230(801)	64(31)	b 15800(1430)	b 4300(433)	
<i>B horizon</i>										
NY	a 1040(454)	a 17302(2050)	38(28)	a 2140(636)	4(1)	794(87)	6(2)	ab 9900(851)	649(582)	
VT	a 929(44)	ac 30600(850)	28(11)	ac 5140(405)	2(<1)	2800(274)	5(1)	a 6190(119)	300(11)	
MA	b 2130(41)	b 53700(14400)	25(23)	b 11640(2220)	2(2)	3820(2220)	4(3)	ab 12100(4090)	696(217)	
NH	a 1300(169)	bc 39900(3860)	12(6)	ac 4350(481)	2(1)	1130(102)	5(1)	b 12900(829)	804(234)	
ME	ab 1500(200)	b 56300(1000)	10(5)	c 5700(816)	2(1)	2630(984)	8(3)	c 20800(1880)	934(113)	

O HORIZON

O horizon pH values ranged between 3.0 and 4.3 for all plots. Percent base saturation ranged between 63 and 92%, considerably higher than in the mineral horizons (Table 2.5). Although pH was not affected by species composition, red oak plots had significantly higher CEC values ($360 \text{ meq kg soil}^{-1}$) than white pine plots ($270 \text{ meq kg soil}^{-1}$) ($\alpha < 0.05$) (Table 2.5). In addition, red oak plots had 63% more total Ca, 35% more total K, and 16 % more total N than the white pine plots ($\alpha < 0.05$). Extractable bases were higher on red oak plots as well. On average, there was 34% more Ca, 75% more K, and 39% more Mg in the O horizon of the red oak plots ($\alpha < 0.05$). The O horizon differences are probably a result of differences in foliar content since this horizon is strongly influenced by litterfall (Spurr and Barnes 1992).

Although there were large differences between foliar Al content in red oak and white pine (Table 2.4), there were no differences between extractable or total Al concentrations in the O horizons of the two species types (Table 2.6). This indicates that Al concentrations may be driven by a different set of nutrient cycling dynamics. For

example, Al concentrations in O horizons are 96 times red oak foliar Al and 39 times white pine foliar Al (Table 2.7). This large difference in concentrations cannot be accounted for by higher concentrations of non-foliage biomass inputs to the O horizon such as roots, twigs, or bark (Rustad and Cronan 1995).

Table 2.7. Ratio of O horizon element concentration to foliar element concentration (mass:mass).

Element	Red Oak	White Pine
Al	96	39
Ca	1	3
Mg	<1	<1
K	<1	<1
N	1	1

Aluminum accumulation in the O horizon suggests that Al is not mineralizing as litter decays, or that Al is being redistributed upward from the lower horizons. Rustad and Cronan (1995) suggested that the incorporation of mineral soil to the O horizon by burrowing animals, insects, tree throw, and anthropogenic disturbance was a potential source of Al to the O horizon. Lawrence et al. (1995) proposed that Al mobilized in the mineral soil by acid deposition is transported via capillary action into the forest floor where it accumulates in a reactive, mostly organically-complexed, form. Also, net accumulation of Al in decaying litter has been documented for litter of both hardwoods and conifers (Rustad 1994; Rustad and Cronan 1995). This concentration or accumulation effect is not as pronounced for any other element (Table 2.7).

Extractable element fraction (extractable divided by total x 100) can serve as an index for potential leaching loss of total nutrient capital if root uptake were removed by harvesting (Table 2.8). Al has the lowest extractable fraction (10%) and Ca has the highest fraction (71%). This emphasizes the susceptibility of base cations (especially Ca) to depletion from the O horizon.

Table 2.8. Percent extractable element concentration (extractable / total concentration x 100), averaged across states and species for each horizon.

Horizon	Element			
	Al	Ca	Mg	K
O	10	71	50	32
A	3	2	1	<1
B	4	<1	<1	<1

O horizon element concentrations increased in the order: N>Ca = Al >K>Mg. Although not significantly different, VT O horizons have extremely high and variable total Al concentrations. This is a result of high Al values for one RO and one WP plot, possibly due to incorporation of mineral soil into the O horizon. The higher O horizon total Ca values in Vermont are reflected in higher foliar Ca (Tables 2.4 and 2.6). Vermont

red oak plots had significantly higher total Ca values than any of the other states (Table 2.4). Total Ca values on the Vermont white pine plots were significantly higher than all states except New York.

A HORIZON

A horizon pH values ranged between 3.2 and 3.8 for red oak and white pine plots and were comparable to the O horizon. Base saturation decreased from an average of 85% in the O horizon to less than 10% in the A horizon (Table 2.5). Species effects are still evident in the A horizon; however, the relationship is reversed. Red oak plots had lower average base saturation (4%) than white pine plots (8%) ($\alpha < 0.05$) (Table 2.5).

Cation exchange capacity is on average about 65% less than that in the O horizon. The CEC did not differ by species, ranging from 41 to 177 meq kg soil⁻¹ for red oak and 51 to 130 meq kg soil⁻¹ for white pine. Extractable Ca concentration on the white pine plots (93 mg kg soil⁻¹) was over twice that of the red oak plots (35 mg kg soil⁻¹) indicating an apparent depletion of Ca from mineral soils by red oak and redistribution to surface soils. This is supported by Alban (1982) who found the same trend for species which take up large amounts of Ca. There were no other significant differences between species for any other element (Table 2.6).

The extractable fraction of total Al (3%) is larger than the extractable fraction of totals for Ca (2%), Mg (1%), and K (<1%) (Table 2.8). All of the extractable element fractions are smaller than those in the O horizon.

B HORIZON

B horizon pH values ranged between 3.9 and 4.7, somewhat higher than the O and A horizons, but still low enough to allow Al^{+3} to dominate soil exchange sites (Bohn et al. 1985). Cation exchange capacity ranged between $105 \text{ meq kg soil}^{-1}$ and $286 \text{ meq kg soil}^{-1}$, or about 1.6 times that of the A horizon (Table 2.5). The low base saturation in both the A and B horizons along with Al dominance suggests these horizons are depleted of exchangeable Ca, Mg, and K. High total concentrations of these elements in the A and B horizons suggest that there are large mineral pools of these elements that are being released slowly via weathering reactions.

Correlations among Foliage and Soil elements

A correlation matrix was constructed to test for significant relationships among foliar element concentrations and soil extractable element concentrations. Only the statistically significant relationships are presented in Table 2.9 ($\alpha < 0.05$). The negative correlations in the mineral horizons show that as the extractable concentration of an element in the soil increases, the foliar concentration decreases. This suggests that the majority of root uptake may be occurring from the O horizon and Al may be interfering with root uptake in the mineral horizons.

Table 2.9. Significant correlation coefficients (r) for relationship between foliar elements and extractable elements in O, A, and B horizons ($\alpha < 0.05$).

Horizon	Element	Red Oak Foliar Element				White Pine Foliar Element			
		Al	Ca	Mg	K	Al	Ca	Mg	K
O	Extractable Ca		0.52				0.62	0.69	
	Extractable K		0.55						
A	Extractable Ca		0.52		-0.53				0.53
	Extractable K		-0.58			-0.66	-0.65		0.56
B	Extractable Ca			-0.52					
	Extractable Al	-0.52				-0.54		-0.77	

Discussion

The sites in this study were selected because they were most likely to be infertile relative to other commercial forests in New England. However, their fertility status did not translate to low growth rates. BAI on these sites was higher than average New England BAI for these species (Smith, R.B. et al. 1990) by 53% for red oak and 115% for white pine. Tolerance of oak and pine to infertile sites is confirmed by Skeffington (1983) who concluded that these species were able to survive without visible damage under conditions of high soil Al, low pH and Ca. Stocking guides for white pine and red oak in New England indicate that these stands are at minimum stocking levels for the region (Lancaster and Leak 1978; Sampson et al. 1983). Growth rates in this study could be a function of tolerance exhibited by these species to poor sites and also reduced competition for resources due to low stocking levels.

The large differences in foliar element concentrations between species was not unexpected. The higher base cation content of red oak foliage indicates an accumulation of these elements in biomass. This causes mineral soil depletion by redistributing these elements to upper horizons via root uptake and litterfall (Alban 1982; Raynal et al. 1992). Studies on the effects of Ca uptake by oak and hickory species indicate that significant depletion of subsoil exchangeable Ca can occur in as little as a decade (Johnson et al. 1988; Johnson and Todd 1990).

Foliar element ratios and concentrations as indicators of health

Low foliar Mg:N ratios have been linked to nutrient imbalances brought about by increased N availability and low soil Mg (Oren and Schulze 1989). Nitrogen deposition

can promote tree growth and soil acidification which in turn leads to low Mg:Al ratios in soil solution, inhibition of Mg uptake, and Mg deficiencies (Ulrich 1994). In a study of high elevation spruce-fir forests across an N deposition gradient in northern New England, McNulty et al. (1991) found a definite trend toward lower Mg:N ratios with increasing N deposition. Although an N deposition gradient was not evident for plots in our study, red oak foliage has the same geographical pattern in Mg:N ratios (Fig. 2.3). White pine foliar Mg concentrations do not change regionally; however, levels were in the severe range as noted in a study on similar soil types and species (Stone 1953). On our sites there are no symptoms such as needle or leaf discoloration and growth reductions which have been associated with low Mg or Mg:N ratios (Stone 1953; Oren and Schulze 1989).

In our study, low Ca and high Al concentrations in white pine foliage resulted in Ca:Al ratios of < 18.5 , within the 50% risk category described by Cronan and Grigal (1995) (Fig. 2.4). The lack of evidence for negative impacts to health or growth in this study do not necessarily mean that using foliar Ca:Al ratios as an index for tree health is invalid. Cronan and Grigal suggested that foliar Ca:Al ratio indicators should only be used in conjunction with information derived from Ca:Al molar ratios in soil solution. Furthermore, most of the 36 studies that Cronan and Grigal used as the basis of their Ca:Al risk assessment were conducted in hydroponic solutions, soil or sand cultures. It is clear from Cronan and Grigal's work that Ca:Al ratios in foliage and soil solution could be used as an assessment tool if risk categories can be established from *in situ* studies.

Another study showed decreased light-saturated photosynthesis and increased dark respiration with lower Ca:Al ratios in Scots pine (*Pinus sylvestris* L.) on polluted sites in Poland (Reich et al. 1994). Red oak and white pine Ca:Al ratios in our study were below those of the affected Scots pine. It is not possible to tell from data in our study whether low Ca:Al ratios are affecting photosynthesis or dark respiration. No relationship was found between foliar Ca:Al and tree growth.

Foliar Ca by itself has a positive relationship with tree growth (Fig. 2.2). Oren and Schulze (1989) suggest that production of stemwood by trees of similar size and leaf area, subjected to similar competition, should increase in relation to foliar N concentration. However, they state that if the supply of another element were in less than optimum proportion to that of N, growth would be proportionately reduced. In our study, the correlation between Ca and BAI in conjunction with the fact that N is less correlated with BAI suggests that tree growth may be somewhat limited by Ca supply. Further development of this idea by looking at this relationship on a variety of site qualities may allow us to establish a foliar Ca concentration index which can be used as a tool for determining whether a site is susceptible to nutrient limitations other than N. This could be accomplished by determining where the relationship between foliar Ca and tree growth becomes non-linear or where the relationship between foliar N and tree growth has a higher correlation coefficient.

Despite the fact that red oak and white pine have foliar element levels that have been linked to forest decline or reduced productivity, there is no evidence of foliar discoloration, branch dieback, or large reductions in BAI over time. These results indicate

that more research is necessary before indices based on foliar element concentrations or their ratios can be used for either white pine or red oak.

Soil nutrient depletion

Low base saturation coupled with the dominance of exchangeable Al in the A and B horizons suggests that they are depleted of extractable nutrients. Other studies have shown that conifers and hardwoods will redistribute Ca from the A and upper B horizons via root uptake to biomass and then to the forest floor via litterfall (Ovington 1958; Rennie 1962). This depletion from mineral horizons appears to be greater on red oak plots. Compared to white pine plots, they average 50% greater extractable base cation contents (Ca, Mg, K) in the O horizon but 50% lower base saturation and extractable Ca in the A horizon.

Although extractable elements appear to be depleted from the A and B horizons, total element concentrations in the A and B horizons range from being equal to (Ca) or up to 7 times greater (Al) than concentrations in the O horizon, with the exception of N which is 9 times more concentrated in the O horizon (Table 2.1). Due to the greater volume of the A and B horizons, the elements they contain make up the majority of the sites' nutrient capital. However, Ca, Mg, and K only become available to plants by mineral weathering.

Studies have found that redistribution of Ca within the ecosystem occurred to a greater degree with species that take up more Ca (Alban 1982; Johnson and Todd 1990). Alban (1982) found that Ca inputs to the soil via precipitation, mineral weathering, or upward translocation by roots were not able to replenish the large amounts of calcium

depleted from soils under aspen and spruce. Federer et al. (1989) pointed out that estimates of Ca inputs from root zone deepening and weathering contain large uncertainties but should not be counted on to counteract measured depletion rates. Currie et al. (1996) modeled base cation cycles in central hardwoods and concluded that quantities of base cations are being removed from the soil exchange complex through acid leaching and forest uptake at rates greater than supplied by weathering, thus depleting soil exchangeable pools.

The nutrient status of our sites indicate that they are susceptible to nutrient depletion and that mineral soils are depleted of plant available nutrients. Most available nutrients are found in the O horizon and make up a high percentage of the total nutrient capital of the O horizon (Table 2.8). Consequently, if O horizons were subjected to disturbance via logging or fire, it is likely that the available nutrients would be leached into mineral horizons or lost to volatilization or erosion. This nutrient capital loss would be greater for red oak than white pine due to the higher base cation content in O horizons of red oak (Table 2.6).

Aluminum

Aluminum toxicity can potentially affect energy transformations, cell division, membrane transport, and nutrient accumulation in vegetation (Cronan 1994; Reich et al. 1994).

Studies have shown that Al mobilization in mineral horizons of acid forest soils interferes with Ca uptake, causes nutrient imbalances in vegetation, and damages fine roots (Marschner 1986; Shortle and Smith 1988; Cronan et al. 1989; Cronan and Grigal 1993).

Furthermore, as Al becomes more available, cations are displaced from soil exchange sites and lost through leaching.

O horizon Al concentrations in our study are 96 and 39 times higher than foliar levels for red oak and white pine respectively (Table 2.7). Only 10% of O horizon Al is in a reactive form (Table 2.8). This is in agreement with Rustad and Cronan (1995) who found that in a spruce-fir O horizon 85% of the Al was in a mineral or nonexchangeable form. Rustad (1994) showed that Al content and concentration increased in decaying hardwood and conifer litter for at least 57 months as opposed to Ca, Mg and N which decreased in content and concentration by the end of the study. This accumulation of Al was probably due to adsorption of Al in throughfall onto litter exchange sites. In a later study, Rustad and Cronan (1995) found that the cycling of Al through O horizons under red spruce in Maine is dominated by below ground detrital and mineral inputs.

If the Al in the O horizon were mobilized, it could impact the nutrient status of the sites in our study by displacing Ca, Mg, and K from exchange sites and interfering with root uptake. Lawrence et al. (1995) suggested that mineral Al in the O horizon could be mobilized by naturally derived organic acids or by addition of H^+ from acid deposition; however, they concluded that exchangeable Al concentrations were probably controlled by organically complexed Al. Rustad (1994), in a 5-year litter decomposition study, was not able to determine when accumulated Al would be released. Exchangeable Ca in the O horizon has been shown to be inversely related to concentrations of exchangeable Al (Lawrence et al. 1995) indicating that if the Al in organic horizons is mobilized, plant available cations (especially Ca) could be leached out of the primary rooting zone. The

results of these studies suggest that Al in the O horizon will remain in a non-reactive form unless H^+ ion concentration increases dramatically or the O horizon is disturbed and decay rates are increased.

Extractable elements and foliage concentrations

A limited number of studies have been completed on the relationship between soil chemical properties and foliar concentrations in forest tree species (Abrahamsen et al. 1994). Ovington (1958) found linear relationships between forest floor Ca and Mg concentrations (extractant solution 2.5% acetic acid) and foliar concentrations for hardwoods and conifers. Mitchell and Chandler (1939) found a non-linear relationship between soil N supply and foliar N concentrations for both hardwoods and conifers. Abrahamsen (1994) found linear relationships between foliar Ca and Mg and exchangeable concentrations in the forest floor only as long as these elements were present in clearly suboptimal amounts. In this study, the significant correlations with O horizon concentrations were all positive and involved only foliar Ca in red oak and foliar Ca and Mg in white pine, possibly suggesting a suboptimal supply of these nutrients (Table 2.9). Mineral horizons are marked by a majority of negative correlations indicating that Al may be affecting root uptake at these depths by binding to apoplast surface adsorption sites and inhibiting uptake of Ca and Mg (Cronan 1994).

Comparison with sites affected by atmospheric deposition

Results from other studies involving forests that have been affected by varying levels of acidic deposition may help determine how close our study sites are to experiencing forest decline symptoms. Tables 2.10 and 2.11 include soil element data from spruce-fir forests

in Germany with pronounced symptoms of forest decline and documented nutrient deficiencies. The USA high-elevation sites in Table 2.10 represent studies of spruce-fir forests in the northeastern United States, some of which have decline symptoms. The USA low elevation sites show element ranges for soils from unaffected pine and mixed hardwood forests in the Northeast.

A general comparison indicates some major differences between our sites and others. German site, B horizon pH values were 0.5 unit lower than our sites (Table 2.10). Total soil Ca concentrations are 5 to 10 times lower for German sites compared to our sites (Table 2.11). Also, extractable Ca in the O horizons of the German sites is 9 to 23 times lower than our sites (Table 2.10). For our sites, extractable K in the O horizon is between 4 and 10 times higher and extractable Mg is between 10 and 17 times higher than German sites. On the other hand, O horizon total K is approximately 10 times higher and total Mg is 2 times higher for the German sites. Total N in the O horizon is 6 times higher on our sites in comparison to German sites.

O horizon total Al is 5 to 20 times higher on the German sites compared to our sites suggesting greater accumulation from throughfall or below ground processes (Lawrence et al. 1995; Rustad and Cronan 1995). O horizon extractable Al is comparable for all sites, supporting the hypothesis that exchangeable Al is not correlated with total Al and is probably controlled by organically complexed Al (Lawrence et al. 1995).

The 4-fold greater extractable Al concentrations in A and B horizons in our study (Table 2.10) can be explained by the double-acid extracting solution used in our study

versus the neutral and or buffered solutions used in other studies. This also explains comparatively low base saturation values in mineral horizons of our study.

The comparison between our sites and the effected German sites suggests that our sites are not close to experiencing forest decline symptoms. However, low extractable element concentrations in the A and B horizons of all sites emphasize the importance of the O horizon in supplying nutrients for tree growth.

Table 2.10. Comparison of pH, extractable element concentration, and base saturation for soil O, A, and B horizons between sites in Germany, USA, and this study (WP, RO).

Location	pH	meq kg soil ⁻¹				% Base Saturation	
		Extractable Al	Extractable Ca	Extractable K	Extractable Mg		
<i>O horizon</i>							
Germany ^a	3.2 - 3.9	18 - 75	5 - 40	3	2 - 4		na
USA Low Elevation ^b	3.6 - 4.7	5 - 54	47 - 95	3 - 17	11 - 28		47 - 88
USA High Elevation ^c	na	45 - 140	20 - 104	6 - 13	8 - 16		20 - 75
WP, RO	3.0 - 4.3	27 - 66	114 - 359	12 - 29	21 - 71		64 - 92
<i>A horizon</i>							
Germany ^a	3.2 - 4.1	43 - 43	8 - 8	na	2		na
USA Low Elevation ^b	4.4 - 5.1	11 - 32	1 - 6	<1 - 2	1		4 - 34
USA High Elevation ^c	na	95	2	1	2		6
WP, RO	3.2 - 3.9	37 - 172	<1 - 8	<1 - 2	<1 - 3		2 - 13
<i>B horizon</i>							
Germany ^a	3.4 - 4.3	33 - 65	<1 - 4	<1 - 2	<1 - 1		3 - 11
USA Low Elevation ^b	4.4	8 - 24	<1 - 6	<1	<1		5 - 28
USA High Elevation ^c	3.9	49 - 49	<1 - 3	1 - 5	<1 - 1		6 - 20
WP, RO	3.9 - 4.8	103 - 284	<1 - 2	<1	<1		<1 - 2

^a (Heinrichs and Maye 1977; Zoetl and Huettl 1986; Huettl and Wisniewski 1987; Schulze et al. 1989; Huettl 1990; Tomlinson 1990)

^b (Heiberg and White 1951; Federer and Hornbeck 1985; White et al. 1990; Eagar and Adams 1992; Wilmot et al. 1995)

^c (Eagar and Adams 1992; Johnson and Lindberg 1992a)

Table 2.11. Comparison of total element concentration (mg kg soil⁻¹) for soil O, A, and B horizons between sites in Germany, USA, and this study (WP, RO).

Location	Total Al	Total Ca	Total K	Total Mg	Total N
Germany ^a USA Low Elevation ^b WP, RO	36000 - 79459	641 - 1900	15000 - 31677	1500 - 4133	2200 - 3300
	na	6558	876	1058	19008
	1733 - 17246	3565 - 13984	1256 - 3505	570 - 2421	13943 - 21006
Germany ^a USA Low Elevation ^b WP, RO	44000	220 - 1300	17000 - 36244	1879 - 1900	1200 - 12740
	na	na	na	na	2005
	10099 - 75186	1550 - 10623	5470 - 16905	492 - 2904	445 - 4336
Germany ^a USA Low Elevation ^b WP, RO	49000 - 87027	200 - 1900	18000 - 37730	2146 - 4133	800 - 11060
	na	na	na	na	1572
	17302 - 63594	2142 - 12144	6188 - 20755	794 - 3963	250 - 934

^a (Heinrichs and Maye 1977; Zoettl and Huettl 1986; Huettl and Wisniewski 1987; Schulze et al. 1989; Huettl 1990; Tomlinson 1990)

^b (Heiberg and White 1951; Federer and Hornbeck 1985; White et al. 1990; Eagar and Adams 1992; Wilmot et al. 1995)

Harvest removals

Federer et al. (1989) addressed the question of whether total amounts of nutrients change significantly over time by examining inputs, outputs, and total pool sizes of several forested sites in the northeastern United States. They concluded that within 120 years, spruce-fir sites in Maine and hardwood sites in New Hampshire and Connecticut could lose between 23 and 62% of the total Ca pool. These projected losses were due to the combined effects of increased leaching losses due to acid rain and intensive harvesting and losses due to biomass removal during harvesting. Depletion of Mg and K were expected, although these losses were not predicted to be as severe as Ca losses.

In another study, Hornbeck et al. (1990a) estimate the effects of intensive harvesting on nutrient capitals of hardwoods and conifers in New England. Table 2.12 compares data, on a kg ha^{-1} basis, from sites in our study and the Connecticut (CT) site in Hornbeck's study. The CT site was selected because it was considered to be the most sensitive site in Hornbeck et al. (1990a). The species on the CT site were central hardwoods with a basal area of $23 \text{ m}^2 \text{ ha}^{-1}$ (Tritton et al. 1987), comparable to the basal area of both WP and RO plots in this study (Table 2.3).

Results of the comparison show that extractable nutrient capitals are similar for all sites in both horizons (Table 2.12). Total nutrient capitals are similar for elements (N and Mg) that are organically bound except for N in the CT O horizon which is approximately twice that of the N capitals in either RO or WP. The digestion procedure used in Hornbeck et al. (1990a) may underestimate total Ca and K contained in mineral horizons

by as much as 10 times (Personal Communication, J. Hislop, U.S.F.S.). Thus, comparisons of total soil capitals are not meaningful.

Measured harvest removals of Ca and K from the CT site are over twice as large as soil extractable pools on our sites. Removals of Mg are approximately equal to extractable element capitals. Nitrogen removals are small, under 10% of total N capitals. It is clear that extractable nutrient capitals cannot replace nutrients lost due to harvesting, especially when disturbance of the O horizon will result in additional depletion of these pools via leaching (Hornbeck et al. 1990a). Results indicate that the sites in our study are at least as sensitive as the CT site to nutrient depletion via whole-tree harvesting.

Table 2.12. Extractable and total element capitals (kg ha^{-1}) compared to capitals and harvest removals from the Connecticut site in Hornbeck et al. (1990a).

Site	Ca		K		Mg		N
	Extractable	Total	Extractable	Total	Extractable	Total	Total
<i>CT harvest removal^a</i>							
	<i>530</i>		<i>160</i>		<i>40</i>		<i>270</i>
<i>O horizon</i>							
RO ^b	108	176	23	68	12	28	430
WP ^c	78	109	12	50	8	20	357
CT ^a	58	96	39	72	8	46	995
<i>Mineral horizons^d</i>							
RO ^b	116	32141	57	80480	19	13263	3460
WP ^c	168	32594	44	67854	23	12483	4394
CT ^a	118	3318	93	5045	27	13286	3570

^a Data from Connecticut site in Hornbeck et al. (1990a).

^b Average values for red oak plots in this study.

^c Average values for white pine plots in this study.

^d Mineral soils to a depth of 60 cm.

Management of sensitive sites

Managing for timber production on sites susceptible to nutrient depletion has been discussed in other studies (Aber et al. 1978; Smith, C.T. et al. 1986; Hornbeck et al. 1987, 1990a). Most of these management considerations apply to all sites. For sites with thin O horizons and low base saturation in mineral horizons, particular attention should be paid to protecting the forest floor during and after harvest. If organic horizons are disturbed and Ca, Mg, and K are lost via leaching, it is not likely that these losses will be recouped.

SILVICULTURAL SYSTEMS

Hornbeck et al. (1990) concluded that clearcuts should be avoided on soil types and conditions with low fertility. The data from our study suggests that for sites with sandy soils and thin O horizons, clearcuts would be especially damaging to long-term site productivity. Canopy removal exposes the forest floor and mineral soil to greater amounts of light, heat, and moisture and accelerates decomposition and mineralization of organic materials (Bormann and Likens 1979). In addition, nitrification rates can be expected to increase after clearcutting (Aber et al. 1978; Vitousek and Melillo 1979). Accelerated decomposition of the O horizon could mineralize organically bound Al. Increased nitrification results in a flush of available NO_3^- and H^+ which also has the potential to mobilize accumulated Al in the O horizon. Vegetative uptake will be minimized, consequently larger amounts of NO_3^- and Al^{+3} in the O horizon will cause Ca, Mg and K to be leached from the soil. Also, whole-tree timber harvest removal of Ca in above ground biomass can increase Ca loss by 100% over what is already being lost by leaching (Federer et al. 1989). Nutrient losses due to biomass removal will be greater for hardwoods such as red oak which have high base cation concentrations.

Selection and shelterwood harvests are more appropriate techniques, both for minimizing impacts to the O horizon and regenerating white pine (Lancaster and Leak 1978; Hornbeck et al. 1990a). In addition, less above-ground biomass is removed; consequently, removals of key nutrients will be reduced. Also, nitrification and decomposition rates will remain lower and leaching losses will be minimized due to nutrient uptake by residual trees. Group selection harvests can be used to minimize impacts to the O horizon by harvesting trees in groups, leaving whole sections of the forest floor untouched.

HARVESTING OPERATIONS

Disturbance of the O horizon should be minimized during the harvesting operation. Compaction and exposure of mineral soils may prolong leaching losses by delaying regeneration and plant development. If the disturbances result in erosion and stream sedimentation, there will be nutrient losses beyond those already discussed (Hornbeck et al. 1990a). Furthermore, mixing of mineral soils with high Al content into the O horizon will increase the potential for problems caused by Al accumulation.

Skid roads in timber harvesting operations will disturb approximately 10% of the stand area (Meyer et al. 1966). Outside of road damage, the type of equipment and the care with which it is used will play an important role in protecting the O horizon. Chainsaw felling and feller-buncher operations are two common harvesting techniques used in New England. Both operations use skidders to drag cut trees to the landing.

Feller-bunchers minimize impact to the soil by cutting a tree and laying it down next to the skid road. There are two types of feller-bunchers commonly used; one is a

fixed-head feller-buncher with an articulating frame and the other is a feller-buncher with a swing-to-bunch long-reach boom. The long reach boom facilitates tree removal while minimizing impacts to the soil because it does not have to drive to every tree it cuts. Both types of feller-bunchers can either be track-mounted or rubber-tired. A track-mounted feller-buncher has less of an impact on the O horizon because the machine's weight is spread over a larger surface area.

Care must be taken to plan harvesting so leaves remain on the site because both types of feller-buncher operations remove the whole tree from the site. Harvesting hardwood stands in the dormant season after leaf fall can reduce nutrient removals by 10% for Ca, 16% for K, and 21% for N and P compared to growing season harvest with leaves (Hornbeck and Kropelin 1982). Hornbeck et al. (1990a) also suggest that felling should be conducted several weeks in advance of skidding to allow leaves to dry and drop on site; this method will minimize nutrient removals for conifers as well.

Chainsaw felling operations can have a greater impact to soils because the skidder has to drive over a greater area to collect felled trees. In addition, many loggers will notch the trees with a saw and use the skidder to push the tree over (Personal Communication, D. Quigley, UNH-TSAS); this method has obvious implications for soil damage given that the skidder must drive to every tree that is cut. Impacts to sites can be minimized by using "precision felling techniques" which are currently the focus of logger training programs in New England (Personal Communication, D. Quigley, UNH-TSAS). The main focus of these techniques is to fall trees in an organized fashion so the skidder makes fewer turns and felled trees do not need to be dragged sideways across the forest

floor. Most chainsaw felling operations will top the trees on the site thereby minimizing nutrient loss from foliage biomass removals.

Winter harvesting should be considered regardless of the type of equipment used. Benefits include reduced root damage and soil disturbance because of snow covered and frozen ground (Isomaki and Kallio 1974; Bruhn 1986). Also, residual stand damage is reduced by almost 50% by using feller-bunchers in the winter season as opposed to summer (Nichols et al. 1993).

POST HARVEST SILVICULTURAL TREATMENTS

White pine and red oak are both commercially valuable species; however, on our sites, white pine growth rates are twice that of red oak, and white pine removes fewer nutrients from the mineral horizons. This suggests that these sites should be managed for white pine. Furthermore, white pine will regenerate easier on infertile sites where hardwood regeneration can not compete (Lancaster and Leak 1978; Seymour 1986).

Managing for white pine presents some dilemmas for the forest manager trying to follow our guidelines for sensitive sites. Lancaster and Leak (1978) suggest that to provide ideal conditions for white pine seedling germination and development, it is necessary to disturb the forest floor to expose mineral soil and to break up the accumulation of litter. A possible solution to this dilemma is to log white pine stands that have advanced regeneration. In fact, following our recommendations to minimize impacts to soils will also preserve this regeneration. Another possibility is that the inevitable disturbance caused by any logging activity on the site will provide enough suitable sites for seedling germination.

Conclusions

Our study of red oak and white pine forests in the northeastern United States found that some soil and foliar elements and ratios (Mg, Mg:N, Ca:Al) are at levels where other studies have observed negative impacts on growth or health. The relationship between foliar Ca and BAI and significant correlations between extractable Ca and Mg and foliar levels of these elements indicate that these elements may be in sub-optimal supply. However, the trees in this study do not exhibit any symptoms of forest decline and in fact, have higher than average growth rates. Further study on a range of site qualities could tell us if foliar levels of Ca and N could be used as an index for a site's susceptibility to cation depletion.

Direct comparisons with other studies in Germany and the United States with forest decline symptoms indicate that our sites are not close to exhibiting decline symptoms because organic horizons of our sites have between 4 and 23 times more extractable Ca, Mg, and K, and O horizon total Al is between 5 and 20 times lower. However, the mineral soils of our sites have total and extractable element concentrations which are similar to the German sites. This emphasizes the importance of the O horizon in supplying nutrients for tree growth. A comparison with other similar sites in New England indicates that biomass removal under intensive harvesting regimes could severely impact extractable nutrient pools.

Available nutrient capitals are susceptible to depletion if harvested. Disturbance of the O horizon should be avoided. Most of the extractable nutrients are found in the O horizon and make up a high percentage of total nutrient capital in the O horizon.

Consequently, if O horizons are disturbed via logging, it is possible that available nutrients would be leached into mineral horizons and lost. This nutrient capital loss would be greater for red oak than white pine because red oak forest floor material has 35% more K and 63% more Ca. Furthermore, red oak appears to be depleting mineral horizons of base cations faster than white pine. Nutrient loss could occur without physical disturbance if the large amounts of total Al in the O horizon are mobilized via soil acidification.

Forest management activities should take into account the potential nutrient losses for each species and focus on protecting organic horizons if sensitive sites are to be harvested. Clearcuts should be avoided on sites with sandy soils and thin O horizons. Selection and shelterwood harvests are more appropriate, both for minimizing impacts to the O horizon and regenerating white pine. Track-mounted feller-buncher harvesting operations may impact a site less if care is taken to leave the foliage on the site. Chainsaw felling operations should consider using “precision felling techniques” to minimize impacts to the soils. Winter harvesting should be considered regardless of the type of equipment used.

CHAPTER 3

MICROWAVE DIGESTION OF FOREST SOILS AND FOLIAGE: TOTAL AL, CA, FE, K, MG, MN, P AND N.

Introduction

Studies on impacts of acid rain on forests have progressed from direct effects of acidic deposition on foliage (Tamm and Cowling 1977; Wisniewski 1982) to the effects of added nitrogen and sulfur to the ecosystem (Aber et al. 1993; Magill et al. 1996), and most recently, to the dynamics of decreasing soil pH and aluminum mobilization (Miller et al. 1992; Cronan and Grigal 1995; Ericsson et al. 1995). Also, impacts of acid rain on nutrient capitals of forest soils coupled with nutrient removals via intensive harvesting have caused increasing concern over the nutrient status of forested ecosystems (Smith, C.T. et al. 1986; Johnson et al. 1988; Federer et al. 1989; Hornbeck et al. 1990a). The scale of these studies has expanded from plots to watersheds to landscapes necessitating the collection of larger numbers of samples for analysis.

The increased concern about nutrient capital depletion and critical nutrient ratios (e.g., Ca:Al (Cronan and Grigal 1995) and Mg:N (McNulty et al. 1991)) necessitates the use of a definitive value for total soil and foliar nutrients. The collection of larger numbers of samples requires efficient analytical methods capable of accurately measuring total Al, Ca, Fe, K, Mg, Mn, P, and N in forest soils and foliage.

Direct current plasma (DCP) and inductively coupled plasma (ICP) atomic emission spectrometry (AES) have the capability to accurately analyze liquid samples for

multiple elements over a wide range of concentrations (Page et al. 1982). Therefore, the limiting factor in analyzing soil and foliage samples for multiple elements is the dissolution or digestion of these samples.

Standard methods for the complete digestion of foliage and especially soils involve concentrated acid mixtures and open vessel digestions that are time consuming and hazardous (Rehcgigl and Payne 1990; Warren et al. 1990). Microwave digestion systems offer the capability of safer, more controlled digestions and have been developed for the determination of total N in mineral soils and foliar samples (Antisari and Sequi 1988; Neas and Zakaria-Meehan 1988; He et al. 1990). Other microwave procedures have been developed for total element analysis in these same materials (Kalra et al. 1989; Rehcgigl and Payne 1990; Warren et al. 1990; Fridlund et al. 1994; Matejovic and Durackova 1994). Disadvantages associated with these methods include: long digestion or sample preparation procedures which preclude high sample throughput, lack of data for some of the elements of interest, and lack of methods and data for digestion of organic soils.

The objective of this study is to test and further develop microwave digestion techniques for soil and tree foliage with attention to precision, accuracy, and maximum sample throughput. This was accomplished by modifying variables in digest protocols, including digest time and power, sample weight, and amounts and types of acids used to arrive at more satisfactory recovery rates.

Methods

Our study used a microwave oven designed for laboratory digestion (Model MLS-1200 Mega, Milestone Corporation; Bergamo, Italy). Its maximum power output is 1000 watts,

which is adequate for the digestion of the soils and foliage. The oven has a Teflon-coated cavity (31x38x32 cm) especially designed for acid digestions and a fan which removes acid vapors to a fume hood. The oven is equipped with a removable rotor that holds ten, 100 ml Teflon vessels. Digestion vessels are capable of withstanding pressures of 30 bar and temperatures of $\leq 225^{\circ}\text{C}$. The vessels used are designed to be a completely closed system with safety features for automatic pressure release if pressure specifications are exceeded.

Certified standard reference materials were used to evaluate the accuracy and precision of the digestion methods (Table 3.1). Currently, there is no certified standard reference material for organic soils. Therefore, we used a forest floor sample (NA17) that had been analyzed using neutron activation analysis (Page et al. 1982). Because NA17 is not a certified reference material, it has not gone through the rigorous homogenization and testing of the other reference materials.

Table 3.1. Reference materials used in this paper.

Type	Reference Material Used	Elements	Certified	OM(%) ^a	n
Mineral Soil	CANMET ^b SO-2 (B horizon)	Al, Ca, Fe, K, Mg, Mn, P, N	Y	11	18
Mineral Soil	CANMET ^b SO-4 (A horizon)	Al, Ca, Fe, K, Mg, Mn, P, N	Y	10	17
Organic Soil	NA17 ^c Forest Floor	Al, Ca, Fe, K, Mg, Mn, P, N	N	88	24
Foliage	NIST ^d Pine 1575	Al, Ca, Fe, K, Mg, Mn, P, N	Y	NR	8

^aLoss on ignition.

^bCanada Centre for Mineral and Energy Technology (Bowman et al. 1979)

^cForest floor sample collected, prepared and analyzed using neutron activation, by Mark David (University of Illinois, Urbana).

^dNational Institute of Standards and Technology.

All glassware and Teflon digestion vessels were acid washed in 2N HCl and rinsed in distilled, deionized water. Prior to weighing, foliage samples were oven-dried (overnight) at 70° C and soil samples were oven-dried at 105° C. All sample weights were recorded to ± 0.0001 g. All reagents used were analytical grade. The reagents were distributed using repipettes set to the correct volume to facilitate sample preparation.

We were attracted to microwave technology for total soil digests because of its reported ability to maximize sample throughput and the increased safety of the closed vessel digestion system. We had intended to use methods developed and recommended by Milestone for the total dissolution of soils and foliage (MLS-1200 Operators Manual, 1994). However, as we began to test these methods against standard reference materials, it became evident that they were not suitable for our needs. Consequently, we began an iterative process of trial and error to develop methods that met our goals of precision, accuracy and maximum sample throughput. The most suitable choices for combinations of acids, sample weight, and time sequences are shown in Table 3.2.

All protocols included a 5-minute vent cycle at the end of the digestion process which allowed the samples to cool inside the microwave before removal. After removal from the microwave, the whole rotor was placed in a running water cooling bath for at least 10 minutes to lower the temperature and pressure to the point where the vessels could be opened safely. After cooling, the samples were rinsed out of the digestion vessels into LDPE Nalgene bottles with 110 ml of distilled, deionized water. Each rotor of 10 vessels was run with one blank and 9 samples.

Analysis of the digestate for Al, Ca, Fe, K, Mg, Mn, and P was conducted with a DCP-AES (SpectraSpan III, ARL Direct Current Plasma, Fisons Instruments Inc., Danvers, MA). Raw analytical values for all elements were reported as the mean of three sequential integrations for each sample. A full description of the analytical capabilities of the DCP as compared to the more commonly used ICP can be found in Page et al. (1982). The digestate was analyzed for total N using a Bran & Luebbe (Technicon) TRAACS 800 Autoanalyzer. The sodium salicylate method (Technicon Method 786-86T) was used for the analysis of total Kjeldahl nitrogen digestate. Final analytical values were determined after subtraction of a blank which was treated and analyzed in the same manner. Mean concentrations of the elements were calculated from multiple digests of each sample type (n listed in Table 3.1).

Results

We were able to maximize sample throughput by having four complete rotor setups with a capacity of 10 samples per rotor. This allowed us to digest 6 to 7 rotors (each holding 9 samples plus a blank) over the course of one day.

The analytical means for the concentrations of total Al, Ca, Fe, K, Mg, Mn, P, and N (for SO-2 only) are reported in Table 3.3. Most analytical values displayed low variability with the coefficient of variation (CV) usually less than 5%. Exceptions were the values for K and Mn in sample NA17 and N for sample SO-2.

Table 3.2. Acid mixtures, microwave time, and power settings for digestion of soil and foliage standards for total element analysis and total N analysis for mineral soil standards.

3.2a. Total Element Foliage (0.1g Pine 1575)				3.2b. Total Element Organic Soil (NA17 and SO-4)			
Digestion Mixture		Microwave Protocol		Digestion Mixture		Microwave Protocol	
Reagent	Amount	Time	Power	Reagent	Amount	Time	Power
	ml	minutes	watts		ml	minutes	watts
HNO ₃ (concentrated)	5	1	250	HNO ₃ (concentrated)	5	1	250
H ₂ O ₂ (30%)	2	1	0	HCl (concentrated)	2	1	0
		5	250	HBF ₄ (50%)	2	5	250
		5	400			5	400
		5	500			1	0
		5	600			5	500
						1	0
						5	600
						1	0
						2.5	650

3.2c. Total Element Mineral Soil (0.2g SO-2)				3.2d. Total N Mineral Soil (0.15g SO-2)			
Digestion Mixture		Microwave Protocol		Digestion Mixture		Microwave Protocol	
Reagent	Amount	Time	Power	Reagent	Amount	Time	Power
	ml	minutes	watts		ml	minutes	watts
HNO ₃ (concentrated)	5	1	250	H ₂ SO ₄ (concentrated)	4	5	250
HCl (concentrated)	2	1	0	H ₂ O ₂ (30%)	1	5	400
HBF ₄ (50%)	2	5	250	K ₂ SO ₄	0.20g	1	0
H ₂ O ₂ (30%)	2	5	400			3	500
		1	0			1	0
		5	500			3	500
		1	0				
		5	600				
		1	0				
		2.5	650				

Table 3.3. Total element concentrations (mg kg^{-1}) for the four reference standards. Measured values, mean analytical values, with coefficient of variation (CV%), % recovery as compared to measured values and 95% confidence interval for certified values. Numbers in parenthesis are values that have not been certified.

Forest Floor (NA17)							A Horizon (SO-4)						
Element	Standard			Measured			Element	Standard			Measured		
	Value	95% CI	Mean	CV	Recovery	%		Value	95% CI	Mean	CV	Recovery	%
Al	(15727) +/-	NA	11662	5	74		Al	54600 +/-	2730	47714	5	87	
Ca	(675) +/-	NA	845	6	125		Ca	11100 +/-	999	11084	2	100	
Fe	(4730) +/-	NA	5559	4	118		Fe	23700 +/-	1422	23695	3	100	
K	NA +/-	NA	2038	12	NA		K	17300 +/-	519	16635	2	96	
Mg	NA +/-	NA	393	4	NA		Mg	5600 +/-	784	5080	3	91	
Mn	(81) +/-	NA	57	42	70		Mn	600 +/-	36	589	2	98	
P	NA +/-	NA	1165	6	NA		P	900 +/-	135	1026	5	114	

B Horizon (SO-2)							Foliage (Pine 1575)						
Element	Standard			Measured			Element	Standard			Measured		
	Value	95% CI	Mean	CV	Recovery	%		Value	95% CI	Mean	CV	Recovery	%
Al	80700 +/-	1800	85283	3	106		Al	545 +/-	30	0	n/a	0	
Ca	19600 +/-	1000	20911	2	107		Ca	4100 +/-	200	3711	1	91	
Fe	55600 +/-	1600	54510	3	98		Fe	200 +/-	10	136	7	68	
K	24500 +/-	400	26006	3	106		K	3700 +/-	200	3530	2	95	
Mg	5400 +/-	300	5567	2	103		Mg	NA +/-	NA	1075	1	NA	
Mn	720 +/-	20	709	2	98		Mn	675 +/-	15	636	2	94	
P	(3000) +/-	NA	3407	2	114		P	1200 +/-	200	1081	3	90	
N	(2200) +/-	NA	2185	9	99								

Recovery rates for total element concentrations ranged between 87% and 114% for the SO-2 and SO-4 samples, between 70% and 125% for NA17, and between 0%(Al) and 95% for pine 1575. The total nitrogen method in Table 3:2 was tested on all four sample types but worked reliably only on the mineral soil sample (SO-2).

Measured values in sample SO-2 for Fe, Mg, and Mn fell within the range of the 95% confidence interval reported with the certified elements (Table 3.3). Al, Ca and K had recovery rates of just over 105% and measured values did not fall within the certified confidence interval. Measured values of Al and K in sample SO-4 had low recovery rates, outside of the 95% confidence interval. Values for K and P in Pine 1575 were the only measured values that fell within the certified 95% confidence interval for that sample.

During the course of the microwave methods development, we also tested the DCP analysis procedure for repeatability. It became evident that samples with high organic matter concentrations appeared to be losing and regaining Al. Consequently, we initiated a series of tests which involved analyzing the digestate from three of the NA17 samples on the DCP over the course of several weeks. The aluminum concentration data for the sequential analysis of the NA17 digestate are presented in Fig. 3.1. The measurable aluminum concentration dropped rapidly in the first 10 days after digestion and then increased sometime between 19 and 52 days after digestion. Ca, Fe, K, Mg, Mn, and P remained constant over the same time period. This sequential analysis over time was carried out for Pine 1575 samples as well, and there was no measurable aluminum in the digestate at any time. Element concentrations in the digestate from mineral soil samples remained constant with time.

Fig. 3.1. Average concentration of total Al (ppm) in sample NA17 (n=3). Sample digestate was measured sequentially over time. Error bars are ± 1 standard deviation.

Discussion

Forest floor (NA17)

The low (70.4%) and highly variable (CV 41.5%) Mn recovery for NA17 (Table 3.3) could be due to the extremely low concentrations of Mn in the digestate, approximately 0.07 ppm. This value is close to the theoretical detection limit (0.003 ppm) for Mn on the DCP. This could be remedied in the future by reducing the initial dilution of the digestate to approximately 50 ml.

The Al in the forest floor sample digestate is capable of moving in and out of solution as illustrated in Fig. 3.1. The small error bars in Fig. 3.1 indicate that all samples behaved consistently. This trend over time was not exhibited by any other element or by Al in any other sample type. In a study by Kalra et al. (1989), it was suggested that low recoveries of Fe and Al after the microwave digestion of NIST foliage standards were due

to incomplete digestion of siliceous material. Kingston and Jassie (1988) also present two possible explanations for low recovery of elements such as Al:

1. Al reacts with fluoride in the fluoroboric acid and forms an insoluble complex.
2. Insoluble metallo-organic molecules are left in the digestate.

Given that we were able to obtain complete recovery of Al from materials of a higher mineral content (SO-2, SO-4), it is not likely that incomplete digestion of any siliceous material is the problem. It is more likely that Al is complexing with fluoride and subsequently moving out of solution over time. The reason Al becomes measurable again is unclear.

Foliage (Pine 1575)

The method outlined in Table 3.2 was capable of providing reproducible results that were close to the certified values for the total concentrations of Ca, K, Mn, and P. Mg concentrations were very precise (CV=1%), however, the accuracy could not be assessed because this standard reference material did not have a certified value reported for Mg. Fe and Al had low recovery rates of 68.1% and 0%, respectively. These elements could have reacted with undigested organic matter as postulated by Kingston and Jassie (1988). It is likely that there was incomplete digestion of organic material. Kalra et al. (1989) obtained complete recoveries of Al and Fe by wet digestion with the addition of perchloric (HClO_4). HClO_4 is a strong oxidizing agent that attacks metals that are unresponsive to other acids and thoroughly decomposes organic materials (Kingston and Jassie 1988). Kingston and Jassie (1988) noted that microwave digestion of organic materials may require additional treatment with HClO_4 if complete decomposition is necessary before analysis.

Total N

The total N method reported in Table 3.2 recovered 99.3% (CV 9.2%) of the N from the B horizon (SO-2) sample. The other sample types in this study were digested with this method and results were unsatisfactory so tests were discontinued. The microwave digestion vessels are not capable of handling the high temperatures necessary for complete decomposition of highly organic foliage and forest floor samples. Studies by Bremner (1960) showed that the most important factor for complete Kjeldahl digestion of soils is temperature. The temperature in a typical Kjeldahl block digestion procedure is usually between 350° C and 370° C (Neas and Zakaria-Meehan 1988). Our digestion vessels are only capable of withstanding temperatures of 225° C. Neas and Meehan (1988) described a microwave digestion technique with specialized equipment that can handle the high temperatures necessary. This method is reported to be 20 times faster than conventional block digestion techniques. However, due to the fact that their setup can only handle one sample at a time, conventional 40 hole block digesters are still more efficient.

Recommendations

We discovered that methods recommended by microwave manufacturers are geared to extracting a consistent percentage of the element or constituent of interest rather than a quantitative total. For research, where total nutrient capitals or element ratios are required, it is important to recover 100% of a wide range of elements with a high degree of precision from a given soil or foliage sample.

Evaluation of digestion methods should include quality assurance steps with samples and standards which have similar physical and chemical characteristics to the

samples of interest. Organic matter concentration of the sample appears to be of particular significance as the organic matter is difficult to decompose in microwave digestion. If highly organic soil samples are to be digested, it is necessary to develop an in house check standard as there is not a certified reference material available. If Al is an element of interest, it is necessary to consider time between digestion and analysis.

CHAPTER 4

PREDICTING ELEMENTS IN WHITE PINE AND RED OAK FOLIAGE WITH NEAR INFRARED REFLECTANCE

Introduction

Forest health and monitoring issues have become a major focus of scientists and research institutions in Europe and North America during the last decade. The interest in forest health has increased because of wide-spread forest decline symptoms in Europe (Global Environment Monitoring System 1990) and high elevation spruce-fir decline in North America (Eagar and Adams 1992). Global change issues such as acid rain and intensive harvesting have been implicated as possible causes of forest decline symptoms (Federer et al. 1989; Hornbeck et al. 1990a; Cook and Zedaker 1992). The regional scale of these stressors presents logistical challenges which necessitate the development of efficient analytical methods to measure foliar elements of forest ecosystems which may serve as indexes related to forest health.

Foliar concentrations of Ca, Al, K, Mg, Mn and N have been shown to be highly correlated with tree growth and health and physiological function for a wide range of species (Mitchell 1936; Mitchell and Chandler 1939; Mader and Thompson 1969; Mader and Howarth 1970; Aber et al. 1989; Reich et al. 1994; Cronan and Grigal 1995). Standard methods for elemental analysis of foliage involve acid digestion of foliar material, which is time consuming and hazardous.

Near infrared reflectance spectroscopy (NIRS) is an environmentally friendly technique, capable of rapid, non-destructive, chemical analysis of vegetative material. The basis for NIRS is the prediction of the chemical properties of biological materials by measuring near infrared light reflected from the sample. NIR spectroscopy has been used to determine concentrations of P, Ca, K, B, Mg, Na, Mn, Fe, Cu, and Zn in forage, grain, and grasses (Shenk et al. 1979; Clark et al. 1987, 1989; Vazquez de Aldana et al. 1993, 1995). More recently, NIRS has proven to be capable of replacing traditional wet chemistry methods for the determination of cellulose, lignin, and N concentrations in dried and ground foliage for a wide variety of tree species (Wessman et al. 1988; McLellan et al. 1991b; Bolster et al. 1995). Further development of this technology has shown that cellulose, lignin, and nitrogen concentrations can be predicted for forest canopies via remote sensing instrumentation (Curran and Kupiec 1995; Martin and Aber 1995).

The purpose of this paper is to evaluate the ability of NIRS technology to replace traditional acid digestion methods for the analysis of Al, Ca, K, Mg, Mn, and Fe in tree foliage using red oak (*Quercus rubra*) and white pine (*Pinus strobus*) foliage.

Methods

Sample Collection

Foliage samples were collected from 75 dominant or co-dominant white pine and 90 red oak trees from northern New England and New York (Hallett and Hornbeck 1996). Two samples were collected from each tree, one from the top of the crown (sun leaves) and one from mid-canopy. For white pine, current year needles were separated from the

previous year's needles yielding 4 samples per tree. A total of 300 pine and 170 red oak samples were collected. Samples were separated from the branch and petiole, oven dried at 70°C, and ground in a Wiley mill to pass a 1 mm mesh.

Wet Chemistry

All foliage samples were digested using a modified TKN digestion with a selenium catalyst (Isaac and Johnson 1976). Analysis of the digestate for total foliar Al, Ca, Fe, K, Mg, and Mn was conducted with a DCP-AES (SpectraSpan III, ARL Direct Current Plasma, Fisons Instruments Inc., Danvers, MA) (Page et al. 1982). Analysis of the digestate for total foliar N was carried out using a Bran & Luebbe (Technicon) TRAACS 800 Autoanalyzer.

Near Infrared Reflectance Spectroscopy Analysis and Statistics

NIR spectral measurements were made on all foliage samples using a NIRSystems Model 6500 Near Infrared Spectrophotometer with a spinning sample cup. The sample is rotated and scanned 32 times in 60 seconds. The sample spectrum is the average of the 32 scans. Two sub-samples were scanned and averaged for each sample. The spectral measurements ranged from 400 to 2498 nm and were converted from reflectance (Fig. 4.1a) to absorbance $[\log(1/R)]$ with respect to a ceramic reference standard. Data are reported at 2 nm intervals with an instrument bandwidth of approximately 10 nm. The software used for data collection and analysis was NIRS2, version 3.00, from Infrasoft International (Silver Spring, MD). The raw absorbance spectra were subjected to a second difference spectral transformation which uses 3 individual bands separated by 10 nm gaps (eq. 1).

$$[\text{eq. 1}] \ A''_{\lambda} = (A_{\lambda+20 \text{ nm}} - A_{\lambda}) - (A_{\lambda} - A_{\lambda-20 \text{ nm}})$$

Where:

A''_{λ} = second difference of absorbance at wavelength λ .

A_{λ} = Absorbance at wavelength λ

The difference spectra is then subjected to a running average smooth across 10 bands (20 nm) (Fig. 4.1b).

Fig. 4.1. (a) Spectral reflectance and (b) 2nd difference of absorbance for red oak and white pine with (c) the equation coefficient at each wavelength for the prediction of foliar Ca.

The second difference is used because it enhances subtle features of the spectral signature, removes baseline shifts caused by differences in particle size, and helps resolve overlapping bands (Dixit and Ram 1985; Hruschka 1987).

Of the total samples (470), 25% of the red oak and 25% of the white pine samples were randomly selected to be used for validation (validation data set) of the equations developed from the remaining samples (calibration data set)(Table 4.1). The chemical analysis data for each element was regressed against the spectral signatures of all samples in the calibration data set using a modified partial least squares (MPLS) regression technique. (Frank 1987; Shenk and Westerhaus 1991; Infracore International 1992). MPLS begins by weighting each wavelength based on its covariance with element concentration. MPLS then uses these weights to reduce the data to a smaller set of independent variables or factors as in principal component analysis (Gunst and Mason 1979). The chemical variability is incorporated into the first factors and variability due to data noise (e.g. light scatter) into the later, less important factors. This results in one loading per wavelength for each factor. The factors are regressed against laboratory values to produce one coefficient value per wavelength for the final equation (Fig. 4.1c). The advantage of the MPLS method lies in its ability to simultaneously account for variability in both chemical and spectral data.

The final equation is selected from the average of 4 cross validation groups and the associated equation statistics. The equations were then used to predict the chemical concentrations of samples in the validation data set. The accuracy of the equations were evaluated using the following statistics:

1. $1-VR$, similar to R^2 = ratio of cross validation error squared, to the standard deviation of the data set squared (Infrasoft International 1992).
2. standard error of calibration (SEC) = square root of the mean square for residuals, where the residual equals actual minus predicted chemical concentrations for samples within the calibration data set (Mark and Workman 1991).
3. standard error of prediction (SEP) = square root of the mean square for residuals, where the residual equals actual minus predicted chemical concentrations for samples outside the calibration data set (Mark and Workman 1991).
4. coefficient of variation (CV) = SEP divided by the mean of the elemental concentration in the validation data set multiplied by 100 for each element (Vazquez de Aldana et al. 1995).

In addition to the foliar element predictions, cellulose and lignin concentrations were predicted using existing NIRS equations developed by Bolster et al. (1995). Correlation analysis was used to test for significant relationships between foliar elements, cellulose and lignin (Neter et al. 1985).

Table 4.1. Statistical data for elemental concentrations (mg kg⁻¹ foliage) determined by wet chemistry methods.

Element	Set	N	Range	Mean	SD
Al	Calibration	351	8 - 458	150	98
	Validation	119	6 - 586	145	100
Ca	Calibration	351	528 - 8709	3650	2009
	Validation	119	514 - 9466	3544	2186
Fe	Calibration	345	4 - 140	45	20
	Validation	116	5 - 334	45	36
K	Calibration	351	1938 - 12818	5997	2459
	Validation	119	1727 - 12545	6145	2355
Mg	Calibration	351	419 - 2408	1211	373
	Validation	119	406 - 2226	1170	330
Mn	Calibration	350	85 - 4520	997	795
	Validation	118	76 - 3729	1031	863

Results

The chemical data for the population sets used in calibration and validation are presented in Table 4.1. The range of element concentrations necessary for accurate calibration was provided by the inherent differences between species, upper and middle canopy, and current and previous year's needles. The concentration ranges in the validation data set fell close to or within the range of calibration data sets in all cases. Element concentrations ranged from 45 mg kg⁻¹ of Fe to 5997 mg kg⁻¹ of K.

The statistics used to evaluate the accuracy of equations created using the MPLS regression technique and the ten wavelengths with the highest regression coefficients (absolute value) are presented in Table 4.2. The magnitude of the regression coefficient at a given wavelength is representative of how important that wavelength is to the prediction equation. This can be seen graphically for the Ca equation in Fig. 4.1c.

The 1-VR statistic reported in Table 4.2 is the amount of variation in the data that is adequately modeled by the calibration equation as a fraction of the total variation in the differences between the measured values for the data points and the predicted values for these points. For example, 97% of the variation in foliar Ca is explained by the MPLS equation (Table 4.2, Fig. 4.1c).

The SEC (Table 4.2) is the standard deviation for the residuals due to differences between measured and predicted values within the calibration data set. The SEC is a useful estimate of the theoretical best accuracy obtainable for a given calibration equation (Mark and Workman 1991). The SEP is greater than the SEC for all elements (Table 4.2). Mark and Workman (1991) state that the SEP is generally greater than the SEC since the

validation samples were not involved in the calibration process but could be smaller in some cases due to chance alone.

The CV's listed in Table 4.2 are a standardized measure of accuracy for the final equation and how well it predicted element concentrations in the validation data set. The relative accuracy of the equations for Al, Ca, Mg, and K (CV<30%) can be seen in Fig. 4.2 where the scatter around the 45° line for Al (CV=28%) is greater than the scatter depicted for Mg (CV=14%). CV's of 48 and 50% for Fe and Mn indicate that NIRS may not be useful for the prediction of these elements in tree foliage.

The theoretical basis for the prediction of foliar cellulose, lignin and N is well documented (Wessman et al. 1988; McLellan et al. 1991b; Bolster et al. 1995). In contrast, there has been little theoretical work done on absorption bands for Al, Ca, Mg, and K in plant material. Consequently, it is necessary to examine whether predictive equations developed for these elements are based on correlations with cellulose, lignin, and N by squaring the correlation coefficients in Table 4.3 and comparing them with the 1-VR statistic in Table 4.2. None of the correlation coefficients in Table 4.3 indicate that cellulose, lignin, or N would be a better predictor of inorganic elemental concentration than the NIRS technique. For example, the largest correlation coefficient is between lignin and K (-0.60) indicating that with an increase in foliar lignin, K content decreases. Although this relationship is significant ($\alpha < 0.05$), the variance explained by the NIR equation for K is much greater (1-VR=0.90).

Table 4.2. Statistical data for NIRS calibration of elements in foliage samples.

Element	1-VR	SEC	SEP	CV	Ranked Wavelengths (nm) ^a									
					1	2	3	4	5	6	7	8	9	10
		mg kg ⁻¹	mg kg ⁻¹	%										
Al	0.87	30	40	28	1588	1592	1024	1132	1020	1136	1584	1028	1016	1812
Ca	0.97	332	864	24	1960	1956	1548	1964	1552	1544	1980	1028	1056	1052
K	0.90	689	1037	18	1564	1560	1568	1572	1556	1064	1060	1068	1576	1056
Mg	0.78	160	169	14	1064	1060	1068	892	888	1264	884	1260	1268	1056
Fe ^b	0.41	13	21	48										
Mn ^b	0.78	288	491	54										

^a Top ten weighted wavelengths from MPLS equation.^b Ranked wavelengths not presented for elements with CV's > 30%.Table 4.3. Pearson correlation matrix of foliar cellulose, lignin, and selected elements ($\alpha < 0.05$).

	Lignin	Cellulose	Al	Ca	K	Mg	N
Lignin	1.00						
Cellulose	-0.42	1.00					
Al	0.48	-0.53	1.00				
Ca	-0.31	0.34	-0.12	1.00			
K	-0.60	0.58	-0.79	0.24	1.00		
Mg	-0.39	0.53	-0.44	0.61	0.55	1.00	
N	-0.26	0.49	-0.42	0.58	0.49	0.49	1.00

Fig. 4.2. Predicted versus actual element concentrations (mg kg^{-1} foliage) using validation data set.

Discussion

The results from this study indicate that NIRS has potential for replacing conventional acid digestion methods for the determination of foliar Al, Ca, K and Mg in forest tree species. Currently, CV's of 14 to 28% for the prediction of these elements in red oak and white pine are marginal for ecosystem nutrient cycling studies where CV's are expected to be 10% or less. However, it is promising that between 78 and 97% of the variation in foliar Al, Ca, K, and Mg can be explained by the NIRS calibration model. Increased accuracy can be expected with new calibration data sets which include a large number of coniferous and deciduous tree species.

Cellulose and lignin in plant material have known absorption bands in the NIR region (Osborne and Fearn 1986; Williams and Norris 1987), N is organically-bound in plant material, and N-H bonds have known absorption features (Weyer 1985). Theoretically, there are no absorption bands for mineral species in the near infrared spectrum (Shenk et al. 1979; Burns and Ciurczak 1992). Previous studies have documented the ability of NIRS to predict element concentrations in grasses and forages (Clark et al. 1987, 1989; Vazquez de Aldana et al. 1995). It is hypothesized that NIRS can determine some cation concentrations because of their association with organic or hydrated inorganic molecules (Clark et al. 1987). It is probable that the association of Al, Ca, K, and Mg with certain organic acids provides the hydrogen bonding detected by NIRS (Clark et al. 1989).

There has been a limited amount of work done to determine which organic compounds the NIRS is detecting to allow us to predict elemental concentrations. Clark et

al. (1987) showed that chlorophyll bands in the NIR region are close to the wavelength used for the calibration of Mg content of various grasses and hays. Clark also demonstrated similarities between bands in the K, Mg, and Ca malate spectra and those used in calibration for those same elements.

Due to the lack of known absorption bands for foliar elements, correlations with cellulose, lignin, and nitrogen were examined (Table 4.3) to determine if the NIRS was indirectly predicting element concentrations via spectral features of these organic molecules. The squared correlation coefficients are not as high as the 1-VR statistic (Table 4.2) from the MPLS equation. Similarly, Shenk et al. (1992) regressed crude protein (CP) and acid detergent fiber (ADF) content (mixed species hay) against K, Mg, and Ca content. In all cases an equation developed using NIRS performed better than the regression using CP and ADF.

The wavelengths cited as being important for calibration of Al, Ca, K, and Mg for various grasses and hays (Clark et al. 1987, 1989; Vazquez de Aldana et al. 1993, 1995) are not among those listed as being important for the calibration of these same elements in red oak and white pine foliage (Table 4.2). This discrepancy could be due to the difference in vegetative materials and the use of the MPLS regression technique, which uses information from the whole spectrum and weights individual wavelengths as to their importance in predicting the constituent in question (Infrasoft International 1992). Another important factor is the ability of the NIRSystems model 6500 near infrared spectrophotometer to detect wavelengths from 400 nm to 2498 nm. The detection range of the spectrophotometers used in all other studies cited here did not extend below 1100

nm. Of the top ten wavelengths listed in Table 4.2, almost half are below 1100 nm. This decreases the relative importance of wavelengths greater than 1100 nm.

The operational use of NIRS in forest ecosystem studies is possible but still depends on the development of data sets which include foliage from species specific to a given study. Acid digestions will still be necessary for accuracy assessment and expansion of calibration data sets if new species are encountered. If accuracy standards are met, it can be expected that fewer acid digestions will be necessary, which could allow greater numbers of samples to be collected for a given study due to the speed of NIR analysis.

With calibration data sets including a wide variety of forest species and an increased understanding of the mineral/organic associations being detected, it may be possible to extend this work to recently developed remote sensing instruments capable of detecting near infrared wavelengths from high altitudes. Aircraft and satellite remote sensing instruments with spectral resolution similar to laboratory instruments include NASA's Airborne Visible/Infrared Spectrometer (in operation) and the NASA/TRW Hyperspectral Imager (1996 launch) (Goetz et al. 1985; Porter and Enmark 1988; Witcher and Stone 1995). Further development of the relationships outlined in this paper could lead to canopy level predictions of Al, Ca, Mg, and K.

Conclusion

These results show that it is possible to predict Al, Ca, K, and Mg concentrations in white pine and red oak foliage with acceptable accuracy. For Fe and Mn, the model developed by NIRS was not successful for the prediction of these parameters. Before NIRS can

replace acid digestion methods for the determination of Al, Ca, K, and Mg in tree foliage, it will be necessary to develop calibration data sets that include a wide variety of species.

Given that there are no absorption bands for mineral species in the near infrared spectrum, it is unclear as to which mineral/organic associations are being detected using NIRS. Additional work is necessary to determine the nature of these associations, perhaps by focusing on the spectral region between 400 nm and 1100 nm.

The results presented in this paper in conjunction with the emerging remote sensing technology could allow us to predict Al, Ca, K, and Mg levels for forest canopies at a landscape or regional scale. This, in turn, might be used to assess forest health and physiological function at a scale that would help in the study of global change issues.

CONCLUSIONS

Decline of commercially valuable spruce-fir forests in Europe and the appearance of similar decline symptoms among high elevation spruce-fir forests in the northeastern United States have been linked to acid deposition. Acid rain can result in the loss of Ca, Mg and K from forested ecosystems. Low elevation forests of New England are not subjected to the high levels of acidic deposition found in high elevations; however, acid rain and intensive land use at lower elevations have the potential to deplete low elevation commercial forests of key nutrients. These facts led us to assess the nutrient status of two commercially valuable forest types in New England.

Our study of red oak and white pine forests on deep sandy soils in the northeastern United States found that some soil and foliar elements and ratios (Mg, Mg:N, Ca:Al) are at levels where other studies have observed negative impacts on growth or health. The good relationship between foliar Ca and BAI and significant correlations between soil extractable Ca and Mg and foliar levels of these elements indicate that these elements may be in sub-optimal supply. However, the trees in this study do not exhibit any symptoms of forest decline and, in fact, have higher than average growth rates. Further study on a range of site qualities could tell us if foliar levels of Ca and N could be used as an index for a site's susceptibility to cation depletion.

Available nutrient capitals are susceptible to depletion if the stands are harvested. Disturbance of the O horizon should be avoided. Most of the extractable nutrients are found in the O horizon and make up a high percentage of total nutrient capital in the O

horizon. Consequently, if O horizons are disturbed via logging, it is likely that available nutrients would be leached into mineral horizons and lost.

During the course of this study, microwave digestion techniques were developed for total element analysis for soils which were safer and more efficient than traditional methods while maintaining a high level of accuracy. The methods development process emphasized the need for QA/QC samples which are similar to the samples being digested.

Finally, NIRS technology has the capability to predict foliar Al, Ca, Mg, and K concentrations for red oak and white pine. Before NIRS can replace acid digestion methods for the determination of Al, Ca, K, and Mg in tree foliage, it will be necessary to develop calibration data sets that include a wide variety of species. In addition, these results indicate that emerging remote sensing technology could be used to predict Al, Ca, K, and Mg levels for forest canopies at a landscape or regional scale. This, in turn, might be used to assess forest health and physiological function at a scale that would help in the study of global change issues.

This study indicates that forests on infertile low elevation soils are susceptible to nutrient loss and care should be taken to protect nutrient capitals. Regional scale assessments of other forest types in New England can benefit from methods developed in this study.

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