

**Acid deposition effects on soil chemistry and forest growth on
the Monongahela National Forest**

by

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Patricia Elias

Abstract

Acid deposition (AD) results largely from the combustion of fossil fuels, and has been found to negatively impact forest ecosystems. AD may acidify soils through base cation leaching or Al mobilization, may cause accumulation of nitrates and sulfates in soils, and in some cases has been related to forest decline. The Monongahela National Forest (MNF) lies downwind from many sources of AD pollution, and average deposition pH is around 4.4. Therefore, managers are concerned about the possible deleterious effects of AD on the forest ecosystem. During the 2006 Forest Plan revision, evaluation of site sensitivity to acidification was specifically stated as a step in the Forest's adaptive management process. To meet this management objective, forest practitioners must understand the effects AD has on the forest, prescribe appropriate practices, and be able to monitor for future changes.

To address the needs of MNF managers we used Forest Inventory and Analysis (FIA) sites to evaluate forest growth patterns on the Forest and determined the relationship between growth and key indicators of soil acidity. Furthermore, we used those relationships to create a map of site resistance to acidification across the MNF. To further develop a monitoring scheme we assessed two soil sampling protocols and two soil analysis methods for their suitability for monitoring AD-related changes in soil chemistry. Additionally, we evaluated the utility of dendrochronological and foliar sampling as AD-specific monitoring methods.

Across all FIA sites on the MNF periodic mean annual volume increment (PMAVI) ranged from $-9.5 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ to $11.8 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$, suggesting lower-than-expected growth on two-thirds of the sites. Growth was compared to soil indicators of acidity on 30 FIA sites. In the surface horizon, effective base saturation (+), Ca concentration (+), base saturation (+), K concentration (+), Fe concentration (-), Ca/Al molar ratio (+), and Mg/Al molar ratio (+), were correlated with PMAVI ($p \leq 0.1$). In the subsurface horizon

pH_(w) (+), effective base saturation (+), Al concentration (-), and K concentration (-) were correlated with PMAVI. Site resistance to acidification was mapped based on site parent material, aspect, elevation, soil depth, and soil texture. There was a significant ($p \leq 0.1$) positive correlation between PMAVI and a resistance index developed using five soil and site factors. Resistance was also compared with key soil indicators of AD-induced decline on 28 sites across the forest, and pH, effective base saturation, and Al content were found to be the best indicators related to resistance index. Resistance index was used to create a map of the MNF, of which 14% was highly resistant ($RI \geq 0.7$), 57% was moderately resistant ($0.7 > RI > 0.45$) and 29% was slightly resistant ($RI \leq 0.45$).

The first of our monitoring program evaluations compared soil sampling and analysis methods on 30 FIA plots. Analyses of variance showed that soil pH, effective base saturation, Ca/Al molar ratio, and sum of bases varied significantly with sampling protocol. We also compared lab analyses methods and found that if sampling by horizon, a linear relationship can be used to estimate Ca/Al_{srCl2} ratio using NH₄Cl extractions. The second monitoring approach evaluated the utility of a northern red oak (*Quercus rubra* L.) dendrochronology on two FIA plots. This analysis suggests that pollution on the MNF caused a decrease in growth rate during the 50-year period from 1940 to 1990. There were no differences among ring width increment and basal area increment between the two sites. From 1900 to 2007 the two sites showed 58.5% similarity in growth trends, but these could not be attributed to a dissimilar influence of AD. The third monitoring approach evaluated the relationship between foliar and soil chemical indicators. Across FIA plots, nutrient concentrations varied by tree species. The first year results from a potted-seedling study suggest that soil acidity influences growth, and foliar concentrations are related to growth rates.

This evaluation of the effects of AD on the MNF can be used to develop adaptive management plans and a monitoring program that will meet the AD-related objectives of the 2006 Forest Management plan.

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“For in the end, we will conserve only what we love. We will love only what we understand. We will understand only what we learn. And we will learn only what we are taught.”

– Baba Dioum

Table of Contents

Abstract.....	ii
Acknowledgements.....	iv
List of Figures.....	ix
List of Tables	xii
I. Introduction	1
Introduction.....	1
Objectives	3
Thesis Organization	5
II. Literature Review.....	6
Introduction.....	6
Acid Deposition	6
Sulfur Pollution.....	7
Nitrogen Pollution.....	8
Acid Deposition and Forest Productivity.....	10
Resistance and Sensitivity to Acid Deposition.....	14
Soil Acidification.....	16
Buffering Mechanisms.....	17
Base cation depletion & aluminum toxicity.....	19
Monitoring for the Effects of Acid Deposition.....	19
Soil Sampling and Analysis	20
Foliar Analyses	21
Epidemiological Approach to Assessing Acid Deposition Impacts	22
Use of Dendrochronology to Assess Acid Deposition Impacts.....	23
Forest Inventory and Analysis Plots	23
The Monongahela National Forest.....	24
Current Deposition Conditions	26
Tree Species Sensitive to Acid Deposition.....	27
Managing for the effects of Acid Deposition	28
Research Gaps.....	29
III. Acid deposition effects on forest composition and growth on the Monongahela National Forest, West Virginia	31
Abstract.....	31
Introduction.....	31
Methods.....	34
Site Description.....	34
Stand Inventory	35

Field Procedures.....	37
Lab Procedures.....	38
Data Analysis.....	39
Other factors influencing stand volume.....	40
Results.....	40
Stand Inventory.....	40
Species Composition.....	41
Periodic Mean Annual Volume Increment 1989 to 2000.....	44
Soil Indicators.....	47
Modeling Growth.....	48
Acid Neutralization Potential.....	53
Discussion.....	55
Conclusions.....	58
 IV. Adaptive Management for Maintaining Productivity on Acidified Sites on the Monongahela National Forest.....	 60
Abstract.....	60
Introduction.....	60
Methods.....	64
Research and Development.....	64
Hypothesized Resistance Relationships (Step 1).....	64
Develop and Validate Resistance Model (Step 2).....	69
Production of an AD Resistance Map (Step 3).....	70
Selection of AD Indicators for Monitoring (Step 4).....	71
Results and Discussion.....	71
Conclusions.....	80
 V. Dendrochronology of Two Sites on the Monongahela National Forest Subjected to Acid Deposition.....	 83
Abstract.....	83
Introduction.....	83
Methods.....	85
Field Analysis.....	85
Lab and Statistical Analysis.....	86
Results.....	87
Discussion.....	88
Conclusions.....	92
 VI. Use of foliar chemistry as an indicator of site acidification – first year results.....	 94
Abstract.....	94
Introduction.....	94
Methods.....	97
Pot study.....	97
Field study.....	99

Results.....	100
Pot Study.....	100
Field Study.....	104
Discussion.....	106
Conclusions.....	107
VII. Soil Sampling and Lab Analysis Techniques for Acid Deposition Related	
Monitoring.....	109
Abstract.....	109
Introduction.....	109
Methods.....	111
Sampling Protocols.....	111
Laboratory Protocols.....	112
Method Comparisons.....	113
Results.....	113
Sampling Protocols.....	113
Applicability of Soil Survey Data for Determining Soil Depth.....	125
Laboratory Protocols.....	126
Discussion.....	129
Conclusions.....	131
VIII. Summary.....	132
IX. Works Cited.....	135

List of Figures

Abstract.....	ii
Acknowledgements.....	iv
List of Figures.....	ix
List of Tables.....	xii
I. Introduction.....	1
II. Literature Review.....	6
Figure 2-1: Plot design of Phase 2 and Phase 3 Forest Inventory and Analysis Plots.....	25
Figure 2-2: Interpretations of FIA Data from the Monongahela National Forest show forest status and changes.....	26
Figure 2-3: Sulfate, nitrate and pH data from 2006 for the Eastern United States, including the study site in Eastern West Virginia.....	27
III. Acid deposition effects on forest composition and growth on the Monongahela National Forest, West Virginia.....	31
Figure 3-1: Approximate locations of Forest Inventory and Analysis (FIA) plots across the Monongahela National Forest. Highlighted plots were used for an intensive study of site and soil relationships.....	37
Figure 3-2: Periodic mean annual volume increment (PMAVI) on Forest Inventory and Analysis (FIA) plots between 1989 and 2000 for A) all plots on the Monongahela National Forest B) and for plots used in an intensive soil-study.....	45
Figure 3-3: Periodic mean annual volume increment as a function of stand basal area in 2000.....	46
Figure 3-4: Periodic mean annual volume increment as a function of stand age.....	46
Figure 3-5: Periodic mean annual volume increment as a function of site index.....	47
Figure 3-6: Site Index as a function of surface Ca/Al molar ratio on FIA plots.....	52
Figure 3-7: Relationship between periodic mean annual volume increment and a key indicator of soil acidification on FIA plots.....	53
Figure 3-8: Range of estimated Acid Neutralization Potential by cation exchange buffering of intensively-sampled FIA plots.....	54
IV. Adaptive Management for Maintaining Productivity on Acidified Sites on the Monongahela National Forest.....	60

Figure 4-1: Basic process of adaptive management	62
Figure 4-2: Hypothesized resistance curves for site factors used to create resistance index.....	67
Figure 4-3: The relationship between periodic mean annual volume increment and general resistance index.	73
Figure 4-4: Correlations between RI_{MNF} and A) surface soil pH, B) subsurface effective base saturation, and C) subsurface Ca/Al molar ratio.....	75
Figure 4-5: Map of resistance to acidification on the Monongahela National Forest.....	77
Figure 4-6: Resistance Index map in the Allegheny Mountains province of the Monongahela National Forest.....	79
Figure 4-7: Correlations between stream water pH and resistance index.....	81
 V. Dendrochronology of Two Sites on the Monongahela National Forest Subjected to Acid Deposition	 83
Figure 5-1: Ring width increment for two sites with differing parent material on the Monongahela National Forest.....	90
Figure 5-2: Basal area increment calculated from tree cores for two sites with differing parent material on the Monongahela National Forest.....	91
 VI. Use of foliar chemistry as an indicator of site acidification – first year results	 94
Figure 6-1: Relationships between tree growth characteristics and foliar Ca concentration for sugar maple and red oak.....	102
Figure 6-2: Range of foliar nutrients of northern red oak and sugar maple on FIA plots	104
Figure 6-3: Relationship between periodic mean annual volume increment and foliar Ca concentration.....	105
 VII. Soil Sampling and Lab Analysis Techniques for Acid Deposition Related Monitoring	 109
Figure 7-1: The effect of different sampling methods on A) on pH values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between pH and periodic mean annual volume increment for the D) surface soil and E) subsurface soil	115
Figure 7-2: The effect of different sampling methods on A) on Ca/Al ratio. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between Ca/Al ratio and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.....	117
Figure 7-3: The effect of different sampling methods on A) on effective sum of bases values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship	

between effective sum of bases and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.....	119
Figure 7-4: The effect of different sampling methods on A) on sum of bases values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between sum of bases and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.....	121
Figure 7-5: The effect of different sampling methods on A) on NO ₃ /NH ₄ values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between NO ₃ /NH ₄ and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.....	123
Figure 7-6: Relationship between sum of bases calculated using field-collected depth data and soil survey depth data	126
Figure 7-7: Relationship between Ca/Al molar ratio by two exchange procedures	128
VIII. Summary	132
IX. Works Cited.....	135

List of Tables

Abstract.....	ii
Acknowledgements.....	iv
List of Figures.....	ix
List of Tables	xii
I. Introduction	1
II. Literature Review.....	6
Table 2-1: Results from a computer model showing chemical conditions under three acid deposition regulation emissions scenarios at the Hubbard Brook Experimental Forest.....	7
Table 2-2: Range of historical forest growth in West Virginia	11
Table 2-3: Untransformed mean foliar chemistry; soil chemistry and physical properties by forest health class.....	12
Table 2-4: Soil properties that influence the soil acid neutralizing capacity of a soil.....	17
Table 2-5: Soil buffering mechanisms.....	18
III. Acid deposition effects on forest composition and growth on the Monongahela National Forest, West Virginia	31
Table 3-1: Range of site and stand characteristics on Forest Inventory and Analysis (FIA) plots across the Monongahela National Forest (MNF) and a 30-plot subset used for soil sampling.....	41
Table 3-2: Average composition and change across all Forest Inventory and Analysis plots in the Monongahela from 1989 to 2000.....	43
Table 3-3: Forest stand and soil properties arranged in PMAVI classes for intensively-sampled FIA plots	44
Table 3-4: Descriptive statistics and results of soil sampling from 30 FIA study plots.	49
Table 3-5: Correlation coefficients among stand factors and hypothesized soil indicators of acidity.....	51
Table 3-6: Site and soil factors in regression model predicting periodic mean annual volume increment on FIA plots.....	53
IV. Adaptive Management for Maintaining Productivity on Acidified Sites on the Monongahela National Forest.....	60
Table 4-1: Range of site factors used to create Resistance Index.....	65

Table 4-2: Geology resistance numbers.....	66
Table 4-3: Sources for each site factor used to create a site resistance index to AD.....	70
Table 4-4: Subsurface horizon soil characteristics, grouped by specific resistance index values.....	78
Table 4-5: Site characteristics used to calculate resistance index at FIA plots on the MNF	79
V. Dendrochronology of Two Sites on the Monongahela National Forest Subjected to Acid Deposition	83
Table 5-1: G-value similarities between two samples sites on the Monongahela National Forest.....	89
Table 5-2: Soil chemistry characterization of two sample sites	89
VI. Use of foliar chemistry as an indicator of site acidification – first year results	94
Table 6-1: Liming and acidification treatments for each soil	98
Table 6-2: Influence of soil treatment on soil pH and element concentrations	101
Table 6-3: Seedling diameter and height measurements for potted study. Soils from Mauch Chunk parent material (MC), Chemung parent material (C), and Pottsville parent material (P).	101
Table 6-4: Correlations between foliar and soil and nutrients for A) Sugar maple and B) Northern red oak seedlings.....	103
Table 6-5: Range of nutrient concentrations for two species on FIA plots. Values are minimum, maximum, mean, and standard error.	104
Table 6-6: Foliar elemental concentrations for red oak and sugar maple grouped by stand periodic mean annual volume increment.....	106
VII. Soil Sampling and Lab Analysis Techniques for Acid Deposition Related Monitoring	109
Table 7-1: Relative differences among cation concentrations extracted by NH ₄ Cl and SrCl ₂	127
Table 7-2: Models of Ca/Al by SrCl ₂ as a function of Ca/Al by NH ₄ Cl	128
VIII. Summary	132
IX. Works Cited.....	135

I. Introduction

Introduction

Acid deposition (AD) results mainly from fossil fuel combustion, which produces sulfuric acid and nitrous oxides. Early in terrestrial AD research, scientists were concerned about the direct effects of acidity on foliage, but this focus has since shifted to the acidification of soils (Van Ranst *et al.*, 2002). The effects on soil include base cation leaching, Al mobilization, and sulfur and N accumulation (Driscoll *et al.*, 2001c). Increased N inputs to the stand may shift composition to nitrophilous species and those that can tolerate low soil-Ca levels (Fenn *et al.*, 1998; Huntington *et al.*, 2000). Furthermore, scientists and forest managers are concerned that N saturation will leave forests more susceptible to frost damage (McNulty *et al.*, 1996; Gress *et al.*, 2007). Additionally, AD predisposes forests to damage from other stresses such as insect infestation (Driscoll *et al.*, 2001b). There is a growing body of evidence that AD has induced productivity losses (Likens *et al.*, 1996; Schaberg *et al.*, 1997; Horsley *et al.*, 2000) and that management practices, such as harvesting, may alter the influence of AD on forest productivity and sustainability (Adams, 1999; Watmough and Dillon, 2003; Gress *et al.*, 2007). Reductions in sulfate emissions since the 1990 Clean Air Act Amendments have reduced associated base cation leaching (Driscoll *et al.*, 2001c); however, although ecosystems vary widely in their ability to absorb N, evidence of N saturation continues to be reported in both Europe and the United States (Fenn *et al.*, 1998; Houle *et al.*, 2006).

The Monongahela National Forest (MNF), located in eastern West Virginia, is situated downwind from sources of sulfate and nitrate pollutants, mostly originating in the Ohio River Valley (USDA Forest Service, 2006). The Forest encompasses over 360,000 hectares of land. This area was designated a National Forest in 1920, after being largely clear-cut in the late-19th and early-20th century. The current forest is second and third growth, and maintains a high level of biological diversity, supporting 13% of the rare plant and animal species in West Virginia (USDA Forest Service, 2006). Situated only a few hours from large urban centers and containing over 1200 kilometers of hiking trails,

the MNF is a popular recreation destination, while still producing about 0.2 million cubic meters of timber annually (Widmann and Griffith, 2004). The MNF covers the Ridge and Valley and Allegheny Mountain provinces of the Appalachian Region. It receives between 76 and 152 cm of rain each year. The pH of the precipitation is about 4.4, and about 20 kg of sulfate and 12 kg of nitrate per hectare are deposited each year (National Atmospheric Deposition Program (NRSP-3), 2006). Elevation ranges from below 400 m to above 1400 m.

The MNF lies at the confluence of the mixed mesophytic and oak-chestnut forest regions, with remnants of the northern hardwoods at high elevations (Braun, 1950). The productivity of these second and third growth forests has historically been between 2 to 7 $\text{m}^3\text{ha}^{-1}\text{yr}^{-1}$ (Hicks, 1998). Some of the earliest growth data for oaks were gathered in West Virginia. Results showed average annual volume increments of 1.79 to 2.39 $\text{m}^3\text{ha}^{-1}\text{yr}^{-1}$ on poor and fair sites, 3.02 to 3.63 $\text{m}^3\text{ha}^{-1}\text{yr}^{-1}$ on average to good sites, and over 4.30 $\text{m}^3\text{ha}^{-1}\text{yr}^{-1}$ on excellent sites (Schnur, 1937). Deviations from these baseline growth rates could be used to evaluate the influence of pollutants and stress on the forest ecosystem.

When the MNF Management Plan was revised in 2006, the Forest Service set objectives to evaluate management actions “that have the potential to contribute to soil nutrient depletion,” specifically evaluating “for the potential effects of depletion in relation to on-site acid deposition conditions” (USDA Forest Service, 2006). To achieve these adaptive management goals for the effects of AD land managers must monitor their prescriptions and determine if they are approaching the desired outcome (USDA Forest Service, 2006).

There is little agreement, however, as to the most effective AD-specific monitoring programs. Monitoring approaches include mapping site sensitivity or resistance, using monitoring plots to evaluate changes in soil or foliar chemistry, and evaluating changes in forest growth. Approaches to mapping site sensitivity or resistance to acid deposition vary, ranging from site characterization (i.e. Kuylenstierna *et al.*, 1995) to meteorological modeling (i.e. Langner *et al.*, 1995). On another scale, the standard monitoring program that uses only productivity measurements may not suffice to evaluate the impact of AD across the landscape (Foster *et al.*, 1997; Adams *et al.*, 2000). Instead, the use of soil sampling to characterize acidity and fertility is commonly used;

however, there is considerable debate between sampling by depth versus sampling by horizon. Also, there are some questions as to which genetic horizons to sample to adequately capture the interaction between AD and the soil system (Bailey *et al.*, 2004). Selection of soil lab analyses will also influence interpretation of results. Foliar analysis has been shown to be a viable method for measuring changes in ecosystem nutrient availability (i.e. Boerner, 1984; Aber *et al.*, 1993; Kogelmann and Sharpe, 2006). Another alternative monitoring scheme is dendrochronological sampling. Tree ring analysis has been used to determine changes in forest dynamics and productivity due to acid deposition (Duchesne *et al.*, 2002).

Objectives

Given the concern of Monongahela National Forest (MNF) managers over the potential effects of acid deposition (AD), our objectives were to determine if there was evidence of growth declines related to AD on the MNF, create a resistance map to acidification, and determine the utility of soil, foliage, and tree core sampling in evaluating the impacts of AD on growth.

First, to evaluate the potential negative effects of AD our objectives were to: 1) determine if there was any evidence of AD-induced growth decline on the Forest and 2) if decline occurred, determine the relationship with key soil indicators related to forest change. We hypothesized that mortality of acid-sensitive species would be higher and productivity would be lower than historical growth during the interval 1989 to 2000 due to chronic input of acid deposition. We predicted that assessing criteria and indicators of soil acidity, potential toxicity level, fertility level, N-saturation, and neutralization capacity would detect forest change and decline.

Our second objective was to create a spatial land-management tool designed to assess resistance to acid deposition. We hypothesized that sites on the MNF were more resistant to productivity losses due to acidification and base depletion as parent material became more calcareous, slopes became steeper, approaching northeast aspects, and as elevation decreased, and if soil on the site was of mixed mineralogy, was deeper, was moderately-fine in texture, and had a lower amount of rock fragments. Also, we

predicted that these soil and site factors could be combined to create a resistance index (RI), which would be related to key soil indicators of AD that could be used to monitor sustainable forestry as a part of a forest-wide adaptive management program.

Our third objective was to determine if dendrochronologies of northern red oak (*Quercus rubra* L.) on two MNF sites, differing only in parent material and soil series, would express the same cumulative effect of AD on productivity. We hypothesized that the analysis would demonstrate differences due to parent material, specifically that productivity declined on the site where parent material had the lowest buffering potential.

To further discern the influence of parent material on growth, and to determine the relationship between foliar and soil nutrients, our fourth objective was to determine if red oak and sugar maple (*Acer saccharum* Marsh.) seedlings in pots grew differently when planted in soils derived from three parent materials at ambient pH or when limed or acidified, and determine if these treatments would be detectible in differences in foliar chemistry after two growing seasons. We hypothesized that the foliar chemistry of both species would be related to soil chemistry and productivity. Specifically, we hypothesized that seedlings grown in acidified soils would show increased mortality, higher levels of foliar Al and Mn, and lower levels of foliar Ca and, while seedlings grown in limed pots would have the opposite responses. Furthermore, we hypothesized that the responses of potted seedlings could be applied on the MNF where foliar chemistry samples will be related to soil chemistry and growth on FIA plots.

Our final objective was to develop a soil sampling and analysis protocol for monitoring the effects of acid deposition on changes in soil chemistry and forest growth, and to compare the results with those obtained using the US Forest Service Forest Health Monitoring sampling protocols. We hypothesized that sampling by depth and by pedogenic horizon would produce the same interpretation for land managers on the MNF. Furthermore, we hypothesized that NH_4Cl and SrCl_2 extracts would produce similar analytical results for estimating Ca/Al ratio.

Thesis Organization

This thesis is organized in chapters addressing each of the above objectives. Each chapter is organized as a journal manuscript draft, with appropriate sections required by the *Soil Science Society of America Journal* and *Forest Ecology and Management*.

II. Literature Review

Introduction

Soil occurs at an environmental interface where the lithosphere, biosphere, atmosphere and hydrosphere converge. Terrestrial life depends on soil; therefore, it is critical to understand this resource in order to sustainably manage the landscape for products and services. Management decisions should be informed by soil condition, and potential for change due to anthropogenic influences.

Atmospheric acid input is an environmental factor that may negatively impact forest growth largely by predisposing forests to damage from other stresses such as insect infestation (Driscoll *et al.*, 2001a), frost damage (Gress *et al.*, 2007), and nutrient imbalance (Vitousek *et al.*, 1997; Fenn *et al.*, 1998). Acid deposition (AD) has also been linked with coastal eutrophication, mercury accumulation, decreased visibility, climate change, and tropospheric elevated ozone (Driscoll *et al.*, 2001c). Acid deposition, therefore, must be a factor considered during the management planning process for those regions of the country receiving significant levels of this pollutant. Potential management practices in response to AD include: monitoring, stand manipulation, changes in harvesting practices, fertilization, liming, and policy or regulatory action (Fenn *et al.*, 1998).

Acid Deposition

Acid deposition in the United States was first observed and reported at the Hubbard Brook Experimental Forest in the late 1960s (Likens, 1972). Comprised of sulfur dioxide (SO₂), N oxides (NO_x), ammonia (NH₃), and particulate emissions, this multi-regional pollution interacts with terrestrial and aquatic ecosystems by altering elemental interactions within the system (Driscoll *et al.*, 2001c). Acidic pollution occurs as both wet deposition and dry deposition. Wet deposition includes rain, snow, hail, sleet and fog. Dry deposition occurs as particulate matter and gaseous forms. The proportion

that each contributes to an ecosystem is dependent on elevation. At high elevations, fog may contribute as much acidity as rain.

Due to concern over this chronic and continuing source of pollution, regulations pertaining to acid deposition were first passed in the 1970 Clean Air Act. Most recently, the 1990 Clean Air Act Amendments (CAAA) set specific target sulfur emissions, and some controls for N emissions. Since the passage of this law, sulfur emissions have been significantly reduced. In 2005, sulfur dioxide emissions by the power sector were 35% below 1980 levels (EPA, 2005). On the other hand, atmospheric N appears to be unaffected by these regulations (Aber *et al.*, 2003). Modeling conducted at the Hubbard Brook Experimental Forest shows that current regulations will not sufficiently address the ecological problems associated with acid deposition (Table 2-1). The data in Table 2-1 show that compared to baseline threshold levels, critical chemical indicators of stream and soil acidity will exceed desired levels despite reduced emissions required by the 1990 Clean Air Act Amendments.

Table 2-1: Results from a computer model showing chemical conditions under three acid deposition regulation emissions scenarios at the Hubbard Brook Experimental Forest From: (Driscoll *et al.*, 2001a). Courtesy of the Hubbard Brook Research Foundation.

Chemical Indicator	Baseline Conditions			Emissions Scenarios		
	1850	Threshold	1970	2050 with 1990 CAAA	2050 with 40% deeper cuts	2050 with 80% deeper cuts
Sulfate wet deposition (g/m ² yr)	0.23	-	1.69	0.89	0.69	0.50
Stream sulfate	9.6	-	62.0	34.3	28.9	23.5
Stream ANC (μmol/L)	42.7	> 50	-5.4	-1.0	0.6	2.5
Stream pH	6.3	> 6.0	4.8	5.3	5.5	5.7
Stream aluminum (μmol/L)	1.5	< 2.0	12.1	6.4	5.6	4.3
Soil base saturation (%)	21.8	> 20	13.4	12.3	13.3	14.4

Sulfur Pollution

Sulfur is a macronutrient needed by plants to make proteins and secondary chemicals. In unpolluted circumstances, the soil has large pools of unavailable sulfur, which enters the system as a salt, and becomes plant available through microbial action (Fisher and Binkley, 2000). In polluted regions, sulfate (SO₄⁻) is deposited as sulfuric

acid. This anion has a strong affinity for base cations, forming salts that leach from the soil system, resulting in an increase in H cation concentration in the soil and a decrease in base saturation (Fisher and Binkley, 2000).

Soil sulfate adsorption occurs by two main mechanisms: 1) equivalent exchange, which results in the release of an OH⁻ ion; or 2) selective absorption, which is a neutral absorption of SO₄⁻. Absorption generally increases as available sesquioxide surfaces increase, pH decreases, organic matter decreases, the concentration of similarly absorbed anions decreases, and with time (Johnson, 1980; Harrison and Johnson, 1992; Fisher and Binkley, 2000).

Since the inception of the Clean Air Act and the 1990 CAAA, S pollution has decreased. Researchers expect soil systems will respond to these decreases through one or more of four scenarios of sulfate desorption: 1) mobilization of additional S pools; 2) complete or near-complete reversibility of absorbed S; 3) partial reversibility of absorbed S; or 4) little or no reversibility of absorbed S (Harrison and Johnson, 1992). While desorption is variable among soils, studies have shown that chronic S deposition, even when reduced, has caused sulfur accumulation in soils, indicating only partial reversibility of sulfate sorption (Driscoll *et al.*, 2001c)

Nitrogen Pollution

Nitrogen is a crucial nutrient for ecosystem function, and has been considered to be the most limiting nutrient resource in forest ecosystems around the globe (Fisher and Binkley, 2000). In unpolluted systems, N enters the forest ecosystem through N-fixation and atmospheric deposition, and is unavailable for vegetative uptake until the N is mineralized into ammonium and nitrate (Fisher and Binkley, 2000). Nitrogen cycling is driven by pools and processes that function at rates ranging from hours in large pools (i.e. microbes) to decades in smaller fractions (i.e. vegetation). Within forested ecosystems, N sinks include uptake by vegetation, microbial immobilization, adsorption to the soil exchange complex, and volatilization (Van Miegroet *et al.*, 1992).

Changes in N sinks influence N sequestration, which is dependent on stand age, land use history, stand vigor and species composition, mineralization potential, N input rates, nitrification rates, previous N stores in the soil, C:N ratio, length of the growing

season, and soil porosity (Van Miegroet *et al.*, 1992; Fenn *et al.*, 1998; Goodale and Aber, 2001). Acid deposition appears to be changing these pools, and acidifying forest systems. The extent to which N input leaches bases and acidifies soils is dependent on the form in which N enters the system. The most common forms of atmospheric N deposition are: HNO_3 , $(\text{NH}_4)_2\text{SO}_4$, and NH_4NO_3 , which could leach up to one, two, or three times their equivalent bases, respectively (Ruess and Johnson, 1986).

Changes in ecosystem N regulatory functions and pools have been observed at experimental N input levels equal to ambient levels of acid deposition (Foster *et al.*, 1997). In a whole-watershed experiment doubling ambient N and S throughfall inputs, Adams *et al.* (1997) recorded nutrient leaching from the upper soil horizons, concluding that NO_3^- may be an important anion for removing Ca from the soil in cases where cation exchange processes dominate neutralization of mineral acidity.

Aber *et al.* (1989) theorized that chronic additions of N will force the system to adjust its structure and function. This will occur in four stages. In stage 0 N cycling will be characteristic of a forest under N-limited conditions. Chronic N deposition will push forests into stage 1, when the added N will act as a pulse of fertilization. After continued deposition, forests will move to stage 2 where the system will become saturated, and stop retaining N. Indices of stage 2 may include nitrate leaching from soils, reduced fine root biomass, and nitrous oxide emissions. Finally, during stage 3 as N deposition continues on a N-saturated system, the forest will decline due to N-luxury consumption or another factor such as light or other nutrients will become limiting.

Systems that are most prone to N-saturation are those subject to high N deposition, with high soil N stores and with low C/N ratios (Fenn *et al.*, 1998). Possible effects of N-saturation are related to lower availability of Ca, P, or water within the plant as N limitations are removed (Gress *et al.*, 2007). Furthermore, scientists and managers are concerned that N saturation may shift species distributions within ecosystems (McNulty *et al.*, 1996).

While sulfuric acid as a source of atmospheric acid deposition has decreased since the passage of the CAAA (Driscoll *et al.*, 2001c) N deposition is still relatively unregulated. Although ecosystems vary widely in their ability to absorb N, evidence of N-saturation continues to be reported in both Europe and the United States (Fenn *et al.*,

1998; Houle *et al.*, 2006). For example, in a comprehensive review of data from the northeastern United States, Aber *et al.* (2003) concluded that surface water data exhibit altered N status in forest systems due to N deposition. Soils data similarly show changes due to atmospheric deposition. In a rare retrospective study on the Allegheny Plateau of Pennsylvania, Bailey *et al.* (2005) determined that soil pH, and Ca and Mg concentrations decreased between 1967 and 1997. These changes have also been exhibited in forest growth data. In the Southern Appalachians, a study determined that decreased basal area growth of yellow birch and American beech was consistent with the later stages of N-saturation (Boggs *et al.*, 2005). In Canada, sugar maple (*Acer saccharum* Marsh.) exhibited a 17% reduction in growth rate on declining stands, which was correlated with N and S deposition and soil exchangeable acidity (Duchesne *et al.*, 2002).

Acid Deposition and Forest Productivity

Biomass accumulation varies with site quality and forest management. For example, in West Virginia growth rates of upland oaks in second-growth stands ranged from $1 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ on poor quality sites to $4 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ on excellent quality site (Table 2-2). Furthermore, forest management practices such as stand thinning can increase rates to over $7 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ (Table 2-2). The USDA Forest Service uses growth rate as an indicator of soil productivity (Burt *et al.*, 2005). Changes in growth can also be used to make inferences about the effects of acid deposition on forested ecosystems. Acid deposition gradients have been associated with differences in basal area growth and decline status of sugar maple (Duchesne *et al.*, 2002; Boggs *et al.*, 2005).

Many studies across the Eastern United States have cited acid deposition as a causal agent in forest decline (Hutchinson *et al.*, 1998; Horsley *et al.*, 2000; Horsley *et al.*, 2002; Duchesne *et al.*, 2003; Kogelmann and Sharpe, 2006). Decline refers to the “irreversible, gradual deterioration of tree health resulting from a complex of biotic and abiotic causal factors that are conceptualized as predisposing, inciting, and contributing” (Kogelmann and Sharpe, 2006). Researchers suspect that AD endangers forest growth by depleting available Ca in the soil system. Between 1967 and 1997 acidic deposition

caused significant decreases in exchangeable soil Ca at all of four study sites on the Allegheny Plateau in Pennsylvania (Bailey *et al.*, 2005).

Table 2-2: Range of historical forest growth in West Virginia. From Hicks (1998)

Site Quality	Upland Oaks	Central Appalachian Sawtimber Stands	Yellow-Poplar
Poor Site (oak SI 50)	2 m ³ ha ⁻¹ per year		
Below Average (oak SI 60)	3 m ³ ha ⁻¹ per year	3.5 m ³ ha ⁻¹ per year	2.5 m ³ ha ⁻¹ per year
Average Site (oak SI 70)	4.5 m ³ ha ⁻¹ per year	5 m ³ ha ⁻¹ per year	3 m ³ ha ⁻¹ per year
Above Average (oak SI 80)	6 m ³ ha ⁻¹ per year	7 m ³ ha ⁻¹ per year	3.5 m ³ ha ⁻¹ per year
Excellent Site (oak SI 90)			8 m ³ ha ⁻¹ per year

In experimental studies, addition of N and S has resulted in Ca and Mg losses from treated watersheds (Fernandez *et al.*, 2003). These observations suggest that Ca may become a limiting resource for the growth of forested ecosystems, ultimately predisposing forests to problems such as increased mortality due to reduced resistance to pests and pathogens (Federer *et al.*, 1989; Huntington *et al.*, 2000). Sugar maple was shown to grow poorly on acidic soil with depleted Ca availability (Watmough, 2002), and exhibited stand decline in soils with depressed Ca concentrations and pH (Sharpe and Sunderland, 1995). Bailey *et al.* (2004; 2005) propose that exchangeable Ca levels below 2% in the B horizon is a threshold below which forests become susceptible to decline. Soil acidification in both experimental and observational studies has been found to cause forest decline. Drohan *et al.* (2002) classified sites with and without sugar maple decline and found significant differences in many soil and foliar chemical characteristics between the two sites (Table 2-3). Non-declining sugar maple stands had higher soil base saturation, Ca concentration, and Ca/Al ratio than declining stands. Foliar Ca, K, and Mg were also significantly higher on non-declining sugar maple stands.

Table 2-3: Untransformed mean foliar chemistry; soil chemistry and physical properties by forest health class. Modified from Drohan *et al.* (2002)

Health Class	n	%BS	Al	Ca	Ca/Al ⁻	ECEC	K	Mg	Mg/Mn ⁻	Mn	pH
Oa horizons [‡]											
Declining	9	54	10	9.3	2.0	20.5	1	1.6	0.5	4.4	3.1
Non-declining	19	60	6.2	6.7	4.0	12.7	0.51	1	0.7	1.8	3.4
<i>P-value</i>		0.520	0.240	0.680	0.650	0.330	0.360	0.800	0.590	0.280	0.023
Horizons ≤ 50 cm											
Declining	9	10	5.6	0.53	0.1	6.2	0.11	0.08	3	0.32	3.7
Non-declining	19	23	5.5	1.63	7.8	7.4	0.17	0.34	4.7	0.29	3.8
<i>P-value</i>		0.037	0.880	0.016	0.031	0.039	0.013	0.007	0.037	0.810	0.010
Horizons > 50 cm											
Declining	9	16	4.5	0.56	0.2	5.6	0.09	0.23	21.1	0.21	3.8
Non-declining	19	27	3.5	1.2	0.9	5.5	0.11	0.38	16.9	0.07	4.1
<i>P-value</i>		0.703	0.045	0.960	0.058	0.074	0.960	0.900	0.530	0.490	0.033
Foliar [‡]											
Declining	9		24.1	4978	163		8444	921	0.7	3169	
Non-declining	19		47	7528	322		9412	1260	2.2	2036	
<i>P-value</i>			0.930	0.046	0.140		0.040	0.050	0.002	0.005	

[‡] Soil ion concentrations are mmol₊ kg soil⁻¹; Foliar ion concentrations are µg g⁻¹

Reprinted from Forest Ecology and Management Vol. 170. Drohan, P.J., Stout, S.L., and Petersen, G.W. Sugar maple (*Acer saccharum* Marsh.) decline during 1979-1989 in northern Pennsylvania. p. 7. Copyright (2002), with permission for Elsevier.

Along with base cation leaching, another consequence of soil acidification is increased solubility and mobility of Al in forested ecosystems (Cronan and Schofield, 1979; Ruess and Johnson, 1986). In the northeastern United States Al mobilization decreased root-available Ca in the forest floor as Al exchanged for Ca, and decreased the number of exchange sites filled by bases (Lawrence *et al.*, 1995). As Al becomes more mobile, and Ca is lost from the system acidified soils will show a change in Ca/Al ratio. Across 116 soil horizons in Pennsylvania, extractable Ca and Al were found to be significantly related (Lyon and Sharpe, 1999).

In an acidification study, Johnson *et al.* (1982a) reported that plants growing in highly acidic environments contained high concentrations of foliar Al. In a controlled experiment northern red oak (*Quercus rubra* L.) seedlings grown in various levels of soil Al responded with significant differences in root branching and foliar biomass production (Joslin and Wolfe, 1989). Because of these biological responses to changes in the soil system, Al contents in biomass may be used to classify the acidity status of forested ecosystems (Johnson *et al.*, 1982a; Cronan and Grigal, 1995).

Kogleman and Sharpe (2006) showed that in acidified soils Mn also may become more mobile and was related to sugar maple decline in Pennsylvania. In their study, red maple (*Acer rubrum* L.) was observed to be more tolerant to high soil Mn concentrations than sugar maple. Manganese does not resorb before senescence; therefore, it may accumulate in the litter layer and prevent Ca and Mg sorption as it leaches through the system.

A study in the northeastern US showed that a loss of exchangeable bases may be aggravated by forest age. Biogeochemical cycles changed with succession from pin cherry (*Prunus pensylvanica* L.) and striped maple (*Acer pensylvanicum* L.) dominated stands to older stands of beech and red maple (Hamburg *et al.*, 2003). This suggests that the impact of AD on cation leaching may be more important on older stands.

To study the effects of AD on forest productivity, basal area increment can be used to estimate woody above-ground net primary productivity (Pastor *et al.*, 1984). This technique is common among acid deposition studies. In Southern Quebec, decline in basal area increment of sugar maple was found to be significantly correlated with visual symptoms of tree decline (irrespective of tree age), with forest floor H and Al concentrations, forest floor base saturation, B horizon K concentration, and somewhat correlated with atmospheric N and S deposition (Duchesne *et al.*, 2003). Horsley *et al.* (2000) used stand percent dead basal area to determine relative health of sugar maple stands in Pennsylvania, and found that basal area monitoring may indicate sugar maple decline before visual canopy symptoms become apparent. Furthermore, growth increment increased due to liming relative to unlimed sugar maple plots in Canada (Moore and Ouimet, 2006).

Aquatic systems are also in peril due to acid deposition. Chronic S and N inputs have decreased acid neutralizing capacity, lowered water pH, and increased concentrations of inorganic monomeric Al in some streams and lakes in the northeastern United States (Driscoll *et al.*, 2001c). On the Monongahela National Forest in West Virginia many streams are limed to increased water pH to a level tolerable by aquatic organisms (Connolly, 2006, personal communication). Aquatic system recovery is slowed by the removal of base cations from the ecosystem and S accumulation in the soil (Driscoll *et al.*, 2001c). Data from the Hubbard Brook Experimental Forest show that

acidification of aquatic systems decreased both the diversity and the abundance of aquatic organisms in affected ecosystems (Driscoll *et al.*, 2001c).

Resistance and Sensitivity to Acid Deposition

To fully understand and assess how AD influences forest productivity, other site characteristics that dictate growth potential must also be understood. Site characteristics such as slope, aspect and elevation are often considered determinant of forest growth along with soil characteristics such as parent material, depth, mineralogy, texture, percent rock fragments, and chemistry.

Parent material is one of the most fundamental site characteristics related to acid-neutralization (Johnson, 1984). Geologic material is considered to be more resistant to acidification if it is more calcareous, providing buffering capacity and more nutrients to the soil system (Johnson *et al.*, 1982a; Johnson, 1984; Lucas and Cowell, 1984). In an Appalachian forest study, N in streams was significantly correlated with bedrock geology (Williard *et al.*, 2005). In this study soil pH, soil percent N concentration, soil C/N mass ratio, soil exchangeable Ca, watershed slope, and certain tree species were significantly correlated with both bedrock geology and stream nitrate levels. The authors suggest that bedrock geology may be a more accurate predictor of stream nitrate concentrations than soil chemistry, suggesting that both the geology and soils should be taken into consideration in assessing forest ecosystem dynamics in relation to AD.

In the Eastern United States, sites with northeast aspect tend to be more productive due to lower moisture losses as the result of decreased solar radiation (Auchmoody and Smith, 1979). Cooler sites will generally be more productive, and therefore use more of the N deposited on the system; N will be biologically absorbed and N-saturation of forest soils will be less likely (Fenn *et al.*, 1998).

Steeper slopes would be less likely to become acidified due to increased run off, and therefore decreased leaching (Fenn *et al.*, 1998). Similarly, the chronic and cumulative effect of leaching would be mitigated on deeper soils (Reuss and Johnson, 1986). The soil is the first geologic acid-sink, and kinetically the most active (Johnson, 1984), and the potential to reduce acidity is expected to be highest when the soil is deeper than 100 cm and lowest when the soil is shallower than 25 cm (Lucas and Cowell, 1984).

Higher elevation sites are more susceptible to acidification for a variety of reasons. These sites receive more acidic deposition, they are prone to have shorter growing seasons, they are more likely to receive AD as fog, and they are more susceptible to soil freezing events (Van Miegroet *et al.*, 1992; Fenn *et al.*, 1998; Driscoll *et al.*, 2001c; Fitzhugh *et al.*, 2003).

Increased rock fragments in a soil profile decrease resistance to acidification because this increase decreases the soil volume available for neutralization; however, higher rock fragment content can increase hydraulic conductivity, which in some soils reduces the equilibrium time between the AD and soil system, increasing resistance to AD (Fenn *et al.*, 1998).

Soil texture appears to be one of the only soil factors related to acid-neutralization that is readily available in spatial data sets (Van Ranst *et al.*, 2002). AD buffering increases with clay content up to a point; however, similar to the influence of rock fragments on hydraulic conductivity, too much clay slows the movement of water through the soil profile, increasing contact time between AD and the soil system, therefore, decreasing resistance. Furthermore, soil texture is correlated with N mineralization and species composition because of its influence on soil water content (Pastor *et al.*, 1984).

In a whole-watershed experiment discerning the effects of elevation on various ecosystem process related to acid deposition, mineral soil depth, organic carbon in the mineral soil, pH of the Oa, and CEC of the Oa and the mineral soil were not found to be correlated with elevation. Leaching of base cations increased with elevation, as did sulfate deposition, while soil exchangeable base concentrations and stream ANC decreased with elevation (Lawrence *et al.*, 1999).

Soil chemistry is complex and highly spatially variable. In a whole-watershed study in the New York Catskills, GIS mapping of slope, aspect, elevation, topographic index, and flow accumulation was not able to predict chemical properties of organic and mineral soils (Johnson *et al.*, 2000). In this study, 4 to 25% of the variance of soil pH, effective CEC, exchangeable bases, exchangeable acidity, total C and N, and C/N ratio could be explained by the topographic factors. The authors suggest that the weak correlations were due to the large scale of the mapped topographic factors, incomplete

characterization of sampling point topography, and the fact that non-topographic factors influence soil chemical properties.

Approaches to mapping site sensitivity or resistance to acid deposition vary, ranging from site characterization (i.e. Kuylenstierna *et al.*, 1995) to meteorological modeling (i.e. Langner *et al.*, 1995). In applying the ecological site factors approach, the most commonly used characteristics include bedrock parent material, soil type, land cover, and moisture regime (Tao and Feng, 2000). Commonly, these characteristics are reclassified into categories, which are then given a weight to produce a relative scale of sensitivity or resistance (Kuylenstierna *et al.*, 1995). Weighting factors are also useful because they may be changed as new data become available through monitoring and research, which are integral aspects of adaptive management (Chadwick and Kuylenstierna, 1991; USDA Forest Service, 2006).

Soil Acidification

Soil acidification occurs when base cations are removed from the system, which may occur through vegetative uptake of base cations or leaching of base cations associated with mobile anions. In unpolluted systems, carbonic and organic acids drive ion mobilization; however, acid deposition adds H and mobile anions to the soil system (Cronan *et al.*, 1978). The effects of added acidity vary by system, depending partially on the buffering capacity of a specific soil.

Acidification is a natural process in soil systems which is understood using three parameters: total acidity, degree of activity, and buffer capacity (Bache, 1980a). Soil acidity forms through carbonation of water, mineralization, input of organic acids from vegetation, oxidation processes, and acid deposited from precipitation (Bache, 1980a). Acidity changes the soil system via cation removal, from vegetative uptake or leaching by natural or anthropogenically introduced acids (Ruess and Johnson, 1986) (Feller, 1977; Cronan *et al.*, 1978). The equilibrium equation:



shows that acidic inputs will cause the equilibrium to shift to the right. Thus, acidification of soils results in a loss of base cations, reduction of cation exchange capacity, mobilization of Al, mineral degradation, and changes in biological activity (Bache, 1980a).

Base saturation is commonly used to characterize the amount of exchange complexes occupied by base cations; however, in the case of soils polluted by acid deposition the acidity degree may also be a useful characteristic (Ulrich, 1994):

$$\text{Acidity Degree (\%)} = 100 * \frac{\text{exchangeable acid cations}}{\text{exchangeable base cations} + \text{acid cations}} \quad (2)$$

The extent to which this soil characteristic will change with the addition of acid depends on the acid neutralizing capacity of the soil system. In non-polluted systems, the extent of base loss and acidification in soil systems is dependent on base saturation, cation exchange capacity and the relative bonding strength of soil minerals for the H ion.

Buffering Mechanisms

The extent to which soil buffering processes may occur will determine the effect of acid deposition on soil chemistry and nutrient status. A variety of soil properties influence the ability and extent of soil buffering (Table 2-4).

Table 2-4: Soil properties that influence the soil acid neutralizing capacity of a soil

Property	Influence on Soil Acid Neutralizing Capacity (ANC)
Base saturation	Increased base saturation increases ANC
Cation exchange capacity (CEC)	Increased CEC increases ANC; CEC is dependent on mineralogy and pH
Bonding strength of soil minerals for H ⁺	Decreased selectivity for H ⁺ increases ANC; Depends on mineralogy
Soil texture	Decreased ANC with increased sand
Soil depth	Increased ANC with increased depth
Sulfate adsorption capacity	Increased adsorption capacity increases ANC

Buffering mechanisms vary with soil pH (Bache, 1980a). A generally accepted scheme for soil buffering begins with carbonate buffering, then moves to silicate, cation, and Al buffering, and ends with Fe buffering (Table 2-5) (Ulrich, 1980). Acid neutralizing capacity (ANC) is positively correlated with soil pH; therefore, a calculated ANC depends on the pH at which it is calculated. For forest soils, pH of 3 is an acceptable reference (Brahya *et al.*, 2000). Also, it is important to recognize that the properties and mechanisms in Table 2-5 are for mineral soils, which must be considered separately from the ANC of organic soils (Bache, 1980a).

Table 2-5: Soil buffering mechanisms.

pH Range	Buffering Mechanism	Example	Notes
6.2 – 8	Carbonate buffering	$\text{CaCO}_3 + \text{H}_2\text{CO}_3 \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$	pH dependent on partial pressure
5 – 6.2	Silicate buffering	$\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	
4.2 – 5	Cation buffering		pH correlated with mole fraction Al
3 – 4.2	Al buffering	$\text{AlOOH} \cdot \text{H}_2\text{O} + \text{xH}^+ \rightarrow \text{Al}(\text{OH})_{3-\text{x}}^{+\text{x}} + \text{xH}_2\text{O}$	pH determined by hydrolysis of Al
< 3	Iron buffering	$\text{Fe}(\text{OH})_3 + \text{xH}^+ \rightarrow \text{Fe}(\text{OH})_{3-\text{x}}^{+\text{x}} + \text{xH}_2\text{O}$	

The buffering capacity of a soil can be expressed as the soil lime potential, which is:

$$pH + [1/3 pAl - 1/2 p(\text{Ca}, \text{Mg})] \quad (3)$$

where the second section of the equation is the Al-base cation balance of the soil system (Bache, 1980b). However, if Fe and Al-bearing silicates act as sinks for protons the ANC equation should be modified to:

$$m\text{ANC}_s (pH 3) = \text{TRB} + 6(\text{Al}_2\text{O}_3) + 6[\text{Fe}_2\text{O}_3_{\text{total}} - \text{Fe}_2\text{O}_3_{\text{d}}] \quad (4)$$

where TRB is the total reserve bases (sum of Na^+ , K^+ , Ca^{2+} , and Mg^{2+}) (Brahya *et al.*, 2000).

Normally, cation exchange capacity and pH are positively correlated because as pH increases variable charge or functional group exchange sites become deprotonated and negatively charged. However, in some acid deposition studies, the opposite relationship has been found (Johnson *et al.*, 2000). This occurs because in acid soils organic matter is

the dominant form of cation exchange sites through carboxyl groups, which provide a high density of ionized sites but also liberates H ions (Johnson, 2002). Organic matter also binds large amounts of Al, which may act as bases in acid forest soils. Therefore, effective cation exchange capacity represents the portion of exchange sites on which Al is not strongly bound. This will influence the response of acid soils under decreased acidic inputs. A majority of properties that influence ANC are dependent on soil mineralogical components, which is determined by parent material and weathering.

Base cation depletion & aluminum toxicity

As the soil system acidifies through leaching of base cations, the nutrient status of the system will change. If base saturation declines below 20%, additional acid input will result in mobilization and leaching of Al, and H neutralization will be incomplete (Driscoll *et al.*, 2001c). This shift from base cation domination of soil solution (above 20% base saturation) to an Al-dominated system (below 20% base saturation) will occur abruptly (Reuss, 1983).

Acidification has caused Ca loss from forest soils, which may lead to forest decline (Huntington *et al.*, 2000; Fernandez *et al.*, 2003). Concern over nutrient loss due to leaching is coupled with concern that Al toxicity may further induce decline. The Ca/Al molar ratio has been used as an indicator, from which levels below 1.0 in soil solution may indicate a predisposition to forest stress due to Al toxicity (Cronan and Grigal, 1995); however, this indicator may not be conservative enough in systems where harvesting removes additional base cations (Watmough and Dillon, 2003).

Monitoring for the Effects of Acid Deposition

Adams *et al.* (2000) call for development of a monitoring system that assesses sustainability of management practices of forested ecosystems, specifically citing acid deposition as a potential threat to sustainability. Studies of acid deposition and N saturation have revealed flaws in some commonly used methods for measuring and

assessing forest systems because they do not account for AD-specific effects (Foster *et al.*, 1997).

Soil and foliar chemical indicators might be used as possible early indicators of tree and forest changes related to acid deposition. To be useful, indicators should meet 11 criteria outlined by White (2004). They should 1) be based on an ecosystem conceptual approach, 2) be useful, 3) be cost-effective, 4) be related to cause and effect mechanisms, 5) sufficiently overcome the signal-to-noise ratio, 6) include quality assurance programs, 7) be anticipatory of future needs, 8) be comparable to a historical record, 9) provide retrospective data, 10) provide new information, while; 11) having a minimal environmental impact.

Soil Sampling and Analysis

To be useful, Adams *et al.* (2000) argue that soil indicators should have five characteristics in addition to those listed: 1) an available baseline against which to compare changes; 2) the ability to provide a sensitive, continuous, and timely measure of soil change; 3) applicability over large areas; 4) discrimination between natural changes and those induced by management; and 5) high correlation to long-term response in long-lived forest ecosystems.

Soil system measurements may be adjusted to meet these criteria, but must be carefully calibrated to do so while addressing management needs. Among researchers and managers, a key concern is proper sampling methodology. Two considerations are how to sample the soil profile and which horizons to sample. The distinct chemical and biological differences among soil horizons will often create large differences in the rate of anion production, consumption, and leaching (Johnson, 1992a). From soil acidity studies, we know that while overall spatial soil variation is difficult to detect statistically, differences among horizons are readily detectable (Yanai *et al.*, 2005). A study conducted across 18 soil series in Pennsylvania found that B horizon Ca/Al ratios were most likely to indicate acidification risks, while organic horizons may not indicate the same risk because Al is complexed with organic material and Ca is coming from litter decomposition (Lyon and Sharpe, 1999). In the Integrated Forest Study, conducted

across the United States, the base saturation of the B horizon was a useful tool in comparing base fluxes among sites (Johnson, 1992a).

Sample analysis will also influence interpretation of results. Lawrence *et al.* (1997) compared NH_4OAc , KCl , NH_4Cl , and BaCl_2 extracts in removing soil Ca and found no significant differences; however, others argue that a buffered salt method (NH_4OAc at pH 7) overestimates cation exchange capacity and 1.0 M NH_4Cl is a better method for determining cation exchange capacity of forest soils (Amacher *et al.*, 1990; Skinner *et al.*, 2001). Exchangeable, easily-weatherable, and relatively unreactive Ca pools can be measured using a sequential extraction of NH_4Cl , HNO_3 , and an acid digestion (Hamburg *et al.*, 2003). Aluminum and Ca/Al ratio, however, may be best estimated using a SrCl_2 extraction (Joslin and Wolfe, 1989).

Foliar Analyses

Foliar chemistry is related to nutrient availability and root absorption ability, so this method could be used to understand nutrient balance in the soil-root system and therefore exchangeable ions in the soil (Leininger and Winner, 1987). Theoretically, increased mobilization of base cations in the soil system due to acidification would increase base cation uptake by vegetation, therefore increasing concentrations in foliage. However, if uptake processes are impeded by free Al or leaching has removed bases from the soil system, this will not be the case (Johnson, 1992b).

Foliar analysis has been shown to be a viable method for measuring changes in ecosystem N availability. Forest ecosystems experiencing N saturation are expected to have elevated N and P, and lowered lignin concentrations in foliage (Aber *et al.*, 1989). After three years of chronic N additions, green foliar N concentrations in pines and hardwoods both increased after the second year (Aber *et al.*, 1993). After four years of ammonium sulfate treatment, sugar maple, red maple, American beech (*Fagus grandifolia* Ehrh.), and red spruce (*Picea rubens* Sarg.) foliage had significantly higher N concentrations than untreated stands. Sugar maple on the treated watershed also had lower Ca and higher Al and Fe foliar concentrations (White *et al.*, 1999).

Bailey *et al.* (2004) confirmed that foliar analysis can address site quality and base cation nutrition. For comparison between soil and foliar elemental content they recommend looking at more than one soil depth because they found correlations between foliar nutrients and soil nutrients as deep as the lower B horizon. In a study focusing on the Ca/Al ratio of both soil solution and plant tissue, correlations were found between the ratios in each system and the health of the forest, and the authors attest to the usefulness of this ratio in ecological monitoring (Cronan and Grigal, 1995).

In declining sugar maple stands, foliar Ca and Mg concentrations were correlated with soil base cation availability (Bailey *et al.*, 2004). Foliar Mn chemistry was found to be related to soil, sap, and xylem wood chemistry in sugar maple in Pennsylvania (Kogelmann and Sharpe, 2006). In another Pennsylvania study, over 35% of the variability of sugar maple decline could be related to foliar Mg content, Mn content and Mg/Mn ratios (Horsley *et al.*, 2000). In this study, glaciation, topography, physiographic position, and elevation were surrogates for foliar concentration of Mg and Ca. Furthermore, foliar concentrations could be used to delineate the landscape into areas of inadequate base cation supply.

Epidemiological Approach to Assessing Acid Deposition Impacts

Historically, one of the problems related to AD investigations is the inability to create cause and effect relationships between the pollutant and forest response. This is because of statistical limitations, a lack of a controlled experiment, incomplete knowledge of all the biotic and abiotic factors and links, and inability to replicate conditions (Johnson *et al.*, 1992). By applying an epidemiological approach, Johnson *et al.* (1992) determined three criteria that, if met, could lead to a rational cause and effect conclusion. These were: 1) consistency, 2) mechanisms, and 3) responsiveness. That is to say, a temporal and spatial consistency of symptoms and suspected agents is necessary. Furthermore, there must be plausible mechanisms for the symptoms, or plausible linked processes leading to the symptoms. Finally, it must be possible to replicate the symptoms in controlled environments. Using this approach, the authors were able to conclude that AD increased red spruce sensitivity to winter injury, Al mobilization, and cation loss.

Use of Dendrochronology to Assess Acid Deposition Impacts

Given that environmental conditions affect tree growth, changes in rates of growth can accurately indicate forest conditions as well as provide historical environmental monitoring (Fritts, 1976; Juknys, 2004). Therefore, tree growth rings, which can also be used to establish stem age, can be compared to ascertain how past and present environmental conditions affect forest productivity. The main abiotic factors influencing tree growth are: topography, soils, elevation and orthographic factors (Fritts, 1976). Developing models to isolate one of these factors can be used to understand the plant-environment system (Fritts, 1976).

Dendrochronological modeling requires objective statistical measurements, calibrations, and reconstructions. Considerations should include proper field procedure, adequate replication, correct specimen mounting, careful measurement, crossdating, and tests for anomalous individuals (Fritts, 1976). Sample variance must be examined to correctly model variance induced by environmental factors. This is commonly accomplished through standardization, filtering, and analysis of variance techniques (Fritts, 1976).

Tree ring growth analysis has been used to determine changes in forest growth patterns due to acid deposition (e.g. Duchesne *et al.*, 2002; Duchesne *et al.*, 2003). Using dendrochronology, changes in forest growth over time can be correlated with changes in soil chemistry. For example, sugar maple growth rings and basal area increment (BAI) have been used to demonstrate productivity declines across ranges of AD (Duchesne *et al.*, 2002). BAI was found to be inversely related to sugar maple dieback class (classified by crown condition) in Canada; therefore, BAI measurements may be more useful in monitoring than waiting for visible symptoms (Duchesne *et al.*, 2003). Similarly, in the Appalachian region BAI from 1980 to 1998 was correlated with AD (Boggs *et al.*, 2005).

Forest Inventory and Analysis Plots

The United States Department of Agriculture (USDA) Forest Service has an on-going effort to monitor the state of the nation's forests through the Forest Inventory and

Analysis (FIA) system. The FIA program's primary objective is "to determine the extent, condition, volume, growth, and depletions of timber on the Nation's forest land." (USDA Forest Service, 2007) FIA plots are located across the country on all land usages (i.e. public, non-governmental, corporate, individual, Native American). Each plot is re-sampled every five years, so that within each state 20% of the plots are measured each year.

The FIA program includes three sampling phases. Phase 1 classifies land using remote sensing classes. Phase 2 plots are ground-plots, where measurements are taken over three 0.017 hectare plots arranged around another 0.017 hectare center-plot (Figure 2-1). Phase 2 measurements include individual tree measurements such as diameter at breast height, total height, species, tree class, and visible damage. All FIA ground-plots include Phase 2 measurements, while only a sub-set of these are measured as Phase 3 plots. Phase 3 measurements include soil sampling, down woody debris measurements, lichens measurements, and other detailed sampling.

The Monongahela National Forest

The Monongahela National Forest (MNF), in Eastern West Virginia, encompasses over 360,000 hectares of forested land. This area was designated a National Forest in 1920, after being largely clear-cut in the late-19th and early-20th century. The current forest is second and third growth, and maintains a high level of biological diversity, supporting 13% of the rare plant and animal species in West Virginia (USDA Forest Service, 2006). Situated only a few hours from large urban centers and containing over 1200 kilometers of hiking trails, the MNF is a popular recreation destination, while still producing about 0.2 million cubic meters of timber annually (Widmann and Griffith, 2004).

Phase 2/Phase 3 Plot Design

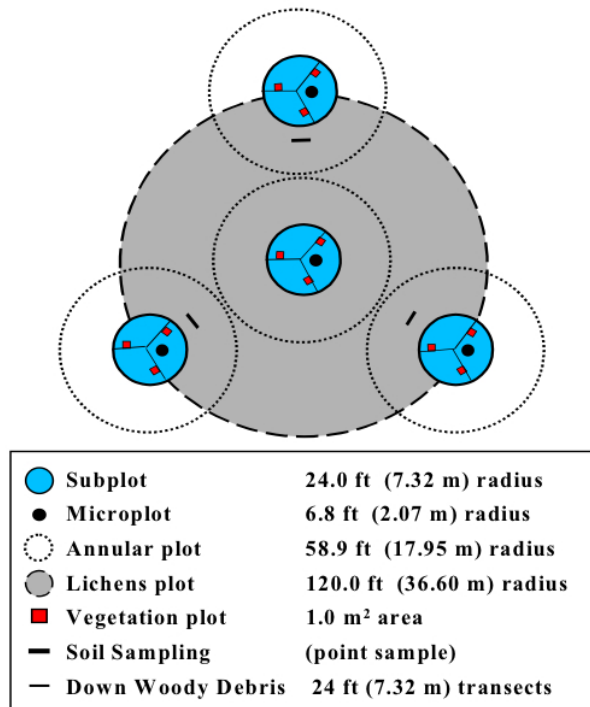
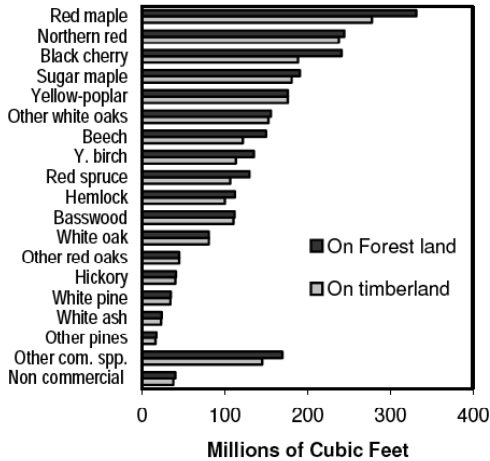


Figure 2-1: Plot design of Phase 2 and Phase 3 Forest Inventory and Analysis Plots.

Based on Forest Inventory and Analysis data published in 2003, 8% of the MNF land area is reserved as wilderness, and 91% is considered to be timberland that grows at least 1.5 cubic meters of timber per hectare per year (Widmann and Griffith, 2004). Of this timberland, 78% is sawtimber-size and 4% is sapling or seedling size stands. Fifty-eight percent of the timberland is fully stocked and 8% is overstocked (Figure 2-2).

Across the MNF, red maple makes up 14% of the volume of all live trees on the forest, and oak species combined make up 23.6% of the volume on timberland. Data from 2002 indicate that net annual growth of trees averaged 0.72 million cubic meters and harvesting averaged 0.2 million cubic meters. Annual mortality averaged 0.54 million cubic meters, which is 0.9% of inventory volume. Thirty-four percent of mortality is accounted for by oak species.

VOLUME OF LIVE TREES BY SPECIES,
MONONGAHELA NATIONAL FOREST, 2000



COMPONENTS OF ANNUAL CHANGE IN
GROWING-STOCK VOLUME

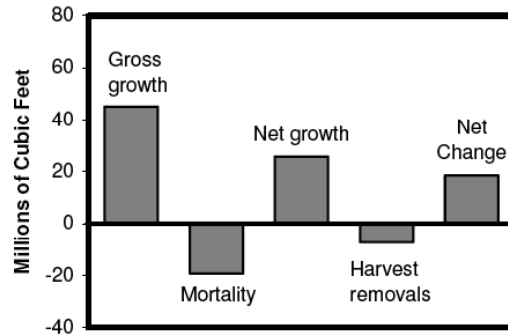


Figure 2-2: Interpretations of FIA Data from the Monongahela National Forest show forest status and changes (Widmann and Griffith, 2004)

Current Deposition Conditions

Historically, levels of acid deposition across the Eastern United States are higher than in other parts of the country. While the amendments to the Clean Air Act passed in 1990 decreased sulfate deposition, the MNF continues to receive elevated inputs of S and N (Figure 2-3). Within 300 kilometers of the MNF there are 311 coal-fired electric generating units, seven of which are among the top ten highest emitting SO₂ units in the United States as of 2003 (USDA Forest Service, 2006).

In 2006 the 1989 MNF Management Plan was revised. The revision process addressed “areas that are highly susceptible to impacts caused by acid deposition” and called to “develop management direction to address and minimize these impacts.” Therefore, the Forest Plan specifically states that, “Management actions that have the potential to contribute to soil nutrient depletion shall be evaluated for the potential effects of depletion in relation to on-site acid deposition conditions” (USDA Forest Service, 2006).

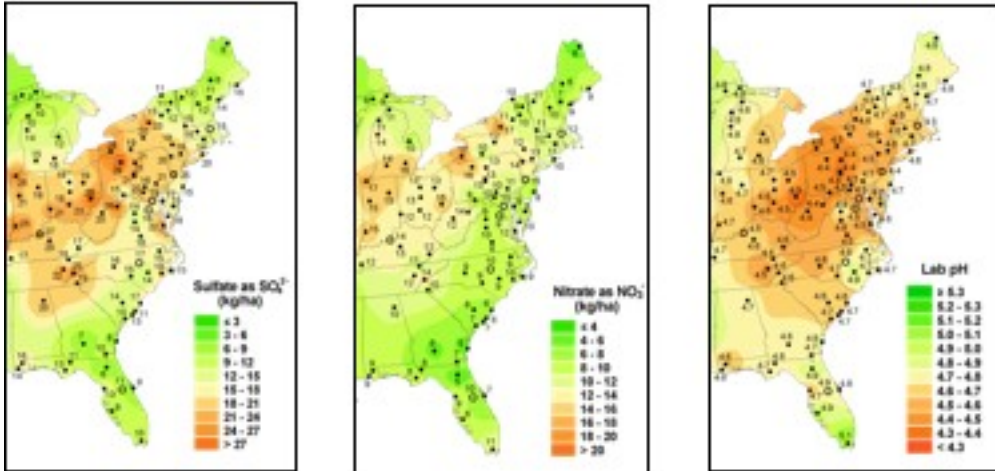


Figure 2-3: Sulfate, nitrate and pH data from 2006 for the Eastern United States, including the study site in Eastern West Virginia (National Atmospheric Deposition Program (NRSP-3), 2006)

Aquatic resources in the MNF are managed to mitigate the effects of acid deposition. Many aquatic fauna are sensitive to low pH levels (Webb, 2004); therefore, many streams in the MNF are limed to mitigate the effects of acid input (Connolly, 2006). The 2006 Forest Plan Revision mentions that soil liming may become a management objective and practice on the MNF (USDA Forest Service, 2006).

Tree Species Sensitive to Acid Deposition

In the central hardwood forest there is variation among tree species in response to acid deposition (Hicks, 1998). One of the most studied species is sugar maple, because AD is one of the abiotic factors causing its decline in the northeastern United States (Horsley *et al.*, 2002). In Quebec, reduced growth rates of sugar maple stands was correlated with soil acidity (Duchesne *et al.*, 2002). In a field-plot experiment Kobe *et al.* (2002) determined that loss of soil Ca may significantly decrease sugar maple canopy dominance within the next 125 years.

Other species also respond to AD, but may do so differently. Red maple mycorrhizal colonization and photosynthesis appear to be less affected by soil pH and base cations than sugar maple (St.Clair and Lynch, 2005). In experimental conditions northern red oak and tulip-poplar (*Liriodendron tulipifera* L.) responded differently to

varying Ca/Al soil ratios and N-additions (Decker and Boerner, 1997). Other species considered to be sensitive to acid deposition include Eastern white pine (*P. strobus* L.) and hickories (*Carya spp.*) (Hicks, 1998).

Managing for the effects of Acid Deposition

Since the adoption of the 1970 Clean Air Act stream water acid neutralizing capacity in the northeastern United States is still below baseline levels (Likens *et al.*, 1996; Driscoll *et al.*, 2001b), therefore many managers are considering treatment options to address this issue. Liming has become one of the most popular mitigation methods because of the positive response to this treatment (Horsley *et al.*, 2002). Sugar maple stands on the Lake Clair Watershed experimental station in Quebec responded to additions of limestone with up to a 90% increase in radial growth in a stand treated with 20 t ha⁻¹, dolomitic lime, compared to a control (Moore *et al.*, 2000). Ten years after these CaMg(CO₃)₂ applications, sugar maple health remained higher on treated than untreated plots; however, there were no detectable differences between rates of 0.5 t ha⁻¹ and 50 t ha⁻¹ (Moore and Ouimet, 2006).

In the central Appalachian region, soils and streams were limed to increase pH and moderate the effects of acid deposition on the landscape (Webb, 2004). The St. Mary's River watershed in Virginia has been subject to stream liming treatments since 1999. In this project, acid neutralizing capacity of the St. Mary's River increased from 0.3 µeq L⁻¹ in January 1999 to 35.4 µeq L⁻¹ in January 2000. Liming can also be combined with fertilization to replenish base cation resources. Sugar maple stands in Vermont were treated with fertilizer + lime (107 kg ha⁻¹ K, 53 kg ha⁻¹ Ca, 11 kg ha⁻¹ Mg, 3000 kg ha⁻¹ Ca(CO₃)₂) resulting in elevated soil pH and Ca, decreased soil Al, increased foliar K, Ca, and P, and less crown dieback (Wilmot *et al.*, 1996). In North Carolina soils, liming treatment showed net retention of applied Ca and Mg in upper soil horizons 23 years after treatment (Johnson *et al.*, 1995); however, long-term field trials on spruce/fir forests in Germany indicate that liming can have deleterious effects on forest ecosystems such as increased nitrification and increased heavy metal movement through the soil profile (Huettl and Zoettl, 1993). Therefore, researchers have experimented with the use of Ca fertilization. At the Hubbard Brook Experimental Forest a watershed was

treated with wollastonite (CaSiO_3) in 1999 at the rate of $0.85 \text{ Mgram Ca ha}^{-1}$. This resulted in increased organic horizon pH, increased foliar Ca, decreased foliar Mn, and improved sugar maple crown condition (Juice *et al.*, 2006).

Webb (2004) suggests that for the central Appalachian region the three options for mitigation are neutralization of surface water acidity by direct application of limestone, watershed-scale application of limestone or other base material, or incorporation of base-cation conservation strategies in forest management. Management practices, such as harvesting, can change the influence of AD on forest productivity and sustainability (Adams, 1999; Watmough and Dillon, 2003; Gress *et al.*, 2007).

Harvesting practices must be considered within the entire management approach in order to protect soil quality from degradation from impacts such as loss of bases and changes in response to increased N-input (Adams *et al.*, 1997; Burger and Kelting, 1999). Nutrients removed via harvesting increase as increased biomass is removed (Adams, 1999). Additionally, although short-term leaching losses will be higher for intensive single-entry harvests, over the whole rotation multi-entry harvests will remove more nutrients than single-entry systems. For example Ca removed through harvesting can range from around 200 kg ha^{-1} in a clearcut to almost 1000 kg ha^{-1} in multi-entry selective harvesting (Adams *et al.*, 2000). Using site-specific management to target areas with lower soil base cation content for either no or less-intensive harvesting, managers can meet sustainability goals. The effectiveness of various harvesting practices to sustain soils above critical acidity levels (i.e. above a pre-determined Ca/Al ratio) can be compared using observational and experimental studies and monitoring (Watmough and Dillon, 2003), and these results may be useful for achieving management objectives such as those outlined in the MNF Plan.

Research Gaps

There have been no documented losses of productivity on the MNF due to AD (Adams, 1999), but continued input, changes in stream chemistry and numerous researcher and forester observations of species changes and low-productivity stands has concerned land managers (USDA Forest Service, 2006). To address these concerns, managers must monitor for the effects of AD across the forest. However, there is no

agreement as to the most effective AD-specific monitoring method. Both the question of AD-related productivity losses as well as monitoring method are gaps in our knowledge and must be addressed to meet the guidelines specifically stated in the 2006 MNF plan.

III. Acid deposition effects on forest composition and growth on the Monongahela National Forest, West Virginia

Abstract

The northern and central Appalachian forests are subject to high levels of atmospheric acid deposition (AD), which has been shown in some forests to negatively impact forest growth as well as predispose the forest system to damage from secondary stresses. The purpose of this study was to determine if AD is affecting the composition and growth of the Monongahela National Forest. Soils adjacent to 30 Forest Inventory and Analysis (FIA) sites were sampled and analyzed for a suite of acidity indicators. These indicators were correlated with the periodic mean annual volume increment (PMAVI) of the forest stands on FIA plots for the 10 year period 1989 to 2000. Periodic mean annual volume increment ranged from -9.5 to $11.8 \text{ m}^3 \text{ ha}^{-1} \text{ yr}^{-1}$, suggesting lower-than-expected growth on two-thirds of the sites. In the surface horizon, effective base saturation (+), Ca concentration (+), base saturation (+), K concentration (+), Fe concentration (-), Ca/Al molar ratio (+), and Mg/Al molar ratio (+), were correlated with PMAVI ($p \leq 0.1$). In the subsurface horizon $\text{pH}_{(w)}$ (+), effective base saturation (+), Al concentration (-), and K concentration (-) were correlated with PMAVI. We hypothesized that NO_3/NH_4 ratio would also be correlated with PMAVI, but it was not. Correlations between soil chemical indicators and PMAVI suggest that AD may be part of the cause or play a role in the lower-than-expected forest growth on the Monongahela National Forest.

Introduction

Located in eastern West Virginia, the Monongahela National Forest (MNF) encompasses over 360,000 hectares of land. The forest is second and third growth, and maintains a high level of biological diversity, supporting 13% of the rare plant and animal species in West Virginia (USDA Forest Service, 2006). Situated only a few hours

from large urban centers and containing over 1200 kilometers of hiking trails, the MNF is a popular recreation destination, while still producing about 0.2 million cubic meters of timber annually (Widmann and Griffith, 2004).

The MNF lies at the confluence of the mixed mesophytic and oak-chestnut forest regions, with remnants of northern hardwoods at high elevations (Braun, 1950). Historically the mixed mesophytic forest was comprised of *Fagus grandifolia* Ehrh. (American beech), *Liriodendron tulipifera* L. (tulip-poplar), *Tilia americana* L. (American basswood), *Acer saccharum* Marsh. (sugar maple), *Castea dentata* Marsh. (American chestnut), *Aesculus flava* Aiton (buckeye), *Quercus rubra* L. (northern red oak), *Quercus alba* L. (white oak), and *Tsuga canadensis* L. (eastern hemlock). Along with the mixed mesophytic forest, the oak-chestnut forest has changed since the loss of American chestnut as a dominant species. It has since shifted towards white oak, tulip-poplar, *Quercus velutina* Lam. (black oak), *Quercus prinus* L. (chestnut oak), *Carya spp.* (hickories), *Nyssa sylvatica* Marsh. (blackgum), northern red oak and *Robinia pseudoacacia* L. (black locust) (Braun, 1950). Braun (1950) characterized the species composition of the northern hardwood forest as dominated by *Picea rubens* Sarg. (red spruce), sugar maple, American beech, American basswood, and *Betula alleghaniensis* Britton (yellow birch).

Historically, the average annual productivity of these second and third growth forests was around $2 \text{ m}^3\text{ha}^{-1}$ on poor sites, and over $7 \text{ m}^3\text{ha}^{-1}$ on excellent sites where management improves growth rate (Hicks, 1998). Some of the earliest growth data for oaks were gathered in upland even-aged stands in West Virginia before the widespread effects of chestnut blight and industrial pollutants influenced forest composition and growth. These measurements were taken mostly in the 1920's and 1930's on second-growth sprout stands across a wide range of site qualities in fully stocked stands (Schnur, 1937). Periodic mean annual volume increment ranged from 1.8 to $2.4 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ on poor and fair sites, 3.0 to $3.6 \text{ m}^3\text{ha}^{-1} \text{yr}^{-1}$ on average to good sites, and over $4.3 \text{ m}^3\text{ha}^{-1} \text{yr}^{-1}$ on excellent sites (Schnur, 1937). These growth rates were expected to plateau at age 50 and remain constant up to age 100. Stand disturbances, such as management practices, can influence and increase average annual growth rate. For example, growth rates five years after thinning on 65 year-old hardwood plots in West Virginia were over $5 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$

(Smith *et al.*, 1994). These documented growth rates provide a baseline against which current measurements can be compared.

Acid deposition (AD) results mainly from fossil fuel combustion, which produces sulfuric acid and nitrous oxides. Early in AD research, scientists were concerned about the direct effect of acidity on foliage, but this focus has since shifted to the acidification of soils (Van Ranst *et al.*, 2002). The effects on soil include base cation leaching, Al mobilization, and S and N accumulation (Driscoll *et al.*, 2001c). Increased N inputs on the stand may shift composition to nitrophilous species and those that can tolerate low soil Ca (Fenn *et al.*, 1998; Huntington *et al.*, 2000). Furthermore, scientists and forest managers are concerned that N saturation will leave forests susceptible to frost damage and other stresses such as insect infestation (McNulty *et al.*, 1996; Gress *et al.*, 2007).

Evidence for forest decline due, in part, to AD has been established for some species in some areas, especially red spruce at high elevations in the Northeastern United States and sugar maple in central and western Pennsylvania (Driscoll *et al.*, 2001c). Symptoms of decline include poor crown condition, reduced tree growth, and high levels of mortality (Driscoll *et al.*, 2001c). Red spruce suffers from both direct effects of AD, such as nutrient leaching from needles, as well as indirect effects such as elevated Al levels in soils (Godbold *et al.*, 1988; Schaberg *et al.*, 1997). Similarly, sugar maple decline, most often cited in the non-glaciated regions of the Allegheny Plateau of Pennsylvania, is reportedly related to soil acidification as well as other site factors (Horsley *et al.*, 2000; Bailey *et al.*, 2005). Northern red oak decline in western Pennsylvania has been associated with more acidic sites, suggesting that nutrient deficiency and Al toxicity may be stressing this species as well (Demchik and Sharpe, 2000). However, in the central Appalachians, there have been no published growth declines related to AD (Adams, 1999).

Soils data show changes due to AD. In Pennsylvania soil pH, and Ca and Mg concentrations decreased between 1967 and 1997 (Bailey *et al.*, 2005). Reductions in sulfate emissions as the result of the 1990 Clean Air Act Amendments reduced associated base cation leaching (Nodvin *et al.*, 1986; Harrison *et al.*, 1989). However, evidence of N saturation continues to be reported in both Europe and the United States (Fenn *et al.*, 1998; Houle *et al.*, 2006).

Systems that are most prone to N-saturation and nitrate leaching are characterized by high N deposition, high soil N stores and low soil C/N ratios (Fenn *et al.*, 1998). N-saturation may lower availability of Ca, P, or water within the plant as N limitations are removed (Gress *et al.*, 2007). Indicators of nitrification and acidification include soil C/N ratio below 20, base saturation below 20% and soil solution Ca/Al molar ratio below 1 (Reuss, 1983; Cronan and Grigal, 1995; Lyon and Sharpe, 1999; Aber *et al.*, 2003).

The MNF is situated down-wind from sources of sulfate and nitrate pollutants; therefore, when the Forest Management Plan was revised in 2006, the Forest Service set objectives to evaluate management actions “that have the potential to contribute to soil nutrient depletion,” specifically evaluating “for the potential effects of depletion in relation to on-site AD conditions” (USDA Forest Service, 2006). For example, a range of harvesting practices will have varying effects on site acidification (Adams *et al.*, 2000). Calcium removed through harvesting can range from around 200 kg ha⁻¹ in a clearcut to almost 1000 kg ha⁻¹ in multi-entry selective harvesting (Adams *et al.*, 2000).

Given the concern of forest managers over the potential deleterious effects of AD, our objectives were to: 1) determine if there was any evidence of AD-induced growth decline on the Forest, and 2) if decline occurred, determine the relationships with key soil indicators related to acidification. We hypothesized that mortality of acid-sensitive species would be higher and PMAVI would be less than expected during the interval 1989 to 2000 due to chronic input of AD. We predicted that pH, Ca/Al molar ratio, effective base saturation, NO₃/NH₄, and sum of bases could serve as indicators of forest change and growth decline.

Methods

Site Description

We used Forest Inventory and Analysis (FIA) plots to gather data along the range of site conditions of the Monongahela National Forest (MNF). The FIA program is a national monitoring network, with plots located across the country on all land usages (i.e. public, non-governmental, corporate, individual, Native American) (USDA Forest Service, 2007). Each plot is re-sampled every five years, so that within each state 20% of

the plots are measured each year. Ground-plot measurements are taken over three 0.017 ha plots arranged around another 0.017 ha center-plot. Data collected include tree diameter at breast height, total height, species, tree class, and any visible damage.

Stand Inventory

FIA data for West Virginia cycles 4 and 5 were downloaded from the Forest Service FIA DataMart webpage (available online at <http://fiatools.fs.fed.us/fiadb-downloads/fiadb3.html> [verified May 21, 2008]). The “TREE” data table was used for stand composition and productivity inventories. The FIA plot locations listed in the public data are only accurate to 1.6 km. Therefore, actual plot locations were obtained from FIA National Spatial Data Services of the Northern Research Station.

Stand measurements were grouped by species to compare changes in composition between 1989 and 2000. Basal area, periodic mean annual volume increment (PMAVI), and number of individuals were allocated among northern red oak, sugar maple, *Acer rubra* L. (red maple), hickories, *Betula spp.* (birches), American beech, tulip-poplar, red spruce, other oaks, other hardwoods and other conifers categories. These species groups were chosen in particular because of their hypothesized sensitivity to AD and their value as wildlife and timber species (Hicks, 1998). Mortality was calculated using total number of dead individuals on each plot summed across all the FIA plots on the MNF. For sites where the species did not exist no value was assigned.

Species turnover (ST) was calculated as a metric of compositional changes between two measurement periods. Values closer to 100% indicate more changes and values closer to 0% indicate smaller or no changes in species composition at each location. ST was calculated using the following equation (Holland, 1978):

$$ST = 100 * (\text{Sum of number of species unique to the first} + \text{unique to second samples}) / (1) \\ (\text{Total number of species found in first} + \text{second samples})$$

Across all the FIA sites on the MNF (Figure 3-1), PMAVI from 1989 and 2000 was determined using average annual growth values calculated in cubic meters per hectare per year ($\text{m}^3 \text{ha}^{-1}\text{yr}^{-1}$) by FIA for each individual tree.

In West Virginia, FIA growth is calculated using the following equations (Scott, 1981):

$$Volume = b_0 + b_1D^{b_2} + b_3D^{b_4}H^{b_5} \quad (2)$$

Where: b is a value estimated for each species,

D is diameter at breast height and H is bole length

$$Average\ annual\ growth = (V_2 - V_1)/(t_2 - t_1) \quad (3)$$

Where: v is volume (Scott, 1981)

t is time, year

Due to changes in FIA plot-arrangement between 1989 and 2000, subplot 1 contained the only re-measured trees between the two sampling periods. Therefore, average annual growth for each tree in subplot 1 was summed to calculate plot PMAVI. Estimates of stand basal area were calculated using individual tree basal area and summing all trees on the plot. Stands were considered adequately stocked if basal area was greater than $16 \text{ m}^2\text{ha}^{-1}$ and less than $46 \text{ m}^2\text{ha}^{-1}$ (Roach and Gingrich, 1968).

Outlying trees were removed from the FIA data set. Outliers had diameters above 45.7 cm, which was larger than the third quartile of the diameter data by over 1.5 times the interquartile range. These trees (95 of 1498) were anomalously large (remnant “wolf” trees from the previous cutting cycle) and did not represent the population of the average stands on the MNF.

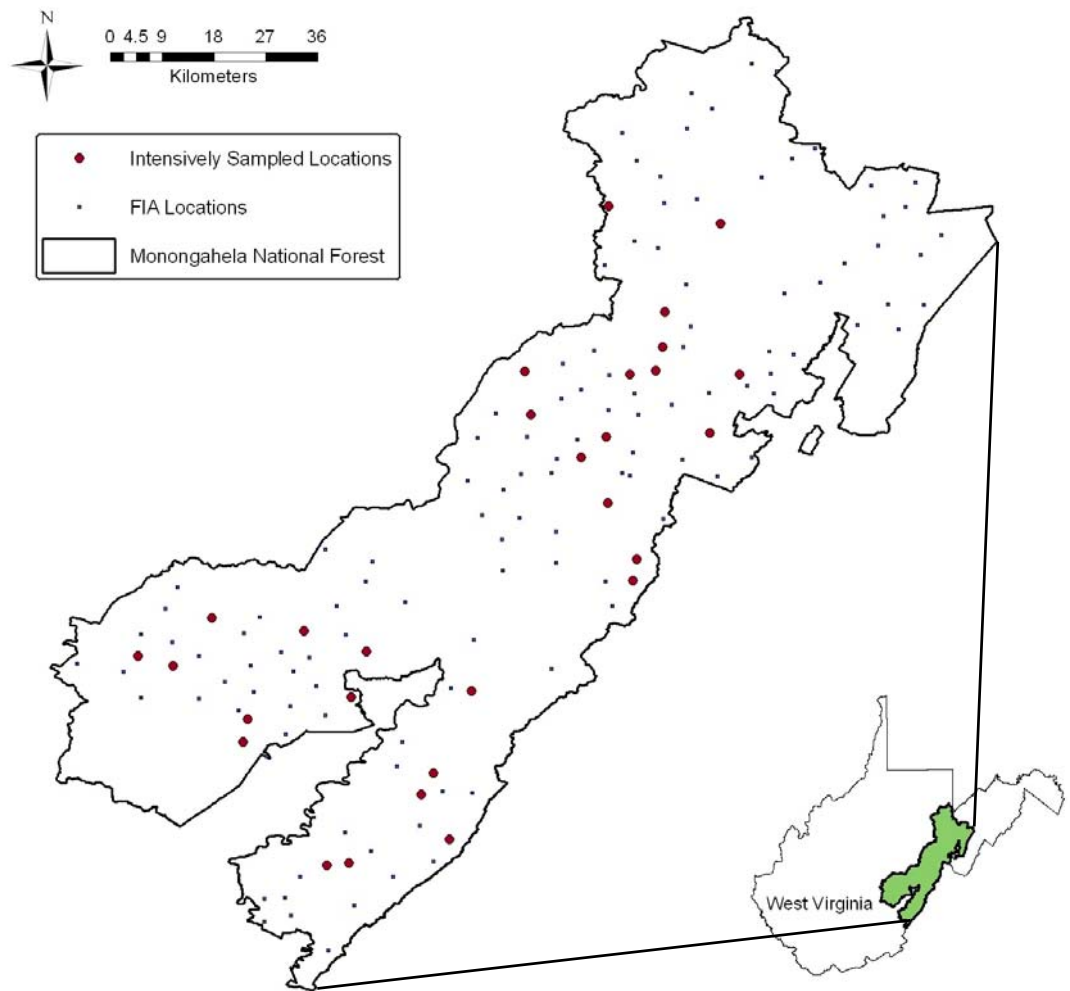


Figure 3-1: Approximate locations of Forest Inventory and Analysis (FIA) plots across the Monongahela National Forest. Highlighted plots were used for an intensive study of site and soil relationships.

Field Procedures

Stand data and soil samples were collected for 30 representative FIA plots across the MNF. Average stand age and site index were calculated using cores from three dominant or codominant trees adjacent to FIA plots. Height was sampled to the nearest 0.33 m using a reloscope. Increment cores were taken at 0.3 m above ground level. A total of 90 trees were sampled, of which 46% were northern red oak, 37% were *Prunus*

serotina Ehrh. (black cherry), 9% were *Quercus coccinea* Muenchh. (scarlet oak), 5% were chestnut oak, and 3% were white oak. Site index (SI) was calculated for each oak species and converted to northern red oak SI using equations from Hicks (1998). For black cherry stands, northern red oak SI was estimated using height and diameter at breast height (Lamson, 1987). Average stand age was calculated by counting the number of early-wood rings on each core. Average ages ranged from 31 years old to 94 years old. Stands in the central hardwoods region are expected to aggrade until age 170 (Hicks, 1998). All stand data were collected in November and December of 2007.

Soils were sampled by digging one narrow soil pit (to 1 m or bedrock) adjacent to each FIA site to determine depth of the master horizons. Representative samples from the A and B master horizons (hereafter surface and subsurface, respectively) from each pit as well as from sub-samples at azimuths of 60, 180, and 300 degrees from the center FIA plot were sampled between July 2006 and August 2007. Soil bulk density was also sampled at these locations using a soil core sampler (approximately 100 cm³) where possible; however, when rock fragment content impeded the core sampler, density was estimated by excavation (Page-Dumroese *et al.*, 1999). All samples used for soil chemical analysis were air-dried, sieved through 2-mm mesh and stored at room temperature until analysis.

Lab Procedures

Criteria for judging soil chemical change due to AD were soil acidity, soil fertility, potential toxicity level, N-saturation, and acid neutralization potential. We analyzed for selected indicators within each of these criteria: pH and exchangeable acidity are indicators of soil acidity, effective base saturation (EBS) is an indicator of soil fertility, Ca/Al molar ratio is an indicator of soil toxicity level, NO₃/NH₄ ratio and C/N ratio are indicators of N-saturation, and sum of bases is an indicator of soil neutralization potential related to cation exchange. Soil pH_(w) was determined using 10 grams of soil in 20 mL of distilled water (Thomas, 1996). Soil exchangeable cations were measured using three different extractants: 1 N NH₄OAc at pH 7, 0.01 M SrCl₂, 1 N NH₄Cl. Total cations were determined by exchanging with 1 N NH₄OAc at pH 7 (Thomas, 1996). Strontium chloride (0.01 M SrCl₂) was used to determine Ca/Al molar ratio (Joslin and

Wolfe, 1989; Sharpe, 2007, personal communication). The Sr-method as been used in the past because soil minerals have a greater selectivity for Sr than for monovalent cations, it is a quick one-step process, and it is considered to be an analytical surrogate for soil solution Ca/Al ratio (Edmeades and Clinton, 1981). Thirty mL of SrCl₂ were added to 10 grams of soil and shaken for 30 minutes. The mixture was centrifuged for 15 min and the supernatant was filtered through a #2 Whatman filter. Effective cation exchange capacity (ECEC) was determined by extraction using 1 N NH₄Cl (Amacher *et al.*, 1990). For each of these procedures, filtrate was refrigerated at 4 degrees C until elemental concentrations were determined using an Inductively Coupled Plasma spectrometer (ICP) (Vista-MIX CCD Simultaneous ICP, Varian, Walnut Creek, CA).

Extractable P was determined by the Bray 1 method (Bray and Kurtz, 1945). Additionally, extractable nutrients were determined using the Mehlich I buffer (Sims, 1996). Carbon values were determined using a C/N analyzer (Vario MAX CNS analyzer, Elementar, Hanau, Germany). Total N was measured on the C/N analyzer, and inorganic nitrate and ammonium were extracted with 2 M KCl (Mulvaney, 1996). Filtrate was refrigerated at 4 degrees C until nitrate and ammonium concentrations were determined by auto-analyzer (Traacs 2000 Analyzing System, Bran & Luebbe, Buffalo Grove, IL). Exchangeable acidity was determined by extraction with 1 N KCl (Bertsch and Bloom, 1996). Filtrate was then titrated with 0.01 N NaOH on a Radiometer Copenhagen auto-titrator using an ABU901 Autoburette, TIM900 Titration Manager.

All soil values were averaged for the three sub-samples for each master horizon. Total profile values were calculated using horizon depths and bulk densities. For concentration values determined through analysis on ICP or auto-analyzer, values below detection limits were assigned a zero.

Data Analysis

Stand and soil properties were correlated with PMAVI and considered significant at $p \leq 0.1$. Non-linear relationships with PMAVI were investigated and transformed for use in linear regression. Soil and site factors that were significantly correlated with PMAVI were used in a multiple regression to assign variation in growth. This data set was filtered for multicollinearity by removing variables with low variance decomposition

factors and high variance of inflation factors. Using the filtered data set, a model was chosen based on maximizing adjusted R-squared, significance of the model, and biological significance.

Other factors influencing stand volume

To evaluate the effects of AD on forest growth other sources of damage were considered and largely ruled-out as influential factors. There are forest pathogens on the MNF; however, most stands have coped with these factors for thousands of years and overall growth would still be around average historical levels (Johnson *et al.*, 1992). Wind and ice damage is common across the Appalachian mountains. These effects, which occur randomly across the forest, could be detected by large drops in basal area. Only 6 FIA plots lost more than 2 m²ha⁻¹ between the measurement periods, and none of these were used for the intensive soil-site study.

Results

Stand Inventory

On Forest Inventory and Analysis (FIA) plots, elevation ranged from 473 to 1386 m, slope ranged from 1 to 80 %, and the plots covered all aspects (Table 3-1). FIA plots were located in the Ridge and Valley and Allegheny Mountain provinces, where they received between 76 to 152 cm of pH 4.4 precipitation per year (National Atmospheric Deposition Program (NRSP-3), 2006; USDA Forest Service, 2006). The plots used for soil analysis were representative of all FIA plots on the Monongahela National Forest (MNF) (Table 3-1). Stocking estimates show that 29% of all plots and 10% of the soil-sampling plots were under stocked, 66% of all plots and 83% of soil-sampling plots were adequately stocked, and 5% of all plots and 7% of soil-sampling plots were over stocked. Periodic mean annual volume increment (PMAVI) ranged from -9.5 to 11.8 m³ha⁻¹yr⁻¹ on all FIA plots, and -9.5 to 6.2 m³ha⁻¹yr⁻¹ on the soil-sampling plots.

Table 3-1: Range of site and stand characteristics on Forest Inventory and Analysis (FIA) plots across the Monongahela National Forest (MNF) and a 30-plot subset used for soil sampling

	All FIA Plots on the MNF	Soil-Sampling Plots
Elevation	473 m to 1386 m	473 m to 1386 m
Slope	1% to 80%	1% to 73%
Aspect	4 deg to 351 deg	4 deg to 351 deg
Physiographic Region	Ridge and Valley Allegheny Mountains	Ridge and Valley Allegheny Mountains
Annual Precipitation	76 to 152 cm year ⁻¹	76 to 152 cm year ⁻¹
Precipitation Characteristics	pH ~ 4.4 SO ₄ ²⁻ ~ 20 to 26 kg ha ⁻¹ yr ⁻¹ NO ₃ ⁻ ~ 12 to 14 kg ha ⁻¹ yr ⁻¹	pH ~ 4.4 SO ₄ ²⁻ ~ 20 to 26 kg ha ⁻¹ yr ⁻¹ NO ₃ ⁻ ~ 12 to 14 kg ha ⁻¹ yr ⁻¹
Basal Area	0.15 m ² ha ⁻¹ to 59.1 m ² ha ⁻¹	12.4 m ² ha ⁻¹ to 57.0 m ² ha ⁻¹
Stocking	29% under stocked 66% adequately stocked 5% over stocked	10% under stocked 83% adequately stocked 7% over stocked
Volume Increment 1989-2000	-9.5 m ³ ha ⁻¹ yr ⁻¹ to 11.8 m ³ ha ⁻¹ yr ⁻¹	-9.5 m ³ ha ⁻¹ yr ⁻¹ to 6.2 m ³ ha ⁻¹ yr ⁻¹

Species Composition

Across all FIA plots on the MNF in 1989 oaks (15%), birches (13%), red maple (13%) and other hardwoods (15%) dominated the stands (Table 3-2). The birch and other-hardwoods categories contained the most dead individual trees, and birches, red spruce, hickories and tulip-poplar suffered over 9% mortality (the percent of individuals within a given species that was dead). In 2000 red maple (15%), birches (14%), and American beech (9%) predominantly occupied FIA sites. The birch and other-hardwoods categories contained the most dead trees, and hickories and birches were the species with the highest level of mortality.

From 1989 to 2000 basal area of red maple increased by 3.3% across FIA sites and basal area of northern red oak, other oaks, sugar maple, hickories, American beech, and other conifers declined. The number of individual red oak, other oaks, hickories, and

tulip-poplar also declined. The percent of each species that was dead increased from 1989 to 2000 for all species but tulip-poplar. In 2000 over 20% of all oaks, over 30% of hickories, over 15% of red spruce and almost 20% of birches were standing dead.

Due to variability across the 30 sites where soils were sampled, sample sizes for species comparisons were small (n = 10 plots with red oak, n = 13 plots with sugar maple, n = 19 plots with red maple, and n = 4 plots with hickories); however, these data allowed us to examine general trends. Hickories were the only species to significantly decline on sites with surface base saturation below 20% and surface effective base saturation below 2.5%. Percent dead northern red oak were highest on sites with surface Al concentrations above $43 \text{ cmol}_+ \text{ kg soil}^{-1}$. Species turnover rate was not statistically related to soil factors; however, there were more unique species in 2000 on sites with subsurface base saturation above 10%.

To further investigate trends in the relationship between species and stand changes with key indicators of soil acidity we grouped sites into classes showing decline (less than $0 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ of growth), stands growing at less-than-expected rates (0 to $3 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$) and stands growing at historically average rates (over $3 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$). Average species turnover and mortality were highest on declining stands and were lowest on stands growing at historically average rates (Table 3-3). Soil pH, an indicator of acidity, was lowest on stands with higher turnover rate and highest on stands with lower values. Calcium/aluminum ratio and sum of bases in the subsurface horizon were highest on stands with lower species turnover values. Surface horizon EBS was similar across all three growth groups. Nitrate/ammonium ratio, an indicator of N-saturation, was lowest on sites with lower species turnover values.

Table 3-2: Average composition and change across all Forest Inventory and Analysis plots in the Monongahela from 1989 to 2000.

	Basal Area (%)	Avg. Dia (cm)	Percent of Individuals	Mortality (% of all dead)	Mortality (% species dead)
1989					
N. red oak	10.4	30.5	8.2	6.9	4.8
Other oaks	16.8	25.1	15.7	7.4	4.4
Sugar maple	6.8	20.8	7.1	6.9	5.6
Red maple	10.7	22.7	12.8	6.4	3.1
Hickories	2.5	25.4	2.8	4.5	9.1
Birches	11.5	21.2	13.4	24.3	11.8
Am. beech	8.5	24.8	8.7	5.0	3.6
Tulip-poplar	5.6	32.8	4.3	6.9	9.3
Other hardwoods	14.5	25.2	15	13.9	-
Red spruce	5.2	28.3	4.7	9.4	11.9
Other conifers	7.5	26.0	7.3	8.4	-
2000					
N. red oak	9.5	28.8	4.7	3.4	10.4
Other oaks	13.5	22.2	11.2	9.7	12.2
Sugar maple	6.5	18.9	7.5	3.4	6.3
Red maple	14.0	21.3	15.4	6.3	5.7
Hickories	1.4	21.2	1.9	4.4	33.3
Birches	11.5	20.8	14.3	20.0	19.2
Am. beech	6.9	18.8	8.9	9.2	14.4
Tulip-poplar	5.6	32.4	2.2	14.6	9.1
Other hardwoods	17.4	21.0	19.2	17.4	-
Red spruce	6.6	21.2	5.7	6.3	15.5
Other conifers	7.1	26.2	9.0	5.3	-
Difference					
N. red oak	-0.9	-1.7	-3.5	-3.5	-
Other oaks	-3.3	-2.9	-4.5	2.3	-
Sugar maple	-0.3	-1.9	0.4	-3.5	-
Red maple	3.3	0.5	2.6	-0.1	-
Hickories	-1.1	-4.3	-0.9	-0.1	-
Birches	0.0	-0.4	0.9	-4.3	-
Am. beech	-1.6	-6.0	0.2	4.2	-
Tulip-poplar	0.0	-0.4	-2.1	7.7	-
Other hardwoods	2.9	-4.2	4.2	3.5	-
Red spruce	1.4	-7.1	1.0	-3.1	-
Other conifers	-0.4	0.2	1.7	-3.1	-

Table 3-3: Forest stand and soil properties arranged in PMAVI classes for intensively-sampled FIA plots

	Less than 0 m ³ ha ⁻¹ yr ⁻¹	Between 0 to 3 m ³ ha ⁻¹ yr ⁻¹	Over 3 m ³ ha ⁻¹ yr ⁻¹
Volume Increment Range	-9.5 to -0.04 m ³ ha ⁻¹ yr ⁻¹	0.03 to 2.9 m ³ ha ⁻¹ yr ⁻¹	3.0 to 6.2 m ³ ha ⁻¹ yr ⁻¹
Mortality (% of individuals that are dead)	10 to 30% Average: 18.5%	0 to 50% Average: 17 %	0 to 35.7 % Average: 10.7 %
Species Turnover Values	9 to 56% Average: 35%	7 to 55% Average: 29%	0 to 45% Average: 22%
Basal Area in 2000	16.7 to 57.0 m ² ha ⁻¹ Average: 31.8	12.6 to 37.3 m ² ha ⁻¹ Average: 23.8	12.4 to 43.2 m ² ha ⁻¹ Average: 27.0
Average pH	Surface: 3.7 Subsurface: 4.1	Surface: 3.8 Subsurface: 4.3	Surface: 3.9 Subsurface: 4.3
Average Ca/Al	Surface: 1.4 Subsurface: 0.31	Surface: 2.3 Subsurface: 0.35	Surface: 3.6 Subsurface: 0.55
Average EBS	Surface: 26% Subsurface: 13%	Surface: 27% Subsurface: 10%	Surface: 26% Subsurface: 10%
Average sum of bases (mol ₊ ha ⁻¹)	Surface: 14732 Subsurface: 31999	Surface: 8051 Subsurface: 36661	Surface: 19099 Subsurface: 43322
Average NO ₃ /NH ₄	Surface: 0.86 Subsurface: 0.56	Surface: 0.95 Subsurface: 0.38	Surface: 0.68 Subsurface: 0.55

Periodic Mean Annual Volume Increment 1989 to 2000

Periodic mean annual volume increment for all FIA plots between 1989 and 2000 ranged from -9.5 to 11.8 m³ha⁻¹yr⁻¹ (Figure 3-2). On 30 sampled plots, PMAVI was negatively correlated with basal area in 2000 ($p = 0.075$) (Figure 3-3), was non-linearly and negatively correlated with age ($p = 0.053$) (Figure 3-4) and was not correlated with site index (Figure 3-5). Basal area, site index, and stand age were not correlated amongst one another. On the FIA sites, 29% of the plots had a negative PMAVI, 40% had PMAVI from 0 to 2.9 m³ha⁻¹yr⁻¹, and 31% had PMAVI over 3 m³ha⁻¹yr⁻¹. Based on historical data an average PMAVI of 3 m³ha⁻¹yr⁻¹ can be expected on sites of average and excellent quality in West Virginia (Schnur, 1937).

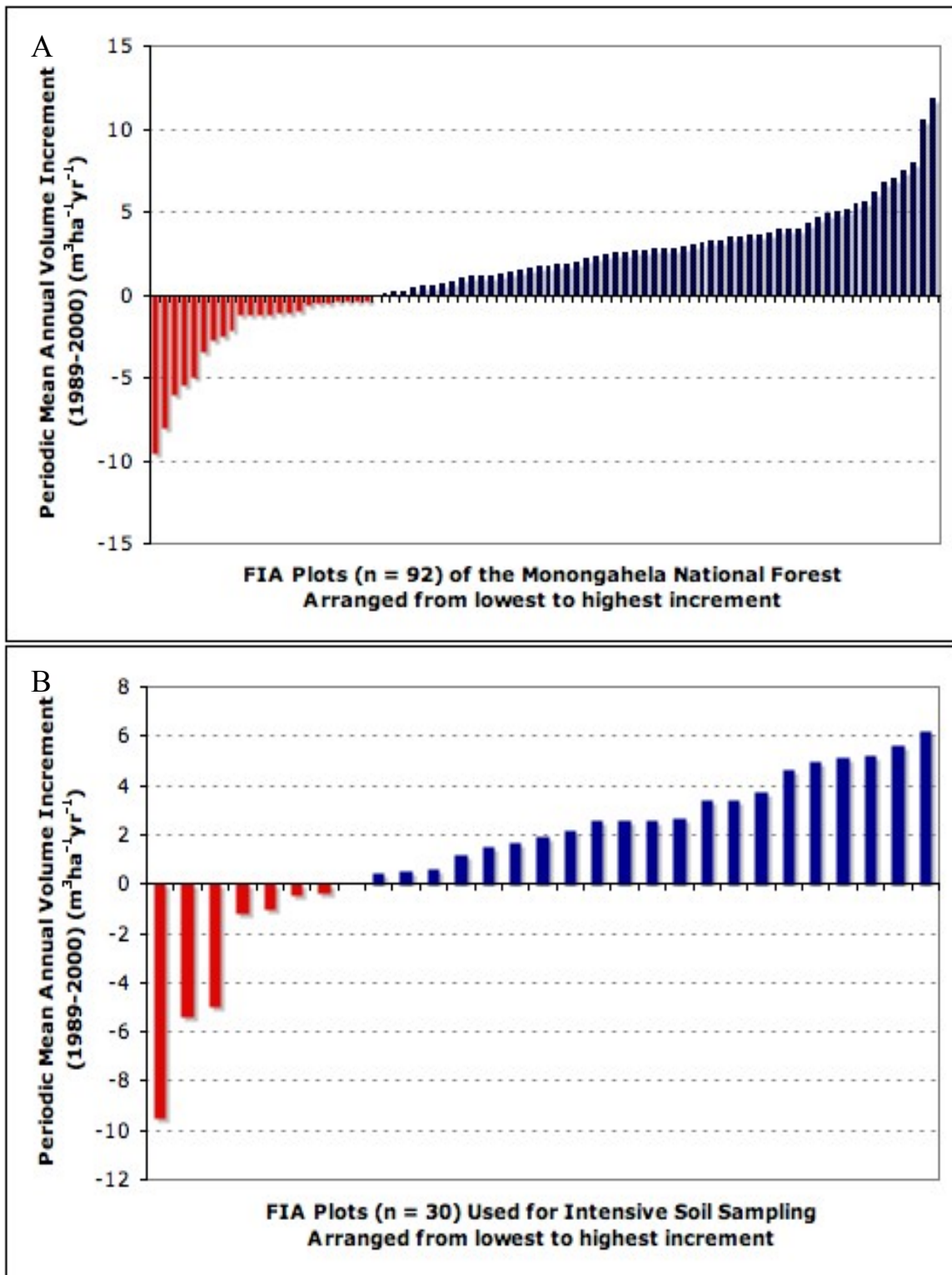


Figure 3-2: Periodic mean annual volume increment (PMAVI) on Forest Inventory and Analysis (FIA) plots between 1989 and 2000 for A) all plots on the Monongahela National Forest B) and for plots used in an intensive soil-study

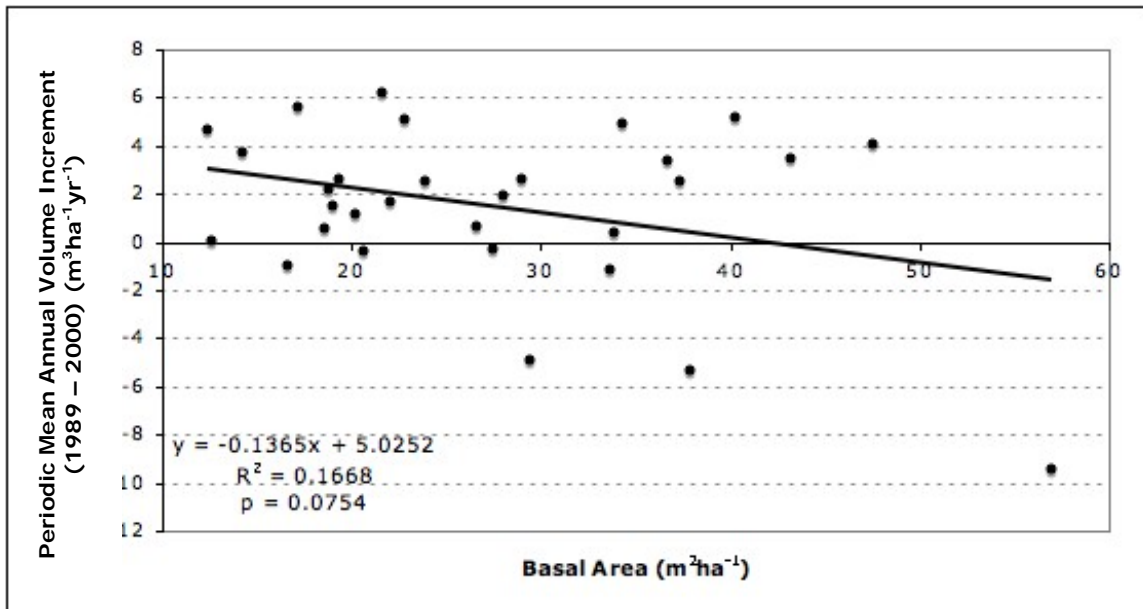


Figure 3-3: Periodic mean annual volume increment as a function of stand basal area in 2000

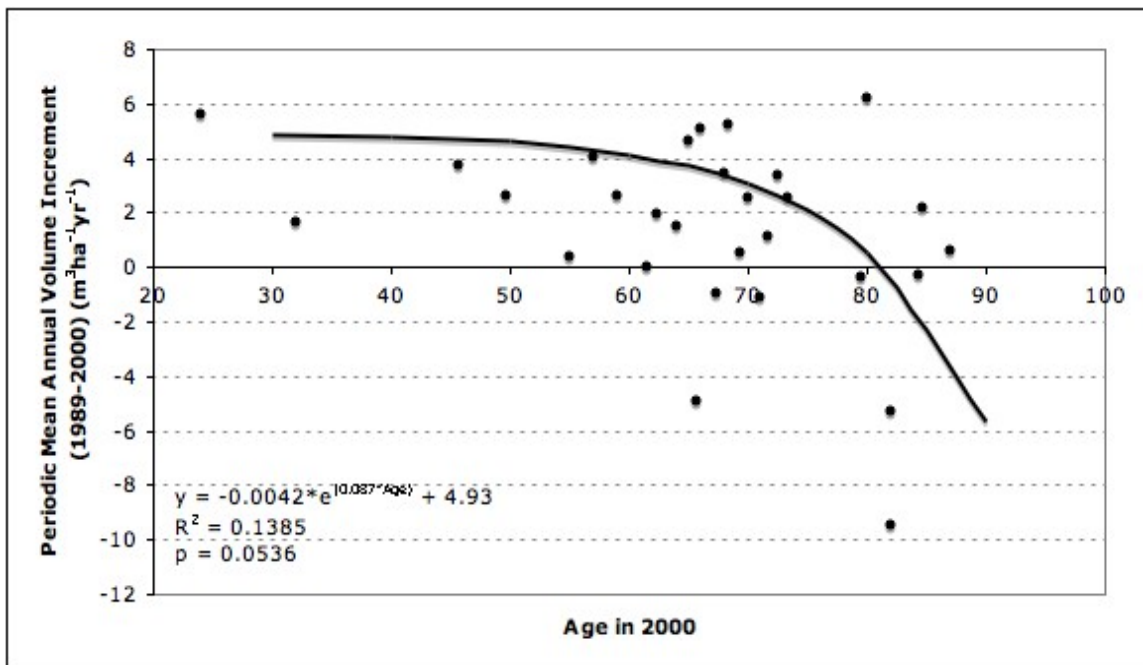


Figure 3-4: Periodic mean annual volume increment as a function of stand age

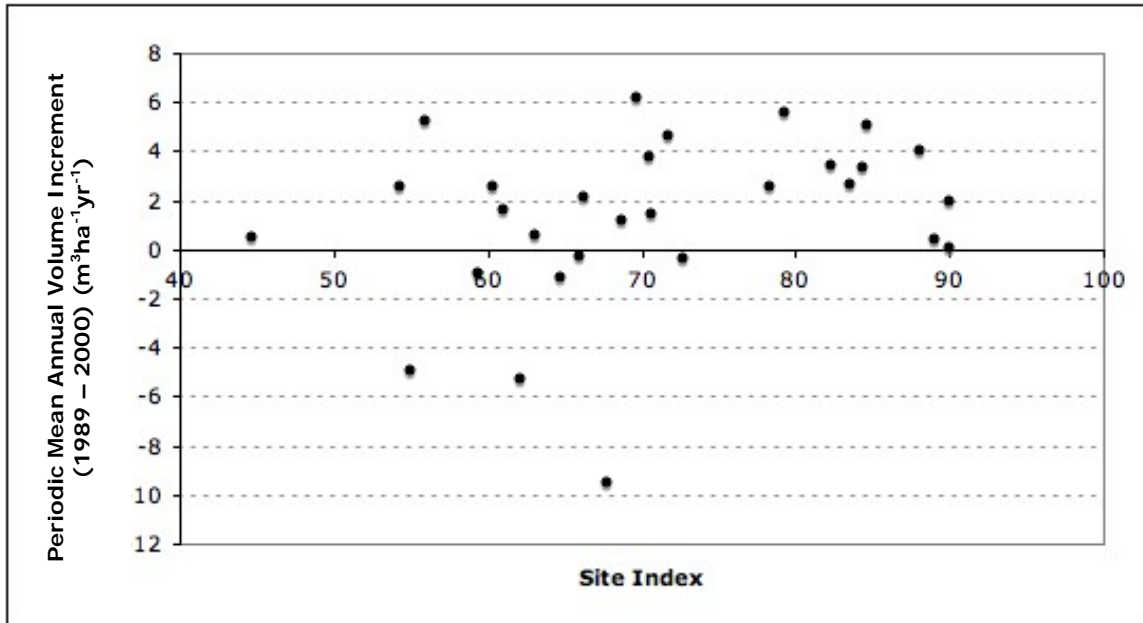


Figure 3-5: Periodic mean annual volume increment as a function of site index

Soil Indicators

Periodic mean annual volume increment was correlated with soil chemical properties considered to be potential acidity indicators (Table 3-4; Table 3-5). Effective base saturation ranged from 5 to 77% and 2 to 28 % in the surface and subsurface horizons respectively, and was significantly correlated with PMAVI in the surface horizon. In the surface horizon Ca concentrations from NH_4Cl exchange, NH_4OAc exchange, Mehlich I extraction, and SrCl_2 exchange were also correlated with PMAVI. Additionally, surface horizon K concentration from NH_4OAc and SrCl_2 exchange and Mehlich I Fe and P concentrations were significantly correlated with PMAVI. Calcium/aluminum molar ratios ranged from 0.17 to 10.2 in the surface horizon, and were significantly correlated with PMAVI (Table 3-4). In the subsurface horizon Ca/Al ratio ranged from 0.09 to 2.2, but was not significantly correlated with PMAVI.

The C/N values ranged from 7.3 to 28.9 for the surface horizon and 6.2 to 34.7 for the subsurface horizon. These values were not significantly correlated with PMAVI. The C/N ratio on 77 % and 87 % of plots was below 20 in the surface horizon and subsurface horizons, respectively. Values for surface and subsurface soil pH ranged from 3.3 to 4.9 and 3.7 to 4.7, respectively. These pH values were significantly correlated with

PMAVI for the subsurface horizon. Exchangeable acidity was not significantly correlated with PMAVI. The ratio of KCl-exchangeable NO_3/NH_4 was not correlated with PMAVI for either the surface or subsurface horizons.

Modeling Growth

We modeled PMAVI as a function of stand and soil factors, to further understand their combined effects on forest growth. All stand and soil factors that were significantly correlated with PMAVI, as well as those hypothesized to influence growth were included as potential variables in the model. The variable screening process, which identified multicollinearity and redundancy and retained the independent and significant correlations, removed all NH_4OAc results, Mehlich I Ca concentration, and NH_4Cl Ca concentration from the modeling process. The remaining soil factors were C/N ratio, pH, exchangeable acidity, and NO_3/NH_4 ratio of both horizons, Fe, P, Ca concentration and Ca/Al ratio of the surface horizon, and Al, effective base saturation and effective cation exchange capacity of the subsurface horizon. From these factors, only those significant enough to enter or remain during selection processes (forwards, backwards, stepwise, max R^2) were included in the model. Due to the relationship between site index and the Ca/Al molar ratio of the surface horizon (Figure 3-6), and the fact that PMAVI was not significantly correlated with site index, the only stand factors used in the regression model were basal area and age.

The first model iteration using all independent stand and soil factors was:

$$PMAVI = 1.2 - 1.8(\ln Ca/Al_{surface}) + 0.14(-0.004 e^{0.09(Age)} + 4.9) + \quad (4)$$

$$0.007Ca_{surface} - 0.06Ex.Acidity_{surface} + 0.03C/N_{subsurface} - 0.07BA$$

The total R^2 for this model was 0.4180, the adjusted- R^2 was 0.2592 and the p-value was 0.0444. To further improve model significance and simplicity we created a second iteration model. The second model iteration was (Table 3-6):

$$PMAVI = 0.6 + 2.2(\ln Ca/Al_{surface}) + 0.18(-0.004 e^{0.09(Age)} + 4.9) - \quad (5)$$

$$0.73(\text{NO}_3/\text{NH}_4_{subsurface})$$

Table 3-4: Descriptive statistics and results of soil sampling from 30 FIA study plots. Significance with periodic mean annual volume increment indicated by: ***: $p \leq 0.01$, **: $p \leq 0.05$, *: $p \leq 0.1$, else there is no significant relationship.

Soil Factor, Level of significance	Min	Max	Mean	Standard Error
<i>Surface Horizon</i>				
<u>Acidity</u>				
pH	3.29	4.90	3.81	0.074
Exchangeable Acidity (cmol ₍₊₎ kg soil ⁻¹)	1.179	19.476	6.40	0.747
<u>Toxicity</u>				
Ca/Al ratio***	0.170	10.2	2.55	0.427
Ca _{SrCl2} (cmol ₍₊₎ kg soil ⁻¹)**	0.137	2.18	0.580	0.082
Al _{SrCl2} (cmol ₍₊₎ kg soil ⁻¹)	0.094	0.805	0.301	0.036
<u>Fertility</u>				
Effective Base Saturation _{NH4Cl} (%)*	4.8	77	26	2.7
ECEC _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	2.3	22	8.4	0.8
Al _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	11.8	103	46.2	3.87
Mn _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.00	1.41	0.470	0.081
Ca _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)**	0.132	3.60	1.48	0.171
K _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.08	0.538	0.284	0.016
Mg _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.008	0.081	0.036	0.003
Na _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.069	0.411	0.168	0.015
Fe _{Mehlich} (mg kg soil ⁻¹)*	22.3	251	103	10.5
P _{Mehlich} (mg kg soil ⁻¹)	2	18	6.4	0.78
<u>N-saturation</u>				
C/N ratio	7.32	29.0	17.4	0.950
Carbon (%)	0.5	17.0	3.7	0.63
Nitrogen (%)	0.03	1.0	0.22	0.04
NO ₃ /NH ₄ ratio	0.008	3.54	0.840	0.178
NO ₃ (mg kg soil ⁻¹)	0.12	62.4	12.7	2.7
NH ₄ (mg kg soil ⁻¹)	4.9	122.7	21.7	4.5
<u>Neutralization</u>				
Base Saturation _{NH4OAc} (%)*	8.30	73.1	27.4	2.86
Sum of bases _{NH4OAc} (mol ₊ ha ⁻¹)	2603	41811	13219	2073

Soil Factor, Level of significance	Min	Max	Mean	Standard Error
<i>Subsurface Horizon</i>				
<u>Acidity</u>				
pH**	3.68	4.70	4.24	0.048
Exchangeable Acidity (cmol ₍₊₎ kg soil ⁻¹)	1.28	12.3	5.49	0.518
<u>Toxicity</u>				
Ca/Al molar ratio	0.087	2.19	0.42	0.083
Ca _{SiCl2} (cmol ₍₊₎ kg soil ⁻¹)	0.018	1.19	0.142	0.040
Al _{SiCl2} (cmol ₍₊₎ kg soil ⁻¹)	0.049	0.737	0.287	0.028
<u>Fertility</u>				
Effective Base Saturation _{NH4Cl} (%)	2.2	28.5	10.9	1.2
ECEC _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	1.5	12.9	6.1	0.53
Al _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)**	15.2	85.7	43.1	3.44
Mn _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.00	1.06	0.102	0.039
Ca _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.052	2.17	0.305	0.074
K _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.049	0.200	0.105	0.008
Mg _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.004	0.094	0.013	0.003
Na _{NH4Cl} (cmol ₍₊₎ kg soil ⁻¹)	0.059	0.413	0.167	0.013
Fe _{Mehlich} (mg kg soil ⁻¹)	26.4	284	72.8	10.8
P _{Mehlich} (mg kg soil ⁻¹)	2	14	2.4	0.4
<u>N-saturation</u>				
C/N ratio	6.23	34.7	17.6	1.04
Carbon (%)	0.62	19.1	4.4	0.61
Nitrogen (%)	0.03	1.0	0.26	0.03
NO ₃ /NH ₄ ratio	0.001	1.72	0.486	0.095
NO ₃ (mg kg soil ⁻¹)	0.02	112.3	26.9	6.3
NH ₄ (mg kg soil ⁻¹)	4.5	170.4	55.9	8.9
<u>Neutralization</u>				
Base Saturation _{NH4OAc} (%)	4.3	39.6	15.0	1.79
Sum of bases _{NH4OAc} (mol ₊ ha ⁻¹)	7763	98526	37636	3936

Table 3-5: Correlation coefficients among stand factors and hypothesized soil indicators of acidity. Bold values are significantly correlated ($p < 0.1$). V is periodic mean annual volume increment; SI is site index; BA is basal area.

	V	SI	BA	Age	Surface pH	Subsurf. pH	Surface NO ₃ /NH ₄	Subsurf. NO ₃ /NH ₄	Surface Ca (SrCl ₂)	Surface Ca/Al	Surface Mg/Al	Subsurf. Ca/Al	Surface Fe (Mehlich)	Surface C/N	Subsurf. C/N	Surface Ex. Acidity	Subsurf. Ex. Acidity	Surface EBS	Subsurf. EBS
V	1	0.3435	-0.069	-0.3684	0.1816	0.0765	-0.0802	-0.0499	0.3606	0.3755	0.2363	0.1695	-0.1313	0.0017	-0.0312	-0.1728	0.0529	0.2132	-0.0916
SI		1	0.0636	0.2883	0.0484	-0.0764	0.1687	0.0852	0.0999	0.3764	0.089	0.2127	0.003	-0.2896	-0.2806	-0.1417	-0.0214	0.2137	0.0981
BA			1	-0.0498	-0.4395	-0.3354	-0.0545	0.1009	0.2914	0.0188	-0.1815	0.0776	0.0632	0.098	-0.1518	0.4156	0.514	-0.1286	-0.1320
Age				1	-0.0313	-0.0281	-0.0907	0.0511	0.0766	0.0479	-0.0772	-0.1022	-0.2984	0.2571	0.1469	0.0326	0.1299	0.1623	0.0942
Surface pH					1	0.5708	-0.2626	-0.3084	-0.0361	0.2799	0.1824	0.423	-0.2684	-0.0928	-0.0734	-0.3981	-0.3939	0.4547	0.5781
Subsurface pH						1	-0.2624	-0.4118	0.0801	0.0826	0.1416	0.3842	-0.1478	0.0267	-0.0785	0.1016	-0.2153	0.1075	0.3568
Surface NO ₃ /NH ₄							1	0.5489	-0.067	-0.0752	-0.2481	0.0999	0.1271	-0.4373	-0.4417	-0.0108	-0.0948	-0.0620	-0.0740
Subsurface NO ₃ /NH ₄								1	0.1168	0.1399	-0.0615	0.2872	0.1651	-0.4834	-0.505	-0.0123	0.1862	0.0517	-0.0939
Surface Ca (SrCl ₂)									1	0.5723	0.295	0.3113	-0.2306	-0.2305	-0.2986	0.254	0.5846	0.3885	-0.0476
Surface Ca/Al										1	0.7271	0.4206	-0.2802	-0.3702	-0.2938	-0.3341	0.2138	0.8200	0.1627
Surface Mg/Al											1	0.1973	-0.3667	-0.129	0.1722	-0.3678	0.0376	0.5675	0.2338
Subsurface Ca/Al												1	-0.0305	-0.4174	-0.6105	0.1012	0.0014	0.1564	0.4684
Surface Fe													1	-0.2154	-0.2682	0.1579	-0.0398	-0.2448	-0.1571
Surface C/N														1	0.7937	0.1049	-0.0027	-0.2954	-0.2777
Subsurface C/N															1	-0.145	-0.1192	-0.1577	-0.1888
Surface Ex. Acidity																1	0.6322	-0.6050	-0.3854
Subsurface Ex. Acidity																	1	-0.1928	-0.6054
Surface EBS																		1	0.3938
Subsurface EBS																			1

The factors in the final model were Ca/Al ratio of the surface horizon, stand age, and NO_3/NH_4 ratio of the subsurface horizon. The model R^2 was 0.4070, adjusted R^2 was 0.3328 and the p-value was 0.0051. After using several regression analysis techniques including stepwise, forward, backward, max R^2 , this model consistently provided the highest level of significance and the highest R^2 values. The Ca/Al molar ratio of the surface horizon alone accounted for over 30% of the variation in PMAVI (Figure 3-7). Other soil factors not included in the model were individually correlated with PMAVI and they could serve as acidity indicators; however, they did not account for additional independent variation in PMAVI in the multiple regression models, or they were covariate with other factors in the model. For example, effective base saturation was highly correlated with Ca/Al ratio and C/N ratio was correlated with NO_3/NH_4 (Table 3-5).

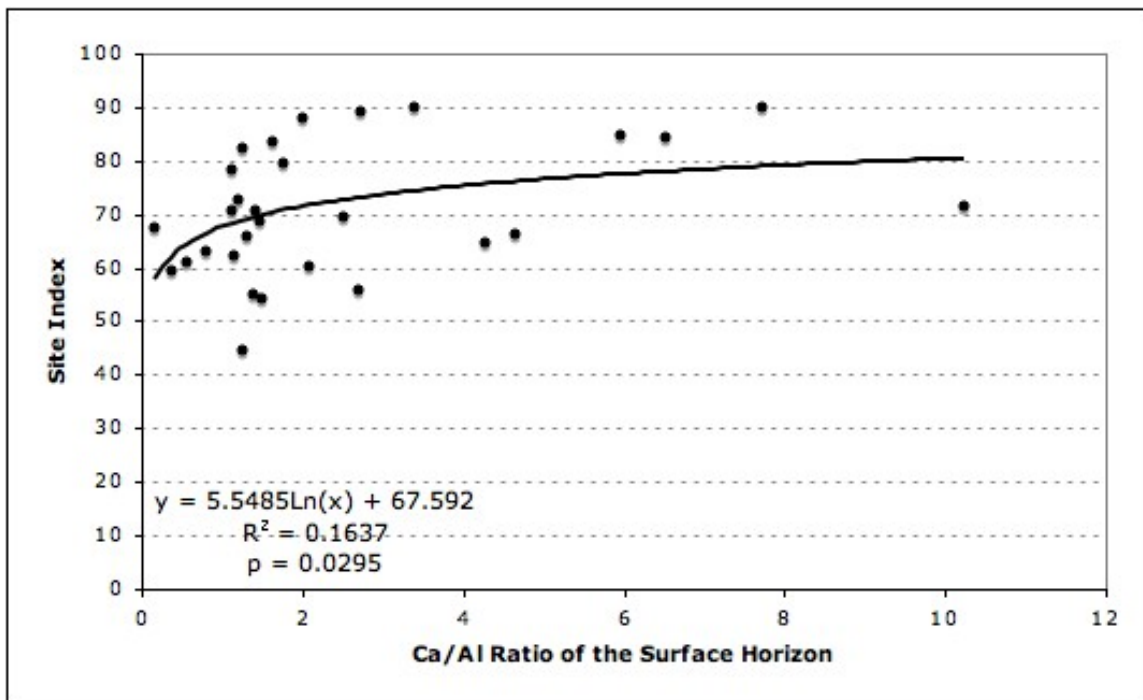


Figure 3-6: Site Index as a function of surface Ca/Al molar ratio on FIA plots

Table 3-6: Site and soil factors in regression model predicting periodic mean annual volume increment on FIA plots

Model: $0.60119 + 2.20299\ln(\text{Ca}/\text{Al}) + 0.17949(-0.00416 * e^{0.09(A)} + 4.9274) - 0.72899N$				
Factor	Coefficient Value	Standardized Coefficient	Partial R ²	Total R ²
Ca/Al: Ca/Al molar ratio of the surface horizon	2.20299	0.53968	0.3270	0.3270
A: Stand age	0.17949	0.27339	0.0703	0.3973
N: NO ₃ /NH ₄ ratio of the subsurface horizon	-0.72899	-0.09947	0.0096	0.4070
Model p = 0.0051; Adj-R ² = 0.3328				

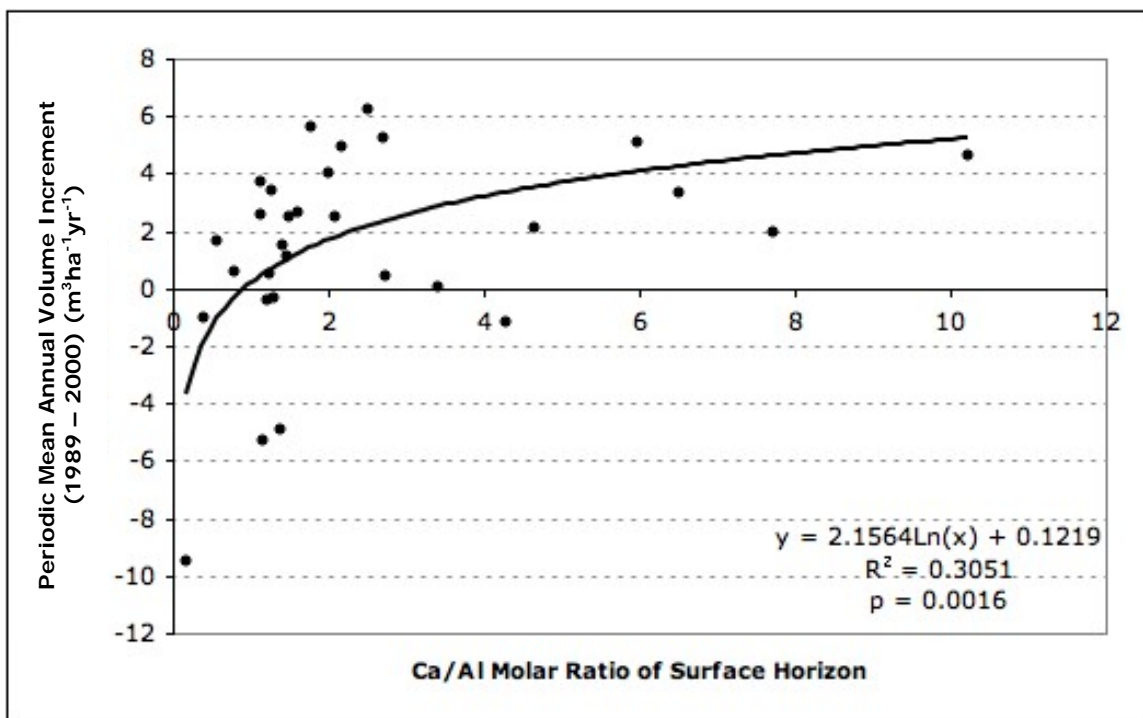


Figure 3-7: Relationship between periodic mean annual volume increment and a key indicator of soil acidification on FIA plots

Acid Neutralization Potential

Soil acid neutralization and buffering mechanisms vary with soil properties such as base saturation, mineralogy, and texture as well as with pH (Bache, 1980a). A generally accepted scheme for soil buffering begins with carbonate buffering, then moves to silicate buffering, followed by cation buffering, Al buffering, and ending with Fe

buffering (Ulrich, 1980). The current soil pH across our plots on the MNF indicates that cation and Al buffering are the dominant acid neutralization processes. We estimated the acid neutralization potential (ANP_{CEC}) produced by base cation buffering. To do so, we multiplied the effective cation exchange capacity times effective base saturation of the total soil depth to a root-limiting layer.

Although this calculation does not include changes in CEC due to weathering, or the possibility of buffering from fragments larger than 2 mm, these calculations provide a comparative range of neutralization potential on the MNF. ANP_{CEC} ranged from 22 to 314 kmoles charge ha^{-1} (Figure 3-8). Assuming 18 $kg\ ha^{-1}yr^{-1}$ of SO_4^{2-} deposition, 12 $kg\ ha^{-1}yr^{-1}$ of NO_3^- deposition, 2.5 $kg\ ha^{-1}yr^{-1}$ of NH_4^+ deposition, 100% nitrification, 50% S retention, and 50% N retention (Adams *et al.*, 1997; Aber *et al.*, 2003) about 0.3 kmoles of negative charge per hectare will leach through the forest soil each year. Therefore, based on this calculation, the least buffered sites will be depleted of ANP_{CEC} within 75 years.

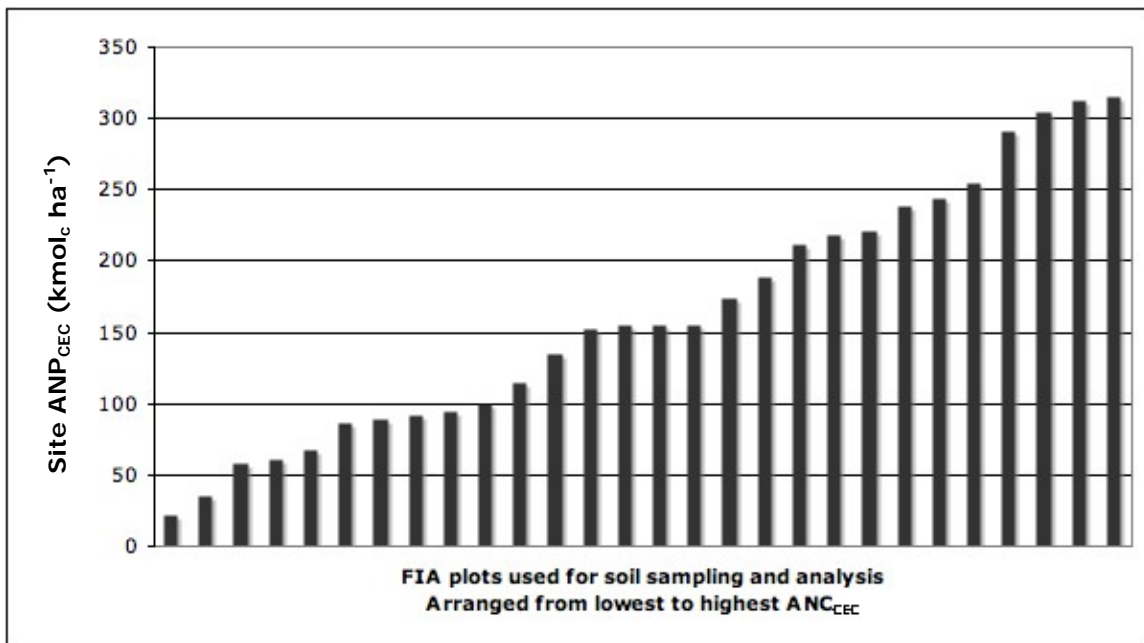


Figure 3-8: Range of estimated Acid Neutralization Potential by cation exchange buffering of intensively-sampled FIA plots

Discussion

We hypothesized that northern red oak, sugar maple, and hickories would decline across FIA sites due to their relatively greater sensitivity to AD, while red maple would increase across the sites. As predicted, basal area of northern red oak, other oaks, sugar maple and hickories dropped from 1989 to 2000. We had not predicted the changes in American beech, but it also declined. Some decline could be due to pathogens and diseases such as beech bark disease, which does occur on the Monongahela National Forest (MNF) (Juergens, 2008); however, previous studies have shown that AD may contribute to site susceptibility to insect damage (Driscoll *et al.*, 2001c). The high mortality of hickories (from 9.1% dead to 33.3% dead) was predicted, and may provide further support for the hypothesis that these species are sensitive to acidification (Hicks, 1998). Changes in hickory composition and hickory mortality may be a useful AD indicator in the central hardwoods region. The dominance of oaks also decreased from 24% to 13%, indicating that these species may be negatively impacted by stress factors compounded by acidification.

Investigating species changes among growth classes (less than $0 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$, 0 to $3 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$, and over $3 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$) showed general trends in relation to soil factors. The declining class (less than $0 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$) had the highest percent of dead individuals, lowest average soil pH values in the surface and subsurface horizons, and the highest average species turnover rates. To further discern the relationship between species changes and soil acidity a larger data set would be needed.

We did not predict the negative relationship between periodic mean annual volume increment (PMAVI) and stand age, given the relatively young age of the stands. This relationship may indicate that tree growth is slowing prematurely. Yield of upland oaks has been positively correlated with age at least through 100 years (Schnur, 1937); however, the chronic nature of AD, in combination with other stresses, may be causing early aging or decline. At these ages, stand dynamics such as stem exclusion may influence individual stem growth. If stand dynamics were the main factor driving PMAVI on these fully stocked stands, then the overall average plot PMAVI would be both positive across the whole forest, and would be closer to average historical values of over $3 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$.

Basal area ranged from 12.4 to 57 m²ha⁻¹, and was weakly correlated with PMAVI. Periodic mean annual volume increment and site index were not related, suggesting that decline is irrespective of site quality. There may be a variety of factors decoupling PMAVI and site index. First, site index values are based on models created with growth data from the early 20th century. The assumptions for factors determining tree growth at that time may not be valid in current conditions. Second, site index models are based on height and age, whereas volume is additionally influenced by diameter. At the age of many of these stands, diameter changes will influence PMAVI more than height change. Furthermore, site index is primarily a gradient related to water availability; however, the acidity of precipitation may counter the otherwise positive effects of mesic conditions. Therefore, the PMAVI of stands in this study may be equally influenced by AD-related stress regardless of initial stand quality. Site index was positively correlated with Ca/Al molar ratio. This relationship suggests that the chronic influence of AD could possibly influence growth on the MNF more than site factors known to influence site index. This is supported by the fact that the Ca/Al ratio accounts for 30% of the variability in PMAVI and is correlated with many other soil acidity indicators.

As hypothesized, the Ca/Al molar ratio of the surface horizon was the soil indicator most related to growth and was correlated with other stand and soil factors, including: site index (+), Ca concentration (+), Mg/Al molar ratio (+), subsurface Ca/Al molar ratio (+), Fe concentration (-), C/N ratio of the surface horizon (-), and effective base saturation of both horizons (+). The Ca/Al ratio, therefore, was the most important factor in our multivariate modeling, and may be the best overall indicator of AD effects.

Effective base saturation below 20% indicates that Al will dominate exchange complexes and soil solution (Reuss, 1983). EBS of the surface horizon ranged from 5 to 77% and from 2 to 28% in the subsurface soil, suggesting that Al dominates the exchange sites on the soils of many FIA plots. Sites where surface horizon base saturation was below 20% and Ca/Al ratio was below 1.0 were considered to be at the highest risk for decline (Connolly *et al.*, 2007). Of our 30 plots, four fit this risk criterion. Forty percent of the plots had base saturation values below 20% in the surface horizon.

By itself, NO_3/NH_4 ratio was not significantly correlated with PMAVI; however, this factor was included in the final multivariate model of growth. Increased nitrate levels are probably due to increased nitrification on sites receiving N input above demand. The negative relationship between NO_3/NH_4 ratio and PMAVI shows that stands with more nitrate are growing at slower rates, or even declining. This relationship suggests that N saturation may be negatively influencing stand growth on the Monongahela National Forest (MNF). Additionally, soil C/N ratio values below 20 indicate N saturation (Fenn *et al.*, 1998). Carbon/nitrogen values ranged from 7.3 to 28.9 for the surface horizon and 6.2 to 34.7 for the subsurface horizon. The C/N ratio was below the N-saturation criterion for surface soils on 77% of plots and on 87% of plots for subsurface horizons. These data suggest that some, but not all, of these plots have reached stage 3 of N-saturation, where excess N may become polluting and cause productivity declines (Aber *et al.*, 1989).

It appears the MNF is between the N-fertilization and N-saturation stages hypothesized by Aber *et al.* (1989). There are some symptoms of N-fertilization on the MNF including sites where base saturation is above 20% and sites where productivity is at or above historical levels of PMAVI (Schnur, 1937). However, growth decline, species changes, depressed base saturation and C/N ratios, and elevated Al concentrations may signify a problem on some sites across the forest. Phosphorus concentration by Mehlich I and Bray I extractions was not correlated with PMAVI, suggesting that the stands have not reached the P limitations hypothesized to occur after Ca limitations have been exceeded as a result of AD and N-saturation (Adams, 1999).

Cation exchange-acid neutralization potential values and Fe concentration were positively correlated with PMAVI. These results suggest that while cation buffering is still important in the system, Al and Fe buffering are probably important mechanisms which are contributing to acid neutralization. Although there were no different relationships among PMAVI and soil nutrient content rather than concentration, these values vary widely across the forest, and management practices affecting nutrient extraction should be site-specific.

We hypothesized that surface and subsurface horizon values would be equally indicative of productivity. While more soil factors of the surface horizon were correlated

with PMAVI, our final productivity model included Ca/Al of the surface horizon, NO₃/NH₄ ratio of the subsurface horizon, as well as stand age. Final model selection was based on maximizing adjusted R-squared, significance of the model, and biological significance. The most significant model included a factor from both the surface and subsurface horizons, which supports the hypothesis that sampling the full depth of both horizons is important in understanding soil chemical status and its relationship with forest growth.

Conclusions

Low periodic mean annual volume increment (PMAVI) values from 1989 and 2000 on some Forest Inventory and Analysis plots suggest that sustainable growth on some parts of the Monongahela National Forest (MNF) may be threatened. Alterations in species composition and levels of key indicators of soil acidity support the hypothesis that AD may be playing a role within the context of other environmental changes such as introduction of non-native species, forest pathogens, climate change, and changes in management activity. The negative relationship between PMAVI and stand age may signify early aging of the hardwood stands on the MNF. Furthermore, the relationship between growth and site index has been decoupled; there was no relationship between PMAVI and site index. Site index and Ca/Al ratio were positively correlated, and the Ca/Al molar ratio of the surface horizon was positively correlated with average stand growth. Calcium/aluminum molar ratio is the most useful indicator in detecting the effects of AD, and is a critical indicator of potential toxicity due to Al mobilization from AD. Effective base saturation, an indicator of site fertility, was also correlated with periodic mean annual volume increment. N-saturation indicators, such as NO₃/NH₄ ratio and C/N ratio, suggest that some stands in the MNF may be approaching N-saturation. The potential for soil cation exchange to neutralize further acidification ranges greatly across the forest, but could be reached in as little as 75 years on the least buffered sites.

While it is difficult to determine cause and effect relationships between forest changes and AD, it is possible to draw a logical conclusion that the two are related if the data show consistency in time and space, if there are plausible mechanisms or linked

processes, and if it is possible to replicate the symptoms in controlled environments (Johnson *et al.*, 1992). In this study, below-historical PMAVI is a symptom of a possible AD effect exhibited across the MNF to varying degrees. This symptom is consistently related to indicators of soil acidification, and not site quality or stocking. It is plausible that the influence of AD creates a scenario in which loss of bases and N-saturation either directly affect growth rates due to changes in nutrient resources, or leave the system susceptible to secondary stresses. Our soil criteria, acidity, potential toxicity, fertility, N-saturation, and potential neutralization addressed a wide range of possible soil mechanisms through which growth could be adversely affected. We determined that indicators representing these criteria were related to PMAVI. Studies in controlled environments as well as historical soil chemistry comparisons have shown that there are relationships between soil acidification and tree growth (i.e. Decker and Boerner, 1997; Bailey *et al.*, 2004).

These results have implications for site-specific forestry, where adaptive management processes and monitoring programs can be used for continued evaluation of AD effects. While there may be other causative factors related to the range in growth observed in this study, such as forest pathogens or other environmental stress factors (although none were observed or recorded in the historical record), the negative impact of these stresses, if they occurred, could be aggravated by acidification; therefore, we recommend that the MNF consider AD effects in site specific-management.

IV. Adaptive Management for Maintaining Productivity on Acidified Sites on the Monongahela National Forest

Abstract

The Monongahela National Forest in eastern West Virginia is subject to high levels of atmospheric acid deposition (AD), which has been shown to negatively impact forest growth by altering nutrient cycles and by predisposing the forest to decline from secondary stresses. To meet forest management objectives, managers must monitor for the effects of acidification and adapt their prescriptions and practices to ensure sustainable forest growth. The objective of this study was to develop an AD resistance map for forest managers to use as a tool in their adaptive management process. Five site factors hypothesized to determine resistance to acid deposition were combined in a single index of resistance and mapped across the forest. These site factors were: aspect, elevation, soil depth, texture, and parent material. Resistance index (RI) was correlated with key soil indicators of acidity-induced decline on 28 sites across the forest. There was a significant ($p \leq 0.1$) positive correlation between periodic mean annual volume increment for the period 1989 to 2000 and RI. A resistance index map was created for the Monongahela National Forest; 14% of area was found to be highly resistant ($RI \geq 0.7$), 57% was moderately resistant ($0.7 > RI > 0.45$) and 29% was slightly resistant ($RI \leq 0.45$). Acid deposition resistance maps can be used to plan monitoring programs and prescribe land-management practices.

Introduction

The Monongahela National Forest (MNF), located in Eastern West Virginia, encompasses approximately 360,000 hectares of land. The current forest is second and third growth, and it maintains a high-level of biological diversity, supporting 13% of the rare plant and animal species in West Virginia (USDA Forest Service, 2006). Situated only a few hours from large urban centers and containing over 1200 kilometers of hiking

trails, the MNF is a popular recreation destination, while still producing about 0.2 million cubic meters of timber annually (Widmann and Griffith, 2004).

The MNF covers part of the Ridge and Valley and Allegheny Mountains provinces of the Appalachian Region. It receives between 76 and 152 cm of rain per year. The pH of the precipitation is about 4.4, and about 20 kg of sulfate per hectare and 12 kg of nitrate per hectare are deposited per year. Elevation ranges from below 400 m to above 1400 m.

The Forest is situated down-wind from sources of sulfate and nitrate pollutants; therefore, when the MNF Management Plan was revised in 2006, the Forest Service set objectives to evaluate management actions “that have the potential to contribute to soil nutrient depletion,” specifically evaluating “for the potential effects of depletion in relation to on-site acid deposition conditions”(USDA Forest Service, 2006).

Acid deposition results mainly from fossil fuel combustion, which produces sulfuric acid and nitrous oxides. This pollutant alters elemental reactions with terrestrial and aquatic ecosystems and threatens productivity through soil base cation leaching, Al mobilization, and sulfur and N accumulation (Driscoll *et al.*, 2001c). There is a growing body of evidence that AD has induced forest productivity losses (Likens *et al.*, 1996; Schaberg *et al.*, 1997; Horsley *et al.*, 2000). Furthermore, management practices, such as harvesting, can change the influence of AD on forest productivity and sustainability by exacerbating base depletion (Adams, 1999; Watmough and Dillon, 2003; Gress *et al.*, 2007). In order to protect soil quality from impacts such as accelerated loss of base cations, harvesting practices must be considered within the entire management approach (Adams *et al.*, 1997; Burger and Kelting, 1999). The effectiveness of various management practices to sustain soils above critical acidity levels (e.g. above a pre-determined Ca:Al ratio) can be determined using experimental studies and monitoring (Watmough and Dillon, 2003) and the results can be used to adapt management guidelines for the national forest.

To effectively practice adaptive management, foresters must address each piece of the process (Figure 4-1). After defining the goals of sustainable forest management, such as management for potential negative effects of AD, data bases are used to develop best management practices guidelines. Monitoring these practices for

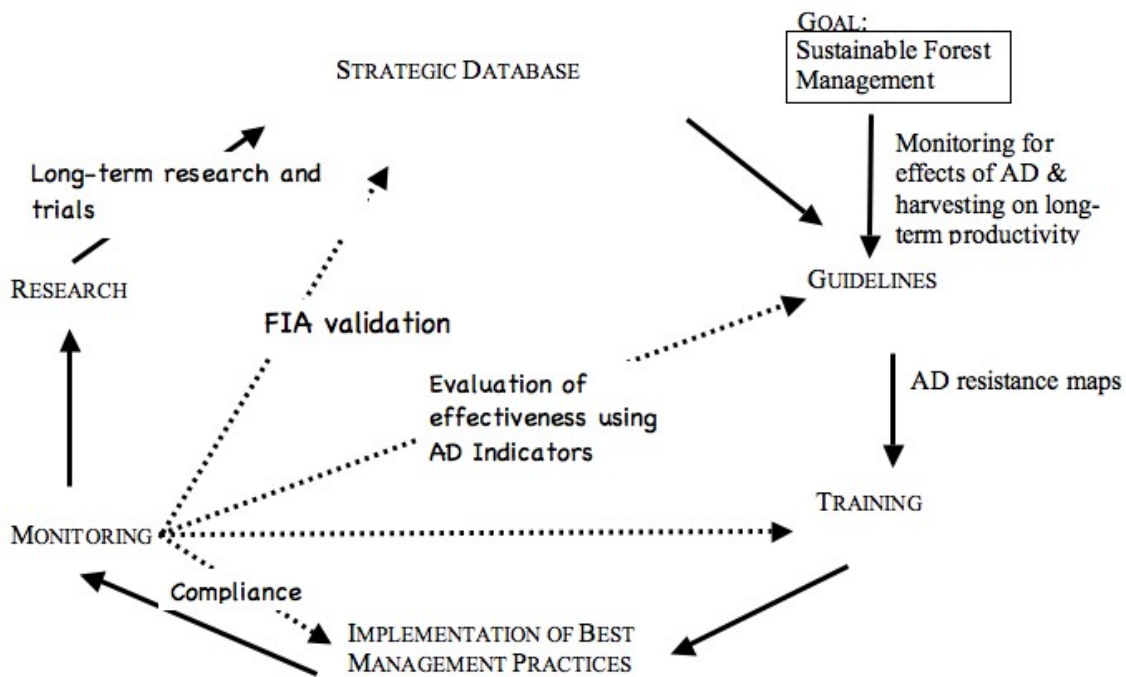


Figure 4-1: Basic process of adaptive management (Adapted from: Heninger *et al.*, 1997).

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both compliance and effectiveness is needed to ensure that sustainability goals are being met, and to modify management practices if needed. Ultimately, FIA data and long-term research data from the Fernow Experimental Forest could be used to validate the strategic database. A preliminary step for applying guidelines is to understand the spatial distribution of resistance to productivity losses due to acidification and harvesting.

Approaches to mapping site sensitivity or resistance to acid deposition vary, ranging from site characterization (i.e. Kuylenstierna *et al.*, 1995) to meteorological modeling (i.e. Langner *et al.*, 1995). In applying the ecological site factors approach, the most commonly used characteristics include bedrock parent material, soil type, land cover, and moisture regime (Tao and Feng, 2000). Commonly, these characteristics are reclassified into categories, which are then given a weight to produce a relative scale of

sensitivity or resistance (Kuylenstierna *et al.*, 1995). The process of creating relative scales or index tools involves three main steps: indicator selection, indicator interpretation, and integration into an index (Andrews *et al.*, 2004). These tools are designed so that they can be modified and updated as new data become available through monitoring and research, which are integral aspects of adaptive management (Chadwick and Kuylenstierna, 1991; Andrews *et al.*, 2004) (Figure 4-1).

To practice adaptive management, forest managers must use monitoring to ensure that best management practices are applied (compliance) and then determine if they are approaching the desired outcome (effectiveness). Proposed monitoring methods for assessing the effects of AD and effectiveness of best management practices are as varied as the publications reporting the problem; however, there is some consensus regarding the critical components of a monitoring program. These include: 1) existence of baseline data/historical record; 2) selection of indicators of change/damage with sufficient signal-to-noise ratio; 3) selection of sustainability criteria; 4) applicability over large areas and ability to be anticipatory; 4) discriminatory between natural changes and management; and 5) provide services with minimal environmental impact while being cost-effective (Adams *et al.*, 2000; Arp *et al.*, 2001; White, 2004).

A spatial analysis of site resistance to loss in productivity due to acidification would provide managers a starting point for implementing guidelines and developing best management practices across a large range of site and soil characteristics. Therefore, to meet the objectives of the MNF plan, our objectives were to create a spatial land-management tool designed to assess resistance to acid deposition and base removals via harvesting. We hypothesized that sites on the MNF were more resistant to productivity losses due to acidification and base depletion as parent material became more calcareous, slopes became steeper, approaching northeast aspects, and as elevation decreased, and if soil on the site was of mixed mineralogy, was deeper, was moderately-fine in texture, and had a lower amount of rock fragments. Also, we predicted that these soil and site factors could be combined to create a resistance index (RI), which would be related to key soil indicators of AD that could be used to monitor sustainable forestry as a part of a forest-wide adaptive management program.

Methods

Research and Development

The overall approach for developing meaningful acid deposition (AD) resistance maps required the following five steps: 1) develop known or hypothesized relationships between AD resistance and mappable site and soil factors; 2) apply resistance relationships to calculate a 0 to 1 score for each site factor; create a general model by equally weighting each site factor score for a general resistance index (RI_{general}); and then testing the model with a validation factor (in this case periodic mean annual volume increment (PMAVI)); 3) generate a precise resistance index (RI_{MNF}) based on weighted site factor scores; which is used to create a map of resistance across the Monongahela National Forest (MNF); and 4) select AD indicators for monitoring the effectiveness of the adaptive management guidelines to attain the goal of sustainable forest management.

Hypothesized Resistance Relationships (Step 1)

We created AD resistance relationships for parent material, slope, aspect, elevation, soil mineralogy, depth, texture, and rock fragments. Resistance relationships or curves were scaled from 0 to 1, where 0 was least resistant and 1 was most resistant to growth losses due to AD (Table 4-1; Figure 4-2). Curves were developed based on published relationships and expert knowledge to encompass the range of each factor found on the MNF.

Parent material is one of the most fundamental site characteristics related to acid-neutralization (Johnson, 1984). Geologic material is considered to be more resistant to productivity losses due to acidification if it is more calcareous, providing buffering capacity and more nutrients to the soil system (Johnson *et al.*, 1982a; Johnson, 1984; Lucas and Cowell, 1984). Current AD sensitivity maps of the MNF classify geology with trace amounts of buffering material as highly sensitive, while geology with substantial amounts of buffering material are classified as low sensitivity (Connolly *et al.*, 2007). The parent material types on the MNF were scaled from 0 to 1 to provide relative resistance for each lithology (Table 4-1; Table 4-2).

In West Virginia sites with northeast aspect are more productive due to decreased moisture losses as the result of decreased solar radiation (Auchmoody and Smith, 1979) and increased soil depth on northeast facing sites. Cooler sites will generally be more productive; therefore, more of the N deposited on the system will be biologically-absorbed and will be less likely to create conditions associated with N-saturation (Fenn *et al.*, 1998). Therefore, we hypothesize that northeast aspects are most resistant to acid deposition (Table 4-1).

Table 4-1: Range of site factors used to create Resistance Index

Factor	Range of Characteristics & Resistance:				
	0				1
Parent Material [‡]	Acidic				Calcareous
Slope	Resistance = $-0.00005x^2 + 0.0055x * 2.7$				
Aspect	235 - 286	197 - 234/ 285 - 325	145 - 196/ 326 - 15	107 - 144/ 16 - 55	56 - 106
Elevation	Resistance = $-0.0005 * e^{0.005x} + 1$				
Mineralogy	Siliceous				Mixed
Depth	Resistance = $1.3 * e^{-55/(x + 0.0001)}$				
Rock Fragments	Resistance = $-0.0175 * e^{0.045x} + 1.015$				
Texture	Resistance = $-0.001x^2 + 0.06x$				

[‡] Table 4-2

We hypothesized that steeper slopes would be less likely to become acidified due to increased runoff, and, therefore, decreased leaching (Fenn *et al.*, 1998) (Table 4-1; Figure 4-2). Similarly, the chronic and cumulative effect of leaching would be mitigated on deeper soils, which we hypothesize to be more resistant (Reuss and Johnson, 1986). The soil is the first geologic acid-sink, and kinetically the most active (Johnson, 1984), and the potential to buffer acidity is expected to be highest when the soil is deeper than 100 cm and lowest when the soil is shallower than 25 cm (Lucas and Cowell, 1984) (Table 4-1; Figure 4-2).

Higher elevation sites are more susceptible to acidification for a variety of reasons. These sites receive more acidic deposition, are prone to shorter growing seasons, are more likely to receive AD as fog, they are more susceptible to soil freezing events (Van Miegroet *et al.*, 1992; Fenn *et al.*, 1998; Driscoll *et al.*, 2001c; Fitzhugh *et al.*, 2003). Therefore, we hypothesized that resistance would decrease at an increasing rate along the elevational gradient (Table 4-1; Figure 4-2).

We hypothesized that increasing rock fragment content in a soil profile will decrease resistance to acidification because this volume decreases the soil fine earth fraction largely responsible for soil buffering (Table 4-1; Figure 4-2).

Table 4-2: Geology resistance numbers


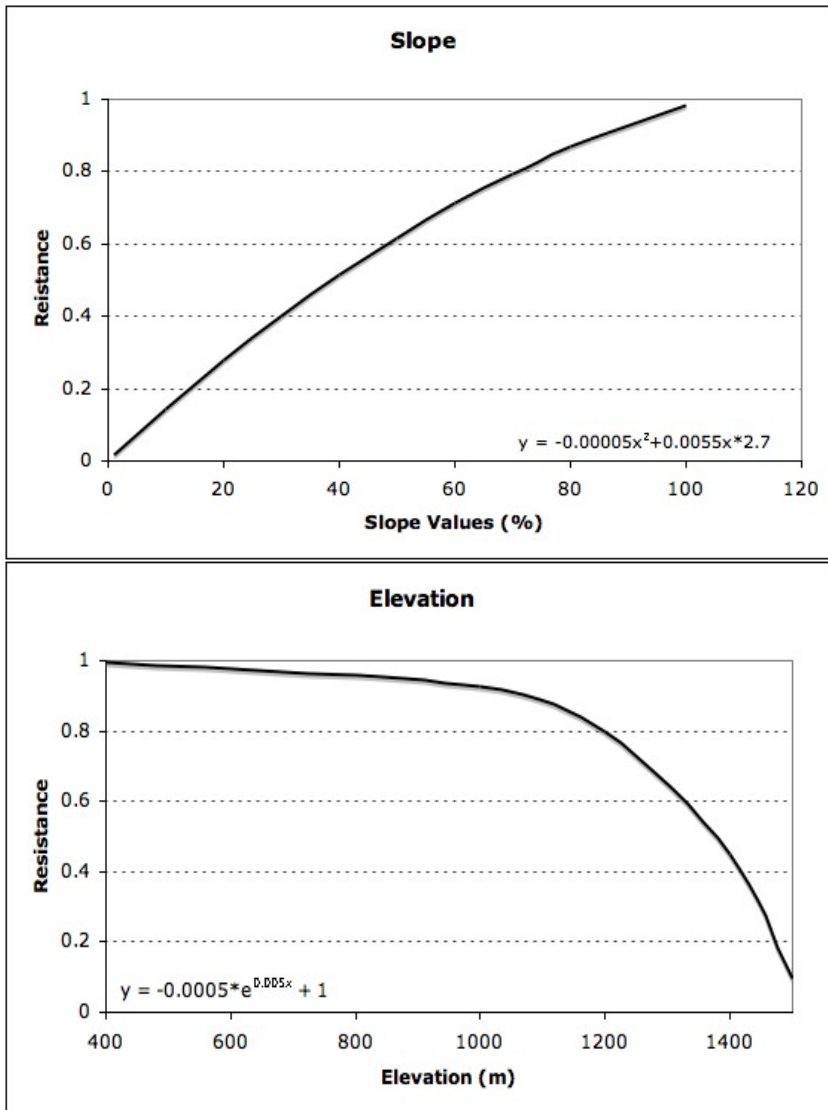
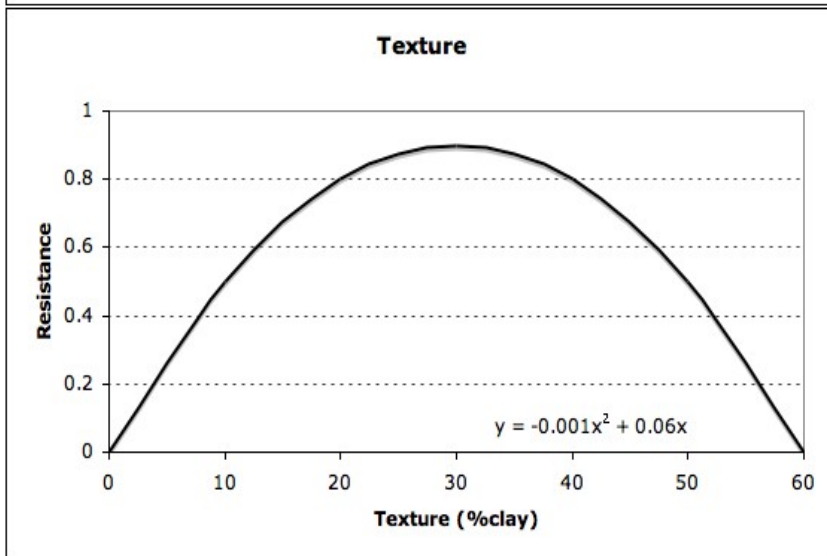
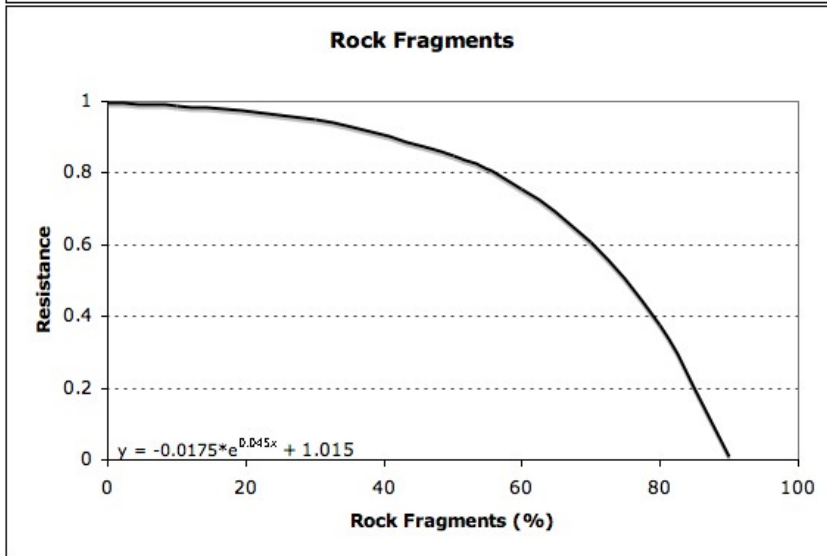
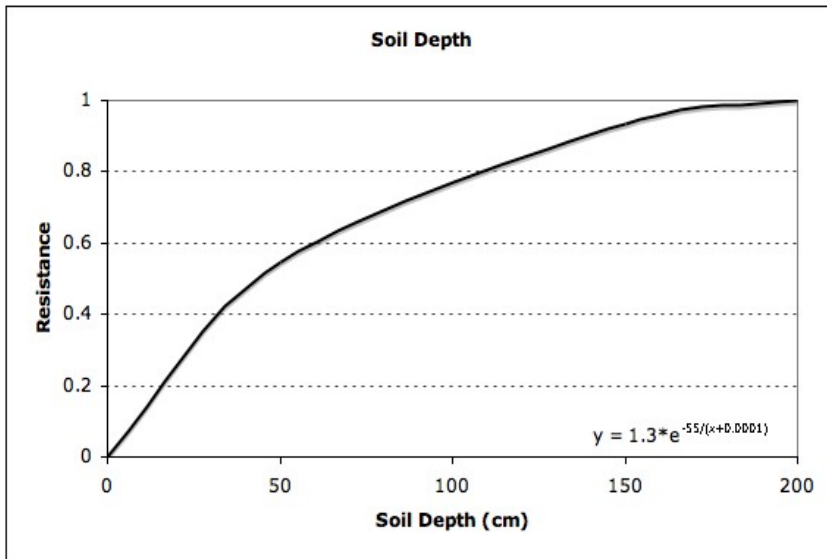
Geologic Formation	Hypothesized Resistance	
Bluefield Formation of the Mauch Chunk Group	0.9	More
Hinton Formation of the Mauch Chunk Group	0.9	
Maccrady Formation	0.9	
Mauch Chunk Group	0.9	
McKenzie Formation & Clinton Group	0.9	
Quaternary Alluvium	0.9	
Chemung Group	0.8	
Conemaugh Group	0.8	
Bluestone Formation of the Mauch Chunk Group	0.7	
Kanawha Formation of the Pottsville Group	0.7	
Brallier Formation	0.6	
Hampshire Formation	0.6	
Allegheny Formation	0.5	
Princeton Formation of the Mauch Chunk Group	0.5	
Pocono Group	0.4	
Juniata & Oswego Formations	0.3	
Oriskany Sandstone	0.3	
Marcellus Formation of the Millboro Shales	0.2	
Tuscarora Sandstone	0.2	
New River Formation of the Pottsville Group	0.1	
Pottsville Group	0.1	
Tonolaway, Wills Creek & Williamsport	0.1	Less

Figure 4-2: Hypothesized resistance curves for site factors used to create resistance index





Soil texture is one of the only soil factors related to acid-neutralization that is readily available in spatial data sets (Van Ranst *et al.*, 2002). We hypothesized that soils with higher clay content will be more resistant to productivity losses due to acidification (Lucas and Cowell, 1984). However, similar to the influence of rock fragments on hydraulic conductivity, too much clay slows the movement of water through the soil profile, increasing contact time between AD and the soil system, therefore, decreasing resistance) (Table 4-1; Figure 4-2).

Using soil factors from the SSURGO database may not fully account for actual soil variability across the MNF. For example, certain soil series with fragipans have a shallower rooting depth than the total soil profile depth reported in the SSURGO database (Connolly, 2006). However, we hypothesize that SSURGO data can be used to develop a spatial AD resistance model, and that it will be related to a gradient in resistance to acidification.

Develop and Validate Resistance Model (Step 2)

We calculated site factor scores at each Forest Inventory and Analysis (FIA) plot on the MNF. The FIA program is a national monitoring network, with plots located across the country on all land usages (USDA Forest Service, 2007). Each plot is re-sampled every five years, so that within each state 20% of the plots are measured each year. Ground-plot measurements are taken over three 0.017 ha plots arranged around another 0.017 ha center-plot. At each FIA plot location on the MNF, values for each site factor were determined using 30 by 30 m United States Geologic Survey Digital Elevation Models (USGS DEM), SSURGO, and MNF maps (Table 4-3). To do this, FIA plots were joined with the MNF map layer for parent material, USGS DEM layers for slope, aspect and elevation, and the USDA Natural Resource Conservation Service's SSURGO layer to obtain component key (cokey) values. The cokey is a value assigned each soil series, providing a unique value for each horizon that can be used to match horizon components among the various data tables provided in the SSURGO database. Horizon depth, rock fragments, and texture values were extracted from the "Component Horizon Table". Mineralogy class values were obtained from the "Component Taxonomy and Mineralogy Table". For rock fragments and texture values the total

horizon value was calculated by multiplying each horizon's value by the weight of that horizon (depth of horizon/depth of profile) and summing over the total profile.

A resistance index was then calculated (RI_{general}) for each FIA plot by equally weighting and summing all resistance scores for each site factor. To scale the function for management purposes the equation was squared. Periodic mean annual volume increment for the 10-year period from 1989 to 2000 was calculated for each FIA plot and regressed with RI_{general} . A significant relationship would validate a relationship between forest growth and an AD resistance gradient.

Table 4-3: Sources for each site factor used to create a site resistance index to AD

Factor	Calculations	Source
Parent Material	Assigned value 0.1 – 1	MNF Map
Slope (%)	Value extracted from DEM	USGS 30-meter DEM
Azimuth of Aspect (deg.)	Value extracted from DEM	USGS 30-meter DEM
Elevation (m)	Value extracted from DEM	USGS 30-meter DEM
Mineralogy	1 – mixed 0 – siliceous	SSURGO Cotaxfminn Table – taxminalogy column
Depth (cm)	Total soil profile depth	SSURGO Chorizon Table – hzdepb_r column
Rock Fragments (%)	$\sum (\text{rock}\% * \text{horizon weight})$	SSURGO Chorizon Table – fraggt10_r and frag30to10_r columns
Texture (%)	$\sum (\text{clay}\% * \text{horizon weight})$	SSURGO Chorizon Table – silttotal_r and claytotal_r columns

Production of an AD Resistance Map (Step 3)

To create an AD resistance gradient specific to the MNF, we regressed PMAVI with the site factors and used the standardized regression coefficients for each site factor as weighting factors. RI_{MNF} was then used to create a map of resistance and sensitivity to AD across the MNF by applying the equation to grids across the forest. The grid size was limited to 30 by 30 meters by the resolution of the USGS DEMs. Each grid was assigned an exact RI value from 0 to 1 based on the specific RI equation; however, for

purposes of applicability and analyses we split the forest into high resistance ($RI \geq 0.7$), moderate resistance ($0.7 > RI > 0.45$) and slight resistance ($RI \leq 0.45$).

Selection of AD Indicators for Monitoring (Step 4)

Indicators of five criteria used to monitor the effects of AD on forest growth were correlated with RI_{MNF} to select those most useful in a monitoring program. The key criteria of soil acidification are soil acidity, potential toxicity level, soil fertility, level of N-saturation, and acidity neutralization potential. Indicators for each criterion were selected and proposed for AD monitoring. pH was used as an indicator of acidity, Ca/Al molar ratio and Al content were used as indicators of potential toxicity, base saturation was used as an indicator of soil fertility, NO_3/NH_4 and C/N ratio were used as indicators of N-saturation, and sum of bases was used as an indicator of acid neutralization potential. Significant indicators were used to determine the breaks in resistance classes (high, moderate, slight) by examining the data for breaks related to previously published soil indicator levels (Cronan and Grigal, 1995; Fenn *et al.*, 1998). To further verify the applicability of this adaptive management tool, we correlated RI with stream water chemistry data collected by forest managers. Stream water pH, conductivity, acid neutralization capacity, and concentration of Ca, Mg, Na, K, Cl, NH_3-N , NO_3-N , and SO_4 were measured. Results from 2001, Spring 2002, Spring 2005, Fall 2006, Spring and Fall 2007, and Spring 2008 stream water samples were compared with average resistance index assigned to watersheds above the sampling locations. Average watershed RI was calculated by using hydrologic data tools to determine watershed area upstream of the sample point, and applying zonal statistics to determine a mean RI value for each watershed.

Results and Discussion

After developing relationships between site factor gradients and AD resistance based on our current collective knowledge (Step 1), the second step in the creation of an AD resistance map was the development of a general model by equally weighting each site factor associated with resistance to acidification. The general resistance model was:

$$RI_{general} = [.2(\text{parent material score}) + .2(\text{aspect score}) + .2(\text{elevation score}) + .2(\text{soil depth score}) + .2(\text{texture score})]^2 \quad (1)$$

Of the eight original site factors considered, parent material, aspect, elevation, soil depth and soil texture were included in the RI model. Due to the limited variation in soil mineralogy on our study plots (only mixed and siliceous), this site factor was dropped from the analysis. Similarly, rock fragment content, despite ranging from 1.9% – 48.6% on the MNF, has little influence on resistance until content exceeds 50% (Figure 4-2).

Slope was also removed from the data set because of the negative relationship ($p = 0.0579$) with soil depth. Depth was a separate site factor in our analysis; therefore, including slope would have produced unnecessary redundancy in the index.

On the subset of FIA plots used for intensive soil sampling, $RI_{general}$ was positively correlated with periodic mean annual volume increment (PMAVI) ($p = 0.0073$) (Figure 4-3). PMAVI ranged from -9.5 to $11.8 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$, suggesting lower-than-expected growth on two-thirds of the sites. Historically, average growth rates of hardwoods in West Virginia were over $3 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ on average sites, and good management practices can increase PMAVI to over $5 \text{ m}^3\text{ha}^{-1}\text{yr}^{-1}$ (Schnur, 1937; Smith *et al.*, 1994). The wide range of growth and decline on FIA plots suggests that current forest conditions, such as pollution and stress, have altered the system from historical baseline levels of productivity. The general model explained 23% of this variability in growth ($p = 0.0087$). This validates our hypothesis of a relationship between forest growth and an AD resistance gradient. The GIS layer of each of these factors is widely available; therefore, AD resistance maps can be developed for the MNF and used to apply site-specific best management practices.

The $RI_{general}$ was based on both established and hypothesized relationships of how soil and site factors buffer the effects of chronic AD. The significant relationship between forest growth on the MNF and $RI_{general}$ shows that forest productivity is connected to the site gradients reflected in the model; however, these factors may buffer the effects of AD to different degrees. The third step in our proposed AD management approach was to produce a more refined AD resistance map by weighting the influence of each site factor to reflect current forest conditions. We regressed PMAVI with the site factors in the general model using data from all MNF FIA plots. The standardized

coefficients were used to weight the relative influence of each site factor to create the following weighted model specific to the MNF:

$$RI_{MNF} = [0.352 \text{ (elevation score)} + 0.083 \text{ (aspect score)} + 0.164 \text{ (texture score)} + 0.218 \text{ (parent material score)} + 0.183 \text{ (depth score)}]^2 \quad (2)$$

The RI_{MNF} , a function of PMAVI, adapted the $RI_{general}$ to be specific to the MNF. The relationship between RI_{MNF} and PMAVI had an R^2 of 0.20 ($p = 0.0160$).

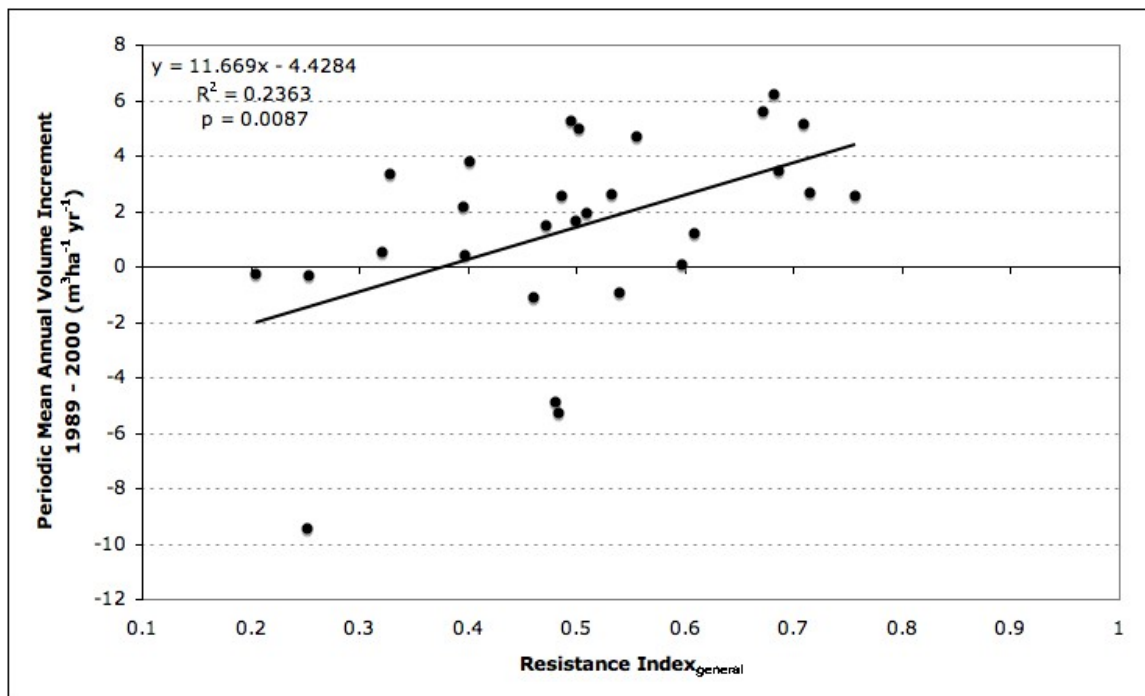


Figure 4-3: The relationship between periodic mean annual volume increment and general resistance index.

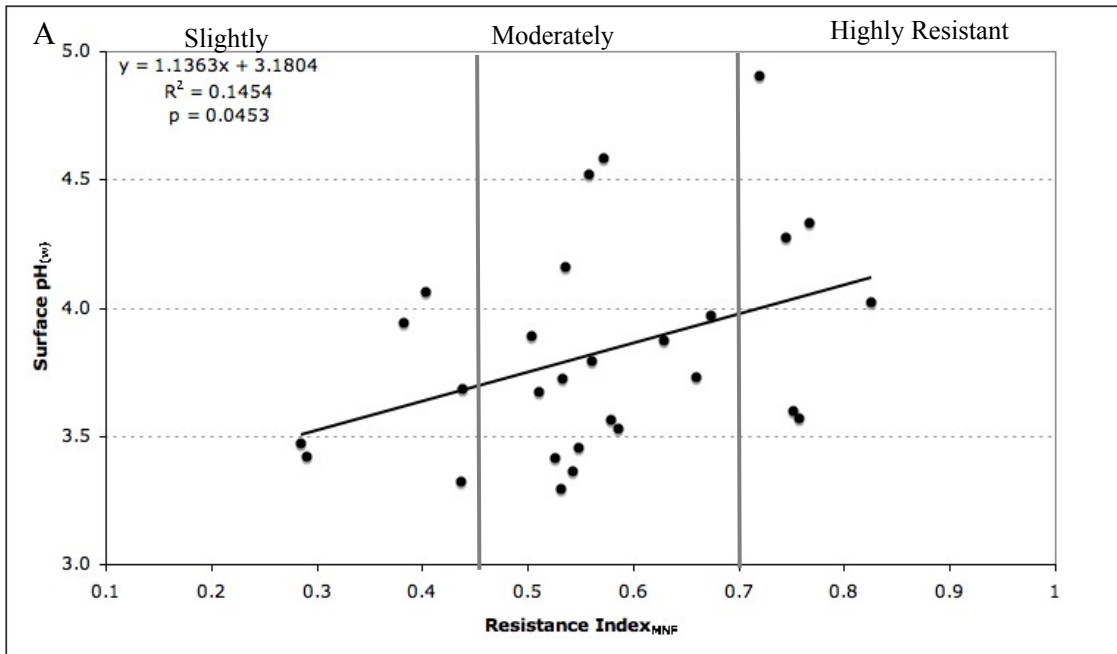
We evaluated the relationship between RI_{MNF} and criteria and indicators of soil acidity, including soil acidity, potential toxicity level, soil fertility, N-saturation, and potential acid neutralization. The key indicator of acidity, pH, of both the surface and subsurface horizons was positively correlated with RI_{MNF} ($p = 0.045$ and $p = 0.0010$, respectively) (Figure 4-4). Key indicators of potential toxicity are Ca/Al molar ratio and Al content. Of these, Al content of the subsurface horizon was negatively correlated with RI_{MNF} ($p = 0.0081$), and Ca/Al molar ratio was positively correlated with RI_{MNF} ($p = 0.0448$) (Figure 4-4). The key indicator of soil fertility, effective base saturation, of the

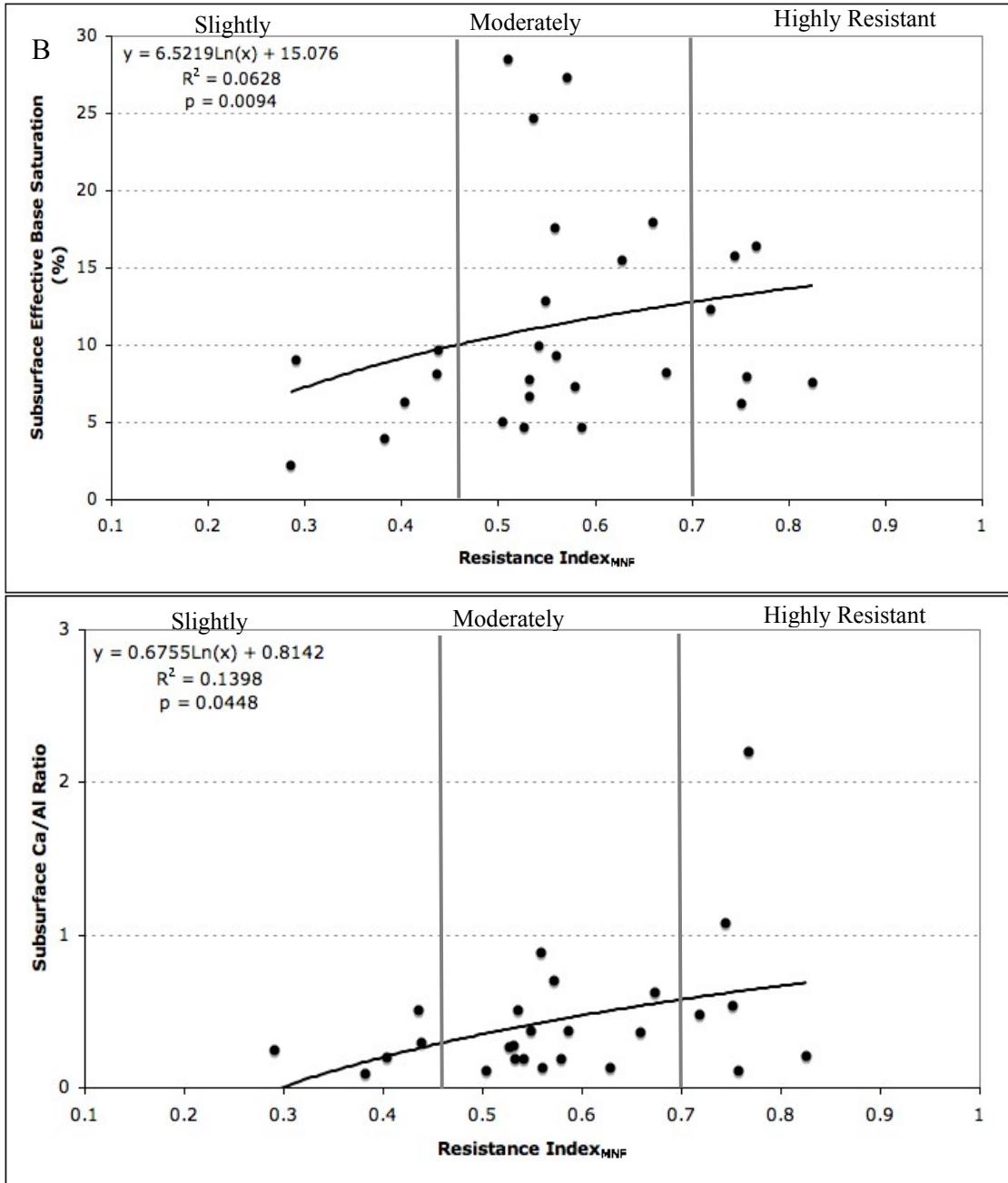
subsurface horizon was positively correlated with RI_{MNF} ($p = 0.0094$) (Figure 4-4). They key indicators of N-saturation, NO_3/NH_4 and C/N ratio were not correlated with RI_{MNF} . The key indicator of potential acid neutralization, sum of the bases, was not correlated with RI_{MNF} .

The relationship between RI_{MNF} and significant indicators (pH, EBS, Ca/Al ratio, Al content) were used to create RI classes (slightly, moderately, and highly resistant). Class breaks were developed at indicator levels established to influence site sensitivity, as well as in breaks in our data (i.e. Cronan and Grigal, 1995, Fenn *et al.* 1998) (Figure 4-4).

A resistance index based on the classes of weighted site and soil factors (RI_{MNF}) was mapped across the Monongahela National Forest (Figure 4-5). The northwestern area of the forest could not be mapped because soils data were not digitized at the time of analysis (July 2008); however, this method could be expanded to that county when those data become available. Across the MNF, 14% of the land area was mapped as highly resistance to acidification ($RI \geq 0.7$), 57% was mapped as moderately resistant ($0.7 > RI > 0.45$) and 29% was mapped as slightly resistant ($RI \leq 0.45$). Average subsurface pH was 4.4 on highly resistant sites, 4.3 on moderately resistant sites, and 4.0 on slightly resistant sites (Table 4-4). Average subsurface effective base saturation was 11 on highly resistant sites, 12 on moderately resistant sites, and 7 on slightly resistant sites (Table 4-4). Average subsurface Ca/Al molar ratio was 0.8 on highly resistant sites, 0.4 on moderately resistant sites, and 0.3 on slightly resistant sites (Table 4-4).

Figure 4-4: Correlations between RI_{MNF} and A) surface soil pH, B) subsurface effective base saturation, and C) subsurface Ca/Al molar ratio





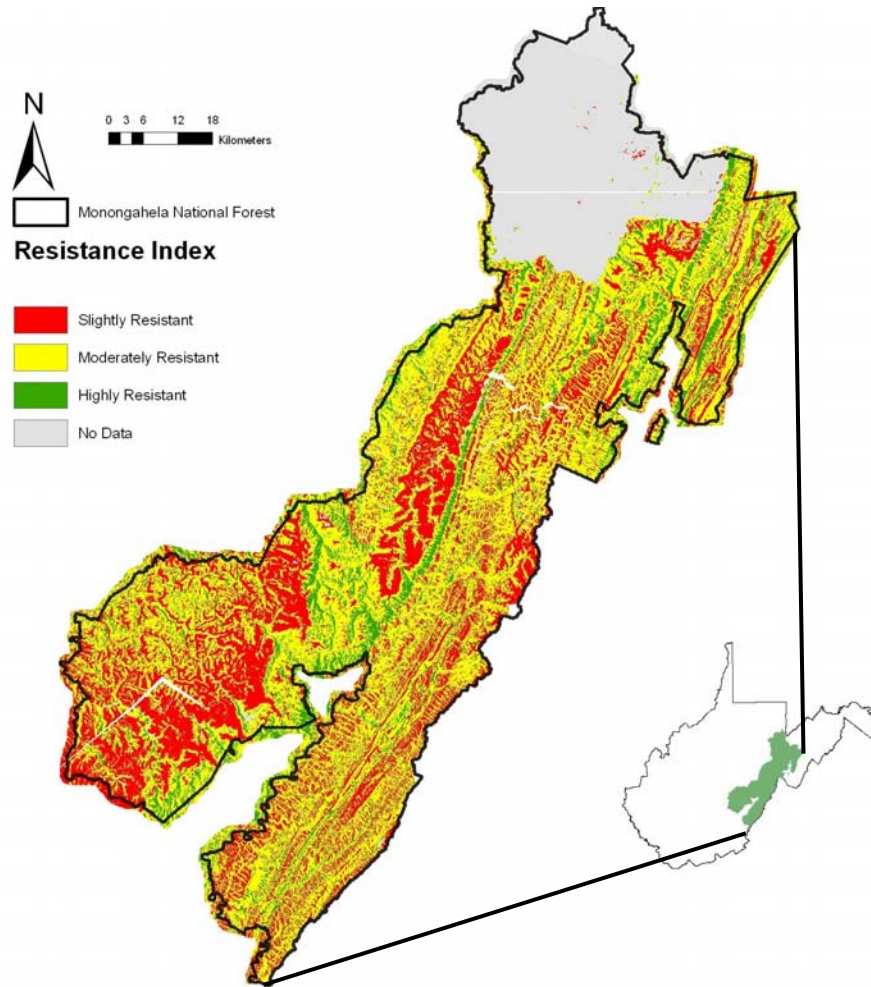


Figure 4-5: Map of resistance to acidification on the Monongahela National Forest.

Cronan and Grigal (1995) determined relationships among Ca/Al values and the risk of forest decline. They suggest that values above 2.0 had a 0% risk, values between 1.1 and 2.0 had a less than 50% risk, values between 0.6 and 1.0 had a 50% risk, values between 0.2 to 0.5 had a 75% risk, and values less than 0.2 had a 100% risk of decline. While the use of these values varies depending on many factors such as soil sampling and analysis methods, relative Ca/Al values for each site resistance class can be used to provide a relative decline scale. For both surface and subsurface horizons, the highly resistant sites had the highest average Ca/Al values, which suggest that these plots have the lowest risk of decline due to acidification by both the RI_{MNF} scale and Cronan and

Grigal (1995) suggestions. On the slightly resistant sites Ca/Al ratio values suggest that these sites may be at risk of decline (Table 4-4).

The map of resistance index can be used in specific land management prescriptions on stand and watershed-sized scales. For example, within a 6000 hectare area of the Allegheny Mountains province, RI_{MNF} was 0.31, 0.42, and 0.64 (Table 4-5; Figure 4-6).

Table 4-4: Subsurface horizon soil characteristics, grouped by specific resistance index values. Values with * were significantly correlated with RI_{MNF}

		pH*	Ca/Al ratio*	EBS (%)*	Sum of bases ($\text{kmol}_+ \text{ha}^{-1}$)	NO_3/NH_4 ratio
$RI \geq 0.7$	Max	4.7	2.2	16.4	57062	0.61
	Min	4.0	0.1	6.2	9986	0.007
	Mean	4.4 ± 0.10	0.8 ± 0.32	11 ± 1.8	35646 ± 9326	0.18 ± 0.1
$0.7 > RI > 0.45$	Max	4.6	0.9	28.4	98526	1.7
	Min	3.7	0.1	4.5	9416	0.006
	Mean	4.3 ± 0.06	0.4 ± 0.06	13 ± 2.0	40571 ± 5967	0.62 ± 0.2
$RI \leq 0.45$	Max	4.2	0.5	9.6	58323	0.99
	Min	3.8	0.09	2.2	7763	0.001
	Mean	4.0 ± 0.07	0.3 ± 0.07	6.5 ± 1.2	31483 ± 8052	0.46 ± 0.2

Resistance index can be applied to management-sized units, where prescriptions can be designed to minimize deleterious effects of acid inputs on low RI sites. For example, managers may choose to apply distinct harvest systems among sites. Whole-tree and bole-only harvesting systems will remove substantially different levels of base cations (Adams, 1999). On an experimental unit within the MNF, whole-tree harvesting removed 1.8 times more nutrients than bole-only harvesting (Patric and Smith, 1975). It is possible for Ca removals to range from around 200 kg ha^{-1} in a clearcut to almost 1000 kg ha^{-1} in multi-entry selective harvesting (Adams *et al.*, 2000). The positive relationship between RI_{MNF} and effective base saturation provides forest managers with an idea of where whole-tree harvesting, which may be used for biomass energy and biofuels, is possible while still maintaining sustainable growth. The impact and weathering rate of parent material on mitigating cation losses or leaching is still unknown on the MNF. However, it is highly unlikely that weathering rates of the acid sandstone and shale bedrock would be rapid enough to replace harvest removals and losses associated with AD. The RI_{MNF} presented here incorporates relative parent material buffering capacity

and may provide site comparisons based on potential weathering on which prescriptions may be determined.

Table 4-5: Site characteristics used to calculate resistance index at FIA plots on the MNF

Plot	RI	Elevation	Aspect	Clay	Parent Material	Soil depth
FIA1	0.31	1149	31.6 deg.	51%	New River Formation, Pottsville Group	94 cm
FIA2	0.42	1252	225 deg.	11.1%	Knawah Formation, Pottsville Group	188 cm
FIA3	0.64	1214	127 deg.	12.5%	Hinton Fomation, Mauch Chunnk Group	96 cm

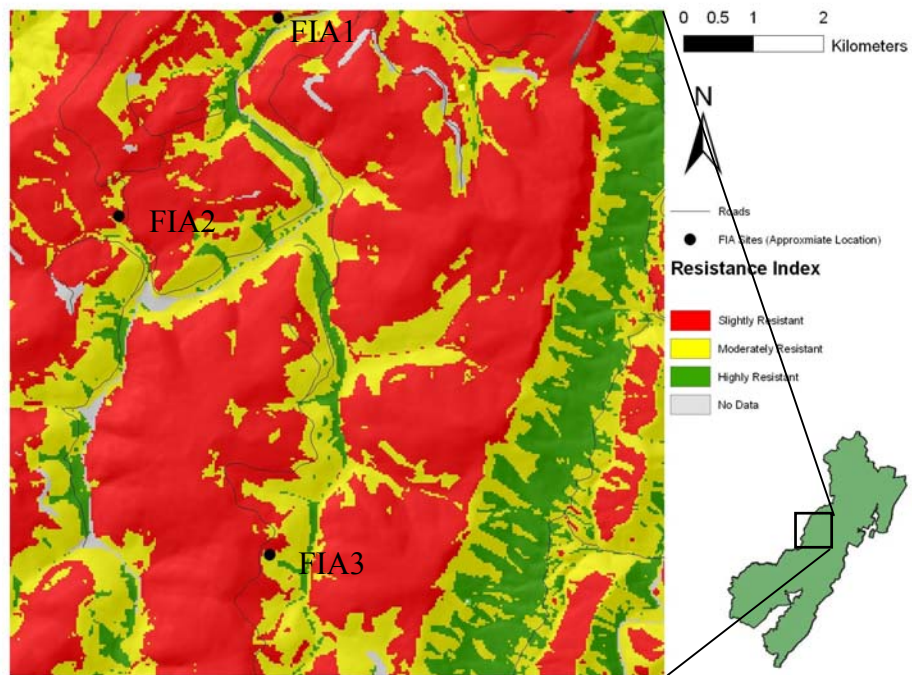


Figure 4-6: Resistance Index map in the Allegheny Mountains province of the Monongahela National Forest.

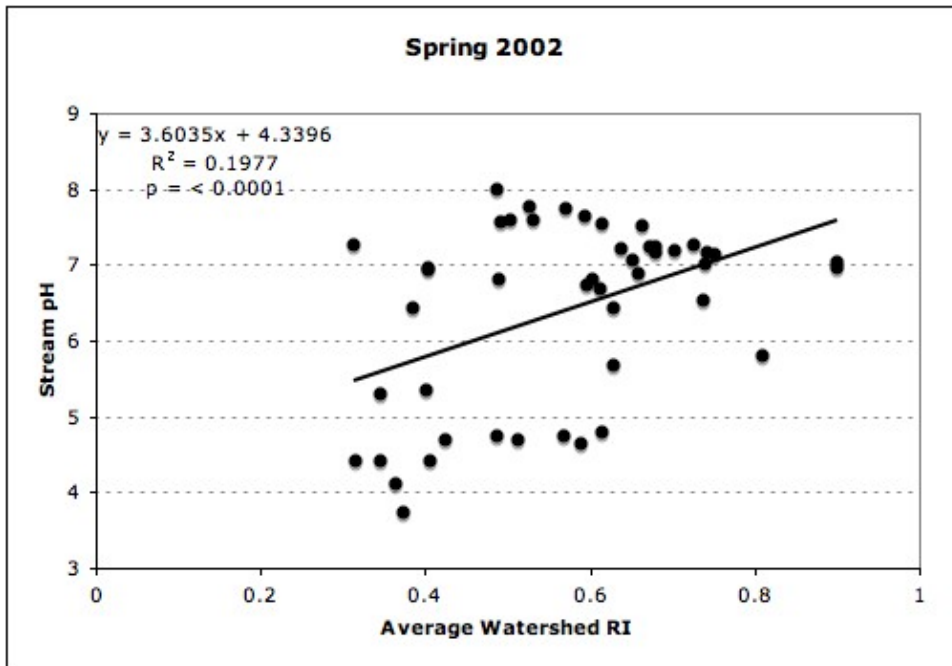
The significant relationship between resistance index and PMAVI and soil acidity indicators demonstrates the versatility of this tool. Previously, managers on the MNF generalized resistance based only on stream chemistry and parent material (Connolly *et al.*, 2007). RI_{MNF} was based on multiple mappable site factors and can be applied at the stand level. It should be useful for making more precise, site-specific management prescriptions.

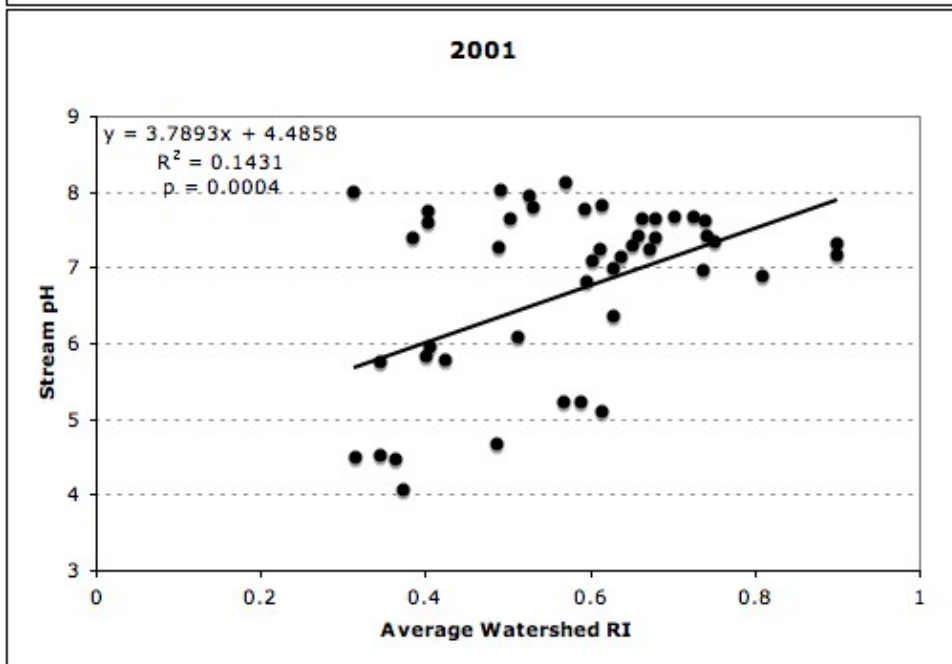
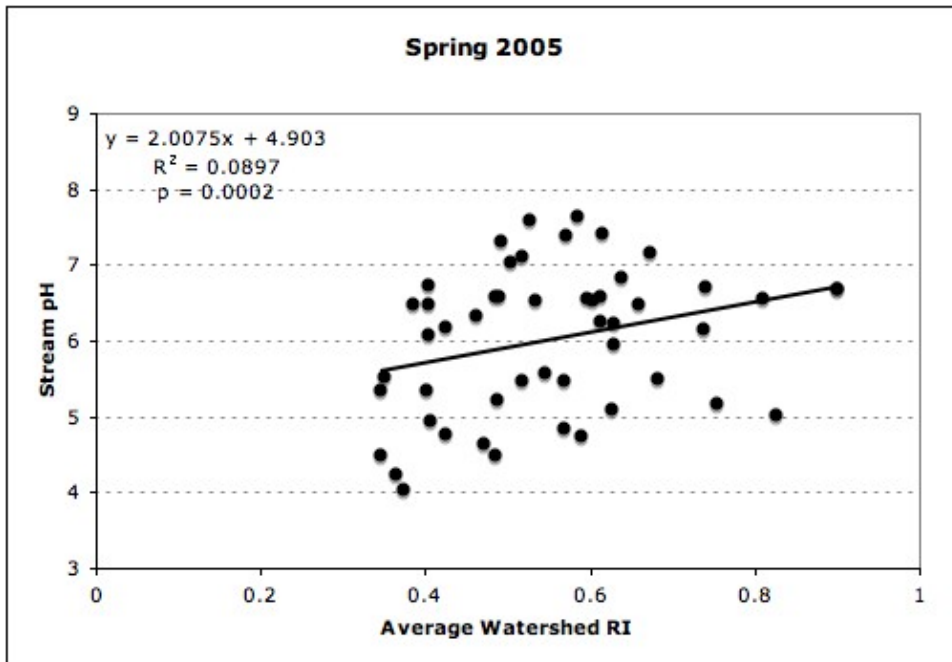
To further verify the applicability of this adaptive management tool, we correlated RI_{MNF} with stream water chemistry data collected by forest managers. Resistance index value and stream water pH were positively correlated in 2001, Spring 2002, Spring 2005, and Fall 2006 (Figure 4-7). During the same time periods, RI_{MNF} was positively correlated with stream acid neutralization capacity and stream Ca, both of which were related to pH.

Conclusions

To meet adaptive management objectives of foresters on the Monongahela National Forest (MNF), we used site characteristics that can be mapped to create a spatial site resistance index to acidification. A general model using elevation, aspect, soil texture, parent material, and soil depth was significantly correlated with periodic mean annual volume increment on 28 FIA plots. Factor weighting of a specific RI model for the MNF (RI_{MNF}) was based on growth from 1989 to 2000. RI_{MNF} was correlated with soil pH (+), effective base saturation (+) and Al content of the subsurface horizon (-) as well as with stream water pH (+), acid neutralization capacity (+), and Ca (+). Resistance index was used to create a map of resistance to acidification on the forest; over 80% of the forest was mapped as only moderately or slightly resistant to acidification. This map can be used for both the development of sustainable management prescriptions as well as the development of an AD-targeted monitoring program. This process and model may be useful in other locations subject to high levels of AD, and the four steps of the process would be similar for other locations. The weighting of the specific RI would be different on other forests, but because FIA is a national program it may be possible to continue to use those data for model validation.

Figure 4-7: Correlations between stream water pH and resistance index.





V. Dendrochronology of Two Sites on the Monongahela National Forest Subjected to Acid Deposition

Abstract

Forests of the Appalachian Mountains are subject to high levels of acid deposition (AD), which has been shown to increase susceptibility to damage from secondary stresses and may decrease productivity. To meet forest management objectives and guidelines, foresters must adaptively manage across the landscape to ensure sustainable productivity. The purpose of this study was to determine the chronic effects of AD on the growth of two sites that overlay different parent materials. We sampled 20 dominant and co-dominant northern red oak (*Quercus rubra* L.) trees from each site to use in creating dendrochronologies of each site. There were no significant differences among ring width increment and basal area increment between the two sites. From 1900 to 2007 the two sites showed 58.5% similarity in growth trends, and these could not be attributed to a dissimilar influence of AD. The highest similarity throughout the 1900 to 2007 period occurred between 1940 and 1990, when the sites were experiencing high levels of AD. During this period the relatively flat basal area increment on both sites suggests that stressors, such as AD, were depressing tree growth. Further investigation would be necessary to fully discern the utility of dendrochronology for monitoring the effects of AD on forest growth.

Introduction

Acid deposition (AD) results mainly from fossil fuel combustion, which produces sulfuric acid and nitrous oxides. There is a growing body of evidence that AD induces forest productivity losses (Likens *et al.*, 1996; Schaberg *et al.*, 1997; Horsley *et al.*, 2000) caused in part by base cation leaching, Al mobilization, and sulfur and N accumulation in forest soils (Driscoll *et al.*, 2001c). Scientists and forest managers are concerned that AD will continue to stress and damage ecosystems, threatening productivity of the forest.

Evidence for forest decline due in part to AD has been established for some species in some areas, especially *Picea rubens* Sarg. (red spruce) at high elevations in the Northeastern United States and *Acer saccharum* Marsh. (sugar maple) in central and western Pennsylvania (Driscoll *et al.*, 2001c). Symptoms of decline include poor crown condition, reduced tree growth, and high levels of mortality (Driscoll *et al.*, 2001c). *Quercus rubra* L. (northern red oak) decline in western Pennsylvania has been associated with more acidic sites, suggesting that nutrient deficiency and Al toxicity may be stressing this species as well (Demchik and Sharpe, 2000). However, in the central Appalachians, there has been no reported evidence of growth declines related to acid deposition (Adams, 1999).

Given that environmental conditions affect tree growth, changes in rates of growth can indicate forest condition, revealing differences in stand productivity in response to a disturbance through time and among sites (Fritts, 1976; Juknys, 2004). Tree ring analysis has been used to determine changes in forest dynamics and productivity due to acid deposition. For example, basal area increment (BAI) growth patterns for sites along an acid deposition gradient in Québec were used to determine tree vigor (Duchesne *et al.*, 2002). In their study, BAI was negatively correlated with N and S pollution levels and was positively correlated with forest floor base saturation. Decline in BAI determined through dendrochronology is a strong indicator of whole-tree growth decline (LeBlanc, 1990). Dendrochronologies have been used in the Appalachian mountains to reflect changes in productivity along N deposition gradients (Boggs *et al.*, 2005).

The ecological site factors most commonly used to estimate site susceptibility to productivity losses due to AD are bedrock parent material, soil type, land cover, and moisture regime (Tao and Feng, 2000). Parent material is one of the most fundamental site characteristics related to acid-neutralization, and is considered to be more resistant to acidification if it is more calcareous, providing buffering capacity and more nutrients to the soil system (Johnson *et al.*, 1982a; Johnson, 1984; Lucas and Cowell, 1984). Soil is the first geologic acid-sink and kinetically the most active (Johnson, 1984). The potential for soils to reduce acidity is expected to be highest when the soil is deeper than 100 cm and lowest when the soil is shallower than 25 cm (Lucas and Cowell, 1984).

The Monongahela National Forest (MNF) is located in eastern West Virginia, and is subject to levels of AD as high as 26 kg SO₄²⁻ ha⁻¹ and 14 kg NO₃⁻ ha⁻¹ per year (National Atmospheric Deposition Program (NRSP-3), 2006); therefore, the influence of acid deposition on sustainable forestry has become an issue with land managers. Our objective was to explore the usefulness of dendrochronology in determining if northern red oak on two MNF sites, differing only in parent material and soil series, would express a different cumulative effect of AD on growth. We hypothesized that the analysis would demonstrate variable AD effects due to differences in parent material, specifically that growth rates would be smaller on the less buffered site where parent material is more acidic.

Methods

Field Analysis

Two forest sites on the Monongahela National Forest (MNF) were used for this study. For both sites, northern red oak composed a large portion of the stand. Stand 1 (Hampshire) was on a Gilpin soil series (fine-loamy, mixed, active, mesic typic hapludult), overlying bedrock of the Hampshire Formation (Devonian interbedded red shale, red mudstone, and red to brown cross-bedded siltstone and sandstone). In 2007, the basal area was 30 m² ha⁻¹, stand age was 125, and periodic mean annual volume increment from 1989 to 2000 was -4.9 m³ ha⁻¹ per year. The elevation was 1262 m, aspect was 287 degrees, and slope averaged 27%. Stand 2 (Marcellus) was on a Berks soil series (loamy-skeletal, mixed, active, mesic typic dystrodept) overlying bedrock of the Marcellus Formation of the Millboro Shales (Devonian grey-black to black carbonaceous shale, containing one or more thin bedded limestones). In 2007, the basal area was 21 m² ha⁻¹, stand age was 109, and periodic mean annual volume increment from 1989 to 2000 was -0.36 m³ ha⁻¹ per year. The elevation was 719 m, aspect was 289 degrees, and slope averaged 22%. These sites were selected for their contrasting geologic parent material. To reduce site variability, sites were selected with similar aspects, slopes, and soil depth. In 2007, there was no evidence of recent disturbance on either site, and stand composition was similar.

Twenty northern red oak trees were sampled on each site. Each tree was cored twice at 0.3 m above ground level. Cores were taken parallel to the ground contour on either side of the tree. Northern red oak was selected because of its value as a wildlife and timber species, and because it is considered to be sensitive to the impacts of acidification (Hicks, 1998).

Lab and Statistical Analysis

Cores were air-dried, mounted on grooved wooden blocks, and prepared for visual analysis using 220, 320 and 400 grit sandpaper. Cores were visually cross-dated, and those that could not be accurately dated were removed from the data set. Cores were measured on an incremental measuring stage at the Dendroecology Laboratory at Virginia Tech, Blacksburg, VA. Accuracy of the cross-dating was then checked using COFACHEA Software (Holmes, 1983).

Untransformed ring width values were used to calculate basal area increment (BAI) for each year, which were then averaged across all cores on each site. BAI was calculated using the following equation:

$$BAI_t = \pi(r^2_t - r^2_{t-1}) \quad (1)$$

where r is the tree radius and t is the year of tree-ring formation.

Additionally, we calculated a measure of similarity between the two sites using the Gleichläufigkeit sign test (g-value) (Schweingruber, 1983). We calculated annual g-values using the following procedure:

1. $\Delta_i = (x_{i+1} - x_i)$ (2)

2. If $\Delta_i > 0$ then $G = 1/2$; If $\Delta_i = 0$ then $G = 0$; If $\Delta_i < 0$ then $G = -1/2$

3. Similarity, $G_{(x,y)} = 1/n-1 \sum |G_{ix} + G_{iy}|$ (3)

where x is ring width, i is annual interval, and $G_{(x,y)}$ is the Gleichläufigkeit similarity value within the annual interval x, y

To evaluate differences between productivity on the sites we compared both BAI averages and average g-values in three time periods: 1900 to 1939, 1940 to 1989, and

1990 to 2007. These periods were chosen because they represent three stages in AD on the MNF. Before 1940 AD was not a significant pollutant on the MNF (Husar, 1986). Between 1940 and 1990 AD increased and while the 1970 Clean Air Act (CAA) addressed some pollutants, sulfate levels declined little and N deposition levels did not decrease (Driscoll *et al.*, 2001c). Nineteen-ninety marked the passage of the Clean Air Act Amendments (CAAA), which required decreases in sulfur emissions in the United States (Driscoll *et al.*, 2001b).

Soil samples were collected at both sites and analyzed for a suite of soil acidity indicators (Chapter III). Additionally, cation-exchange acid neutralization potential (ANP_{CEC}) was calculated as effective cation exchange capacity times effective base saturation of the total soil depth for each site.

Results

Ring width increment increased for both sites throughout the 1900 to 1930 time period (Figure 5-1). Around the 1940s this increment peaked and then decreased through the early 1960s. After the early 1960s, average ring width increment for both sites remained relatively flat and close to the average value of 1.95 mm per year. During 1900 to 1939 the Marcellus site had larger annual ring width increments than the Hampshire site; however, this trend reversed through the 1940 to 1989 time period and reverted since then.

The general trend in basal area increment was similar for both sites (Figure 5-2). Similarly to ring width increment, BAI on the Marcellus site was larger than the Hampshire site from 1900 to 1939; however, this trend reversed for the 1940 to 1989 time period and reverted since then.

Gleichläufigkeit values show the level of similarity between the two sites (Table 5-1). The largest similarities were in the 1940 to 1989 time period, during which the stands were 65% similar. The greatest differences were in the 1900 to 1939 time period, during which time the stands were 53% similar. The average similarity between the stands was 59%.

Soil chemistry data from the two sites are summarized in Table 5-2. The greatest difference in soil chemistry was in the surface horizon pH, which was 3.53 for the Hampshire site and 4.06 for the Marcellus site. Surface pH and subsurface Ca/Al molar ratio were significantly different between the two sites. The Marcellus site had higher surface pH and EBS than the Hampshire site. The Hampshire site had higher subsurface pH, Ca/Al molar ratio, and ANC_{CEC} than the Marcellus site.

Discussion

We hypothesized that the two sites had different buffering capacities due to differences in parent material, and would, therefore, be differently affected by the cumulative effects of AD. Despite differences in parent material, and some differences in soil chemistry, there was little difference between changes in ring width (RW) increment. The overall trends may provide insight into the factors affecting growth on these sites. There are many factors that could have influenced the increase in RW on the Hampshire site around 1940, including changes due to loss of *Castanea dentata* Marsh. (American chestnut) or other stand disturbances, elevated levels of carbon dioxide, or increased pollutants such as acid deposition (Abrams *et al.*, 1997). While all of these factors could be playing a part in growth changes, there was no evidence of American chestnut stumps or other disturbance at either site.

Negative trends in basal area increment are a strong indicator of growth decline (Duchesne *et al.*, 2002), but neither stand exhibited these trends. There are, however, trends in RW and BAI that indicate climatic or management influences on growth patterns. BAI and RW trends are similar: they sharply increase around 1940, plateau between the 1950s and 1990s, and then return to average rates.

During the pre-AD period of 1900 to 1939, RW and BAI are larger on the Marcellus site, indicating that it may have had a higher initial site quality than the Hampshire site. From the mid 1930s through the mid 1940s there was a large jump in RW on both sites. While stand history is unknown, the distance between the two sites suggests that simultaneous management probably is not the cause of this increase; therefore, this change is probably a climactic effect. Increasing AD during this time may

have fertilized the stands, which would have had more of an effect on the stand of poorer site quality (Hampshire), where there is a larger increase in RW during this time.

Table 5-1: G-value similarities between two samples sites on the Monongahela National Forest

Time Period	Approx. Stand Age (years)		Avg. Basal Area Increment (cm ² per year)		Avg. g-value similarity
	Hampshire	Marcellus	Hampshire	Marcellus	
1900-1939	18 – 57	1 – 39	2.75	2.94	52.6%
1940-1989	58 - 107	40 – 89	11.17	10.34	65.3%
1990-2007	108 – 125	90 – 107	16.42	20.95	58.8%
1900-2007	18 – 125	1 – 107	8.93	9.43	58.5%

Table 5-2: Soil chemistry characterization of two sample sites, significance ($p \leq 0.1$) indicated with *

	Hampshire Site	Marcellus Site
Surface soil pH*	3.53	4.06
Subsurface soil pH	4.56	4.19
Surface EBS	10.6%	12.5%
Subsurface EBS	6.0%	6.3%
Surface Ca/Al	1.4	1.2
Subsurface Ca/Al*	0.4	0.2
ANC _{CEC}	91.3 kmol _c ha ⁻¹	88.69 kmol _c ha ⁻¹

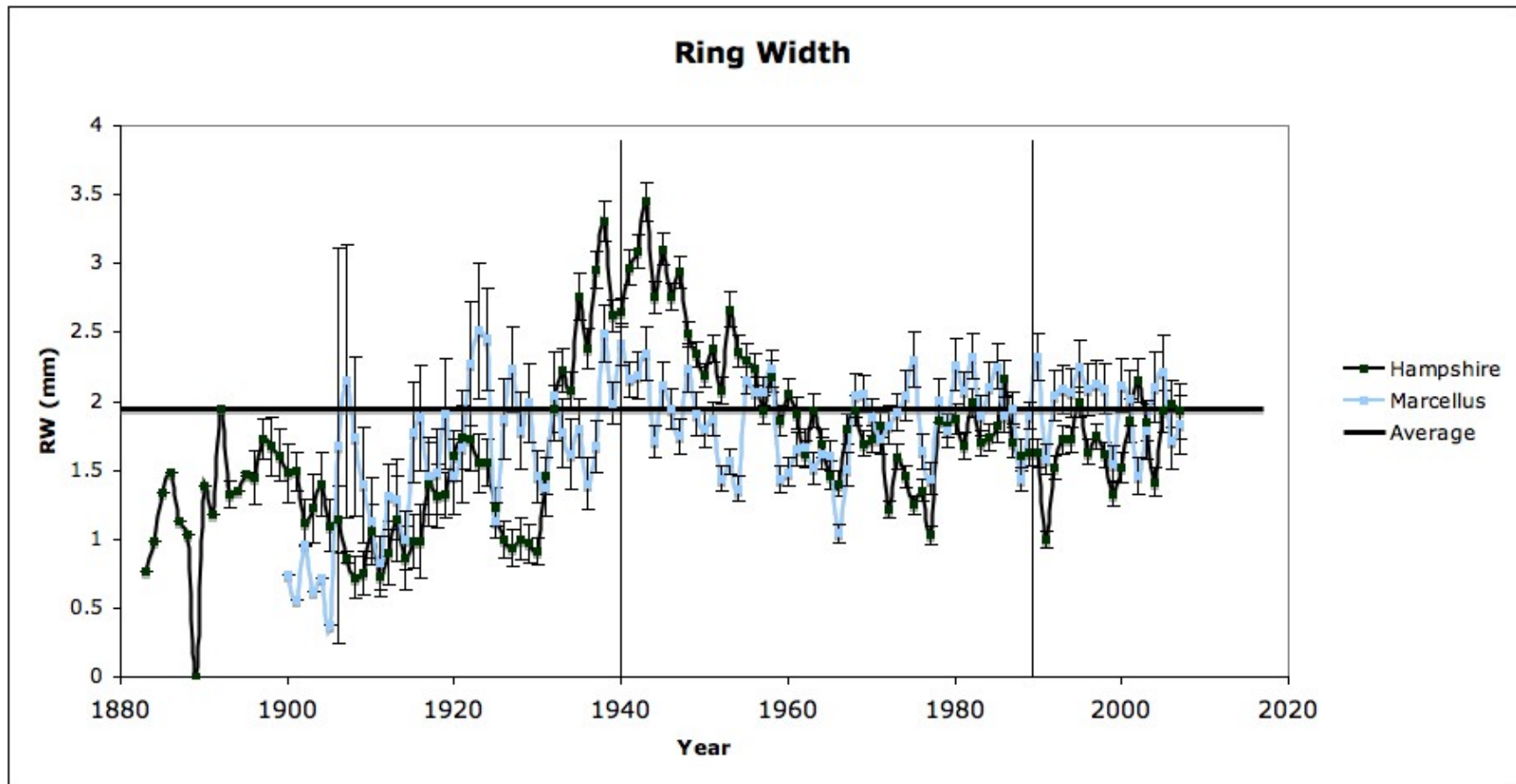


Figure 5-1: Ring width increment for two sites with differing parent material on the Monongahela National Forest.

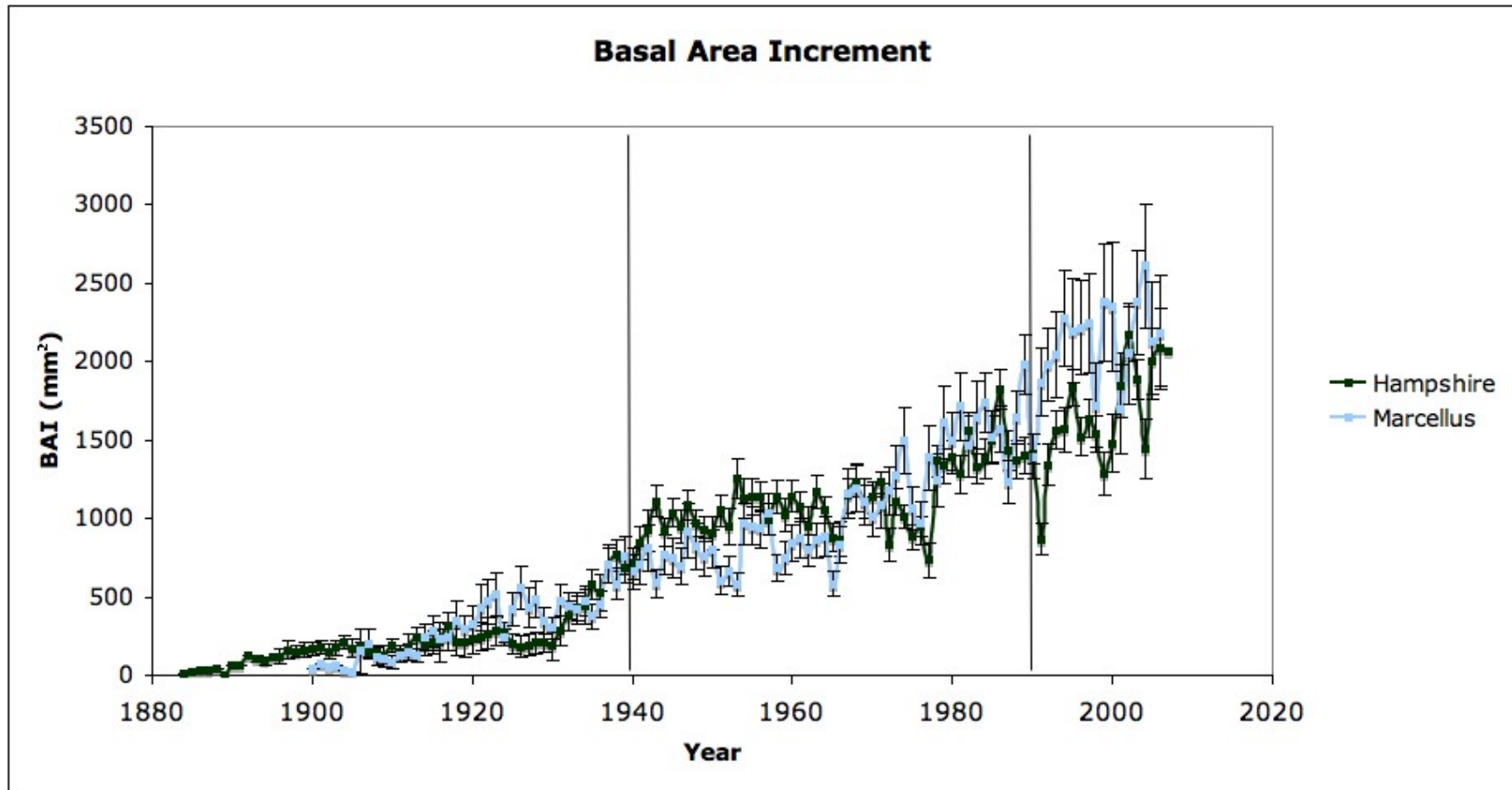


Figure 5-2: Basal area increment calculated from tree cores for two sites with differing parent material on the Monongahela National Forest

The decline and subsequent flattening of RW on both sites around the mid-1960s may be indicative of a sustained decrease due to pollution (Schweingruber, 1983). Many of the documented effects of AD, including base cation leaching, Al toxicity, and stress related to N-saturation are cumulative. These AD impacts may have started to negatively affect the stand around this time. The decline is sustained for multiple decades, implying it is not in response to annual climactic variations. Although other factors such as droughts during the 1960's could have affected RW and BAI, scientists do not agree on the possible simultaneous effects of drought and AD. It appears that drought and acid deposition may work either synergistically, increasing site stress, or drought may ameliorate the impact of AD because of less input (Long *et al.*, 1997; Demchik and Sharpe, 2000).

Since the implementation of the 1990 CAAA, AD-related pollution emissions have declined (Driscoll *et al.*, 2001b). While levels of N and S deposition on the MNF are still elevated above pre-AD conditions, it is possible that resilient stands have somewhat recovered from peak AD conditions as shown by the divergence in BAI of the two stand after 1990. While analysis of a broader range of sites would have made it possible to further investigate the relationship between soil factors with basal area increment (Duchesne *et al.*, 2002), comparison of these two sites suggests that the Marcellus site has more potential for acid neutralization through cation exchange, and may be a more resilient system. RW and BAI results suggest that the Marcellus site has, since 1990, returned to pre-AD conditions of growing at a faster rate than the Hampshire site.

Conclusions

The dendrochronology of two sites with different parent material showed that similar environmental factors were affecting basal area increment during the 50-year period from 1940 to 1990; however, the pre-AD and post-CAAA growth on the Marcellus site suggest that this site is a more resilient system. The relatively flat growth rate during this period may be related to stresses induced by, or associated with, acidic deposition. The influence of different parent materials on these two sites cannot be

determined by this study of dendrochronology alone. Further investigation would be necessary to fully determine the relationship between ring width or basal area increment and soil chemical status.

VI. Use of foliar chemistry as an indicator of site acidification – first year results

Abstract

Forest managers on the Monongahela National Forest in West Virginia need monitoring programs that can effectively evaluate the impacts of management prescriptions on AD-related forest changes. Foliar elemental concentrations are often correlated with soil chemical status and nutrient availability. Therefore, foliar chemistry might be used as a monitoring technique to measure the effects of acid deposition (AD) in forested systems. *Acer saccharum* and *Quercus rubra* seedlings were planted in native soil from three parent materials on the Monongahela National Forest. These soils were amended with lime, sulfur, or left at ambient pH. After one growing season, *Acer saccharum* growth factors were correlated with foliar Ca concentration. Second-season growth and foliage values will be used for final analysis and comparison with foliage and soils trends adjacent to eight long-term monitoring plots on the Monongahela National Forest. Foliar elemental concentrations varied between *Acer saccharum* and *Quercus rubra*. On these plots, nutrient concentrations were compared to periodic mean annual volume increment growth for the period from 1989 to 2000. Generally, *Quercus rubra* foliar Ca and Mg concentration decreased on plots growing at below-average rates. Both *Quercus rubra* and *Acer saccharum* foliar elemental concentrations indicate N concentrations elevated from reference levels, and Ca and Mg concentrations lower than reference levels. With further development it may be possible to develop foliage-based monitoring programs on the Monongahela National Forest.

Introduction

Acid deposition (AD) results mainly from fossil fuel combustion, which produces sulfuric acid and nitrous oxides. This pollutant alters elemental reactions with terrestrial and aquatic ecosystems and threatens productivity through soil base cation leaching, Al mobilization, and sulfur and N accumulation (Driscoll *et al.*, 2001c). There is a growing

body of evidence that AD has induced productivity losses (Likens *et al.*, 1996; Schaberg *et al.*, 1997; Horsley *et al.*, 2000). Furthermore, elevated N inputs on the stand may shift composition and leave forests susceptible to frost damage and other stresses such as insect infestation (McNulty *et al.*, 1996; Fenn *et al.*, 1998; Huntington *et al.*, 2000; Gress *et al.*, 2007).

Land managers are interested in adaptively managing for the effects of AD (USDA Forest Service, 2006). To achieve this goal, managers must monitor their prescriptions and determine if they are approaching the desired outcome. Soil sampling is a common monitoring tool but can be time-consuming, requires expertise of the field crew, and can be expensive (Palmer *et al.*, 2002); therefore, alternative sampling methods may be useful. Foliar analysis has been shown to be a viable method for measuring changes in ecosystem nutrient availability (i.e. Boerner, 1984; Aber *et al.*, 1993; Kogelmann and Sharpe, 2006). Forest ecosystems experiencing N saturation are expected to have elevated N and P, and lowered lignin concentrations in foliage (Aber *et al.*, 1989). Documented changes in foliage concentrations include a study by Aber *et al.* (1993), where after three years of chronic N additions green foliar N concentrations in pines and hardwoods both increased after the second year of experimental treatment. After four years of ammonium sulfate treatment *Acer saccharum* Marsh. (sugar maple), *Acer rubrum* L (red maple), *Fagus grandifolia* Ehrh. (American beech), and *Picea rubens* Sarg. (red spruce) foliage showed significantly higher N concentration than untreated stands. Sugar maple on the treated watershed also had lower Ca and higher Al and Fe foliar concentrations (White *et al.*, 1999). Along a deposition gradient in the southern Appalachian region, foliar nutrient concentrations of American beech, sugar maple, and *Betula alleghaniensis* Britt. (yellow birch) all responded to variations in N deposition (Boggs *et al.*, 2005).

Theoretically, as with elevated N inputs, increased mobilization of base cations in the soil system due to acidification would increase base cation uptake by vegetation, and therefore higher concentrations of cations in foliage; however, if the uptake process is impeded by Al or if leaching has reduced base cation availability in the soil this will not be the case (Johnson, 1992b). Bailey *et al.* (2004) found that in declining sugar maple stands, foliar Ca and Mg concentrations were correlated with soil base cation availability.

In another Pennsylvania study, over 35% of the variability of sugar maple decline could be related to foliage Mg, Mn and Mg/Mn ratios (Horsley *et al.*, 2000). In this case, foliar concentrations could be used to delineate the landscape into areas of inadequate base cation supply. The correlation between foliage concentration and soil chemistry has been found to be valid through 0.5 m of soil depth (Drohan *et al.*, 2002).

Foliar chemistry may also be used to monitor the effectiveness of mitigation treatments. On a liming study in Canada, sugar maple foliage Ca and Mg concentrations remained elevated even ten years after treatment on limed versus control plots (Moore and Ouimet, 2006). Furthermore, potted seedling studies can be useful in further discerning the relationship between soil chemistry and foliar nutrients. Sugar maple is considered to be highly sensitive to decline due to acidification, and it may be one of the most responsive species in soil acidification studies as well (Hicks, 1998; St.Clair and Lynch, 2005). A study of potted sugar maple was used to determine threshold toxicity levels to Mn at which the individuals exhibit detrimental physiological responses (McQuattie and Schier, 2000). Potted tree studies have also shown that red oak productivity declines if soil Ca/Al levels drop below 4.0 (Decker and Boerner, 1997).

The applicability of foliar nutrients as an indicator of site acidity status may be useful for the Monongahela National Forest (MNF) to achieve monitoring objectives relative to AD. Therefore, our objectives were to 1) determine if red oak and sugar maple seedlings in pots grow differently when planted in soils derived from three parent materials at ambient pH or when limed or acidified, and 2) determine if these growth responses would be correlated with differences of foliar chemistry after one growing season. Additionally, 3) use the relationships found in potted seedling study as a basis for interpreting foliar nutrient content differences across an acidity gradient on the MNF. We hypothesized that seedlings grown in acidified pots will show increased mortality, higher levels of foliar Al and Mn, and lower levels of foliar Ca and Mg after two growing seasons while trees grown in limed pots will have the opposite responses. Also, we hypothesized that the foliar chemistry of both species would be related to soil chemistry and productivity. Furthermore, we hypothesized that the responses of potted seedlings could be applied in the field where foliar chemistry samples will be related to soil chemistry and growth on Forest Inventory and Analysis plots.

Methods

Pot study

Soil from the surface horizon was sampled over Mauch Chunk, Chemung, and Pottsville formations. These parent materials were selected because they are considered to be representative of the broad range of parent material that exists on the Monongahela National Forest (MNF). Of these parent materials, Mauch Chunk is most calcareous and Pottsville is least calcareous. All three sampling locations were in the northeastern portion of the MNF near Parsons, West Virginia. Samples were obtained in March of 2006 within a two-day period and transported to Blacksburg, VA for treatment.

Soils were treated to achieve one of five treatments: ambient, three-times limed, limed, three-times acidified, and acidified (Table 6-1). There were no additions to the ambient treatment. The lime treatment was achieved by adding $\text{Ca}(\text{OH})_2$ to the soil and mixing it thoroughly. The SMP buffer was used to determine the level of lime treatment, and applying equivalent $\text{Ca}(\text{OH})_2$ to achieve the desired pH (Sims, 1996). To determine the amount of powdered sulfur needed to further acidify soils, we incubated samples with various levels of S for one week, measured change in soil pH, and used these calculations to apply the amount necessary to reach our pre-determined level of acidity. After treatment, all soils were incubated outdoors for one summer and then stored for the winter and spring.

In early April of 2007 soils were removed from storage and five replicates of 1-year old red oak and sugar maple seedlings were planted in each soil treatment. Seedlings were obtained from a nursery in southwest Virginia, and kept cool and moist until planting. After planting, each pot was covered with wood mulch and then placed in a fenced garden about 6.5 kilometers north of Blacksburg, VA, for the duration of the growing season.

Table 6-1: Liming and acidification treatments for each soil

	Mauch Chunk	Chemung	Pottsville
Ambient	--	--	--
3 x Limed	N/A	6.96 g Ca(OH) ₂ kg ⁻¹ soil	10.4 g Ca(OH) ₂ kg ⁻¹ soil
Limed	2.71 g Ca(OH) ₂ kg ⁻¹ soil	2.32 g Ca(OH) ₂ kg ⁻¹ soil	3.48 g Ca(OH) ₂ kg ⁻¹ soil
3 x Acidified	N/A	32.1 g S m ⁻²	19.1 g S m ⁻²
Acidified	10.7 g S m ⁻²	10.7 g S m ⁻²	6.35 g S m ⁻²

Total rain in Blacksburg between April 1, 2007 and August 31, 2007 was 35.6 centimeters; the temperature ranged from -6.1 to 35.6 degrees C and average temperature was 18 degrees C. Trees received supplemental water to keep soil moist throughout the growing season.

Initial tree height and diameter at root collar (diameter) were measured on the day of planting. These measurements were repeated on August 5, 2007 when soils were sampled by removing about 50 grams from each pot. On the same day foliage was sampled by removing about 5 leaves from each tree. Soils and foliage of replicates were composited by treatment and species. When possible an equal number of leaves was sampled from each tree within each treatment. If one tree produced no leaves, or fewer leaves, we adjusted the number sampled from the other trees within the treatment to have an amount sufficient for analysis. Soils were air-dried and sieved through 2 mm mesh, and stored at room temperature until analysis. Foliage was dried at 65 deg, ground through 1 mm mesh, and stored at 65 deg until analysis.

Soil pH was measured in water, and samples were analyzed for exchangeable cations using 0.01 M SrCl₂ (Joslin and Wolfe, 1989; Sharpe and Sunderland, 1995). Thirty mL of SrCl₂ were added to 10 g of soil and shaken for 30 min. The mixture was centrifuged for 15 min and the supernatant was filtered through a #2 Whatman filter. Filtrate was refrigerated at 4 deg C until elemental concentrations were determined using an Inductively Coupled Plasma spectrometer.

Foliar nutrients were measured using an acid digest. Five-tenths of a g of foliage were burned at 450 deg C for 24 hours. Ten mL of 10% HCl was added to the ash, mixed, and allowed to settle for two hours. Forty mL of water was then added to the digest and the solution was filtered through a #1 Whatman filter. Filtrate was refrigerated

at 4 degrees C until elemental concentrations were determined using an Inductively Coupled Plasma spectrometer.

Foliar nutrient concentrations were correlated with seedling diameter growth, total shoot growth, and number of leaves as well as with results from soils analyses.

Field study

We used Forest Inventory and Analysis (FIA) plots as sampling locations so that we could relate soil chemical characterizations with growth values. The FIA program is a national monitoring network, with plots located across the country on all land usages (i.e. public, non-governmental, corporate, individual, Native American) (USDA Forest Service, 2007). Each plot is re-sampled every five years, so that within each state 20% of the plots are measured each year. Ground-plot measurements are taken over three 0.017-ha plots arranged around another 0.017 ha center-plot.

Foliage was sampled on ten FIA plots on the Monongahela National Forest (MNF). Plot periodic mean annual volume increment (PMAVI) from 1989 to 2000 ranged from -4.9 to 5.2 m³ha⁻¹yr⁻¹. Aspect ranged from 7 to 309 degrees, elevation ranged from 713 to 1262 m, and slope ranged from 10 to 52%. These sites spanned a range of parent material type on the MNF. Northern red oak site index (base age 50) ranged from 54 to 90, and average stand age ranged from 57 to 80 years old. Sugar maple and northern red oak were sampled on any plot where they existed. Three red oaks on each of eight plots were sampled, and three sugar maples on each of four plots were sampled. Shoots from the top half of the canopy were shot down with a shot gun. Foliage was sampled between the last two weeks of July and first two weeks of August 2006. Samples were dried at 65 deg C, ground through 1 mm mesh, and stored at 65 deg C until analysis. Elemental content was determined in the same method as the potted study foliage. Soils were also collected and analyzed similarly to the potted study soils at all plots where foliage was sampled. To determine the relationship between foliar and soil nutrient content we ran correlation analyses and considered relationships significant at $p \leq 0.1$.

Results

Pot Study

Acidification and liming treatments created significant differences among pH levels as well as concentration of soil Al, Ca, K and Mn. Final pH levels ranged from 3.4 to 7.7 in Mauch Chunk soils, 3.0 to 7.9 in Chemung soils, and 2.4 to 8.2 in Pottsville soils (Table 6-2). Average Al concentration ranged from 0.015 to 2.3 mmol₊ mg soil⁻¹ in Mauch Chunk Soils, 0.018 to 10.1 mmol₊ mg soil⁻¹ in Chemung soils, and 0.0001 to 7.3 mmol₊ mg soil⁻¹ in Pottsville soils. Average Ca concentration ranged from 5.6 to 36.8 mmol₊ mg soil⁻¹ in Mauch Chunk soils, 5.3 to 9.5 mmol₊ mg soil⁻¹ in Chemung soils, and 3.9 to 72.1 mmol₊ mg soil⁻¹ in Pottsville soils.

Treatments affected first-year shoot growth and final diameter growth of seedlings (Table 6-3). Across all treatments and parent materials sugar maple shoot growth was positively correlated with foliar Ca/Al ($p = 0.054$). Number of leaves per tree was positively correlated with foliar Ca ($p = 0.042$) and Ca/Al ($p = 0.034$) (Figure 6-1). Tree diameter growth was positively correlated with foliar Ca ($p = 0.006$) (Figure 6-1). Across all treatments and parent materials northern red oak growth values were inconsistently correlated with foliar elemental concentrations.

For both sugar maple and red oak, many foliage and soil nutrients were correlated (Table 6-4). Sugar maple foliar Ca and Ca/Al ratio were positively correlated with soil pH ($p = 0.05$ and < 0.001 , respectively), and foliar Al and Mn were negatively correlated with soil pH ($p = 0.05$ for both). Red oak foliar Ca and Ca/Al ratio were positively correlated with soil pH ($p < 0.001$ for both) and Al and Mn were negatively correlated with soil pH ($p = 0.04$ and 0.07 , respectively).

Sugar maple foliar P was positively correlated with soil Ca/Al ratio ($p = 0.06$). Red oak foliar Al and Mn were negatively correlated with soil Ca/Al ratio ($p = 0.06$ and 0.09 , respectively), and foliar Ca/Al and soil Ca/Al were positively correlated ($p = 0.004$). Sugar maple Al and Mn foliage and soil nutrient levels were positively correlated. Red oak Ca and Mn foliage and soil nutrient levels were positively correlated.

Table 6-2: Influence of soil treatment on soil pH and element concentrations

	pH	Al	Ca	K	Mg
	------(mmol+ mg soil ⁻¹)-----				
MC Ambient	4.9	0.247	5.610	0.454	1.297
MC Acidified	3.4	2.302	9.666	0.7634	2.105
MC Limed	7.7	0.015	36.799	0.431	0.529
C Ambient	4.8	0.576	5.417	0.707	1.610
C 3x Acidified	3.0	10.09	5.351	0.442	1.420
C Acidified	3.6	3.59	9.486	0.934	2.341
C 3x Limed	7.9	0.018	36.66	0.467	0.309
C Limed	7.7	0.019	37.15	0.454	0.343
P Ambient	3.3	1.240	3.916	0.451	1.438
P 3x Acidified	2.4	7.237	9.677	0.376	1.357
P Acidified	2.9	1.68	4.656	0.448	1.134
P 3x Limed	8.2	0.0047	72.12	0.481	5.744
P Limed	7.9	0.00095	27.95	0.164	1.89

Table 6-3: Seedling diameter and height measurements for potted study. Soils from Mauch Chunk parent material (MC), Chemung parent material (C), and Pottsville parent material (P).

	Average Diameter Growth (mm)	Average Shoot Growth (cm)	Average Leaves per Tree (#)
MC Ambient - Red oak	1.1 ± 0.26	31 ± 9.4	42
MC Acidified - Red oak	1.8 ± 0.49	56 ± 16	68
MC Limed - Red Oak	0.66 ± 0.08	9.2 ± 3.7	17
C Ambient - Red oak	1.6 ± 0.54	29 ± 11	44
C 3x Acidified - Red oak	0.17 ± 0.12	25 ± 12	15
C Acidified - Red oak	1.3 ± 0.38	56 ± 13	56
C 3x Limed - Red oak	0.67 ± 0.14	18 ± 4.5	23
C Limed - Red oak	0.52 ± 0.22	12 ± 4.7	21
P Ambient - Red oak	1.1 ± 0.09	18 ± 2.6	22
P 3x Acidified - Red oak	0.28 ± 0.09	9.1 ± 3.8	15
P Acidified - Red oak	1.1 ± 0.28	20 ± 7.6	33
P 3x Limed - Red oak	0.34 ± 0.08	6.7 ± 1.7	17
P Limed - Red oak	0.43 ± 0.08	9.1 ± 2.2	21
MC Ambient - Sugar maple	0.01 ± 0.56	17 ± 4.0	20
MC Acidified - Sugar maple	0.92 ± 0.20	18 ± 5.6	22
MC Limed - Sugar maple	1.2 ± 0.32	30 ± 2.5	23
C Ambient - Sugar maple	1.0 ± 0.33	28 ± 7.9	21
C 3x Acidified - Sugar maple	0.61 ± 0.34	18 ± 7.5	12
C Acidified - Sugar maple	1.1 ± 0.33	20 ± 4.5	17
C 3x Limed - Sugar maple	2.1 ± 0.43	26 ± 5.3	34
C Limed - Sugar maple	0.69 ± 0.23	24 ± 8.3	18
P Ambient - Sugar maple	0.26 ± 0.33	22 ± 6.5	16
P 3x Acidified - Sugar maple	0.07 ± 0.15	13 ± 2	10
P Acidified - Sugar maple	0.78 ± 0.25	17 ± 5.0	16
P 3x Limed - Sugar maple	0.91 ± 0.10	22 ± 9.8	21
P Limed - Sugar maple	1.2 ± 0.54	18 ± 7.6	17

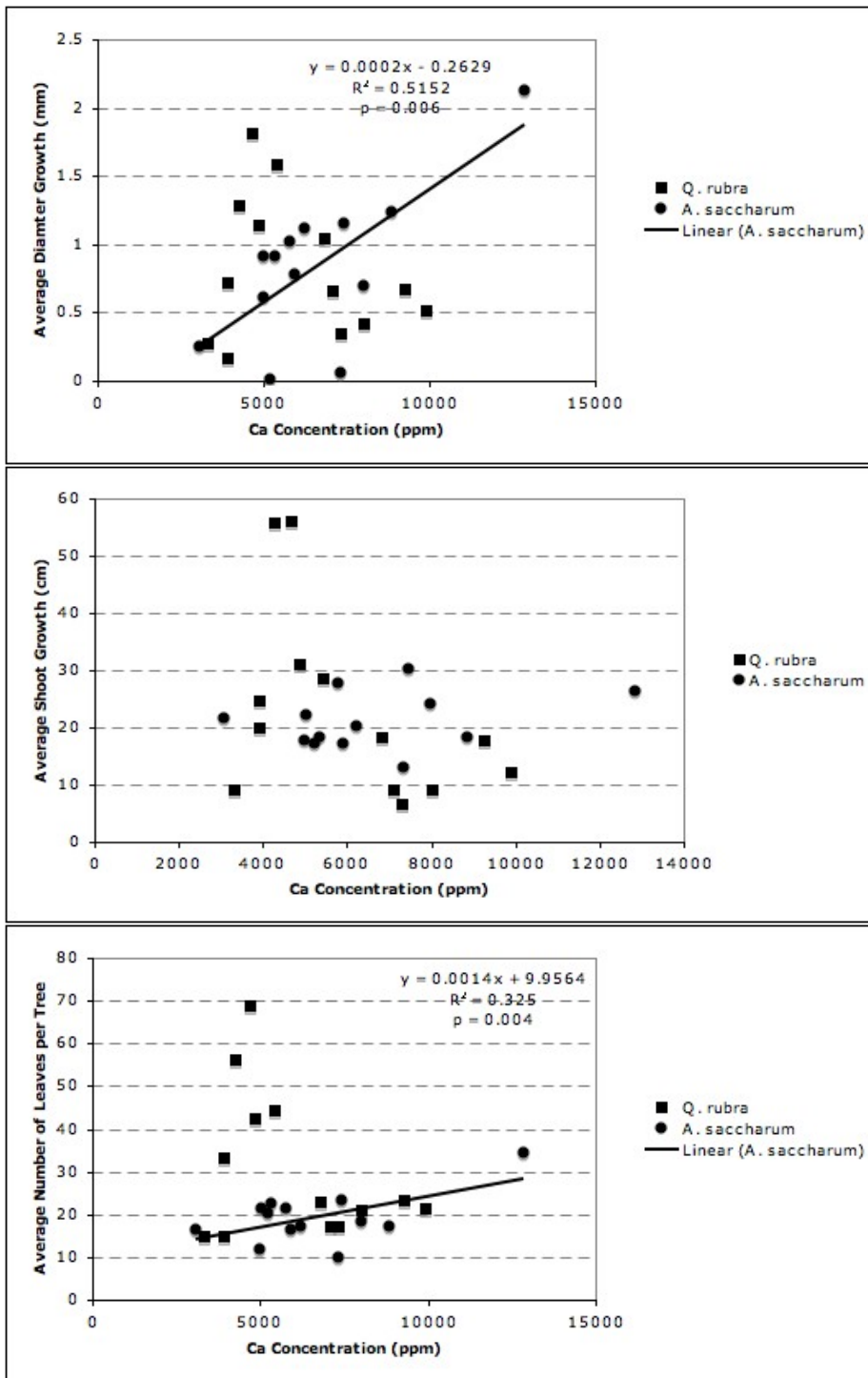


Figure 6-1: Relationships between tree growth characteristics and foliar Ca concentration for sugar maple and red oak

Table 6-4: Correlations between foliar and soil and nutrients for A) Sugar maple and B) Northern red oak seedlings

	Soil Al	Soil Ca	Soil K	Soil Mg	Soil Mn	Soil Na	Foliar Al	Foliar Ca	Foliar K	Foliar Mg	Foliar Mn	Foliar Na	Foliar P	Fol Ca/Al	
A	Soil Al	1	-0.4329	-0.1634	-0.1651	0.379	-0.1719	0.7246	-0.2259	0.2904	0.5802	0.3101	0.7181	-0.0285	-0.7476
	Soil Ca		1	0.0903	0.7258	-0.4469	0.6716	-0.358	0.1718	-0.5698	-0.4588	-0.4688	-0.2546	0.0397	0.7557
	Soil K			1	0.4645	0.6213	0.4951	0.1681	-0.4077	-0.1623	-0.2925	0.6839	-0.4121	-0.5706	-0.1773
	Soil Mg				1	0.0026	0.9192	-0.1131	-0.3859	-0.5588	-0.3402	-0.0074	-0.2262	-0.3548	0.2401
	Soil Mn					1	-0.0224	0.5355	-0.3796	0.1225	0.1472	0.9434	-0.0886	-0.384	-0.6952
	Soil Na						1	-0.1803	-0.4876	-0.6619	-0.4644	-0.0171	-0.2514	-0.5224	0.1881
	Foliar Al							1	-0.0846	0.6082	0.7124	0.6348	0.5215	0.0719	-0.6977
	Foliar Ca								1	0.3304	0.274	-0.3419	0.224	0.8568	0.5012
	Foliar K									1	0.8457	0.3165	0.3877	0.4712	-0.4127
	Foliar Mg										1	0.2828	0.7184	0.4854	-0.5369
	Foliar Mn											1	-0.0477	-0.3261	-0.7071
	Foliar Na												1	0.3163	-0.3972
	Foliar P													1	0.3411
	Fol. Ca/Al														1
B	Soil Al	1	-0.3983	0.2143	0.2121	0.2835	0.0854	0.2378	-0.5672	0.0421	-0.315	0.0299	0.3503	0.0596	-0.4309
	Soil Ca		1	-0.2692	-0.1357	-0.5201	-0.064	-0.5228	0.8161	0.2082	0.317	-0.7137	-0.2495	0.4917	0.7748
	Soil K			1	0.1532	0.7407	0.7639	0.449	-0.3503	-0.1045	-0.2694	0.4834	0.1065	-0.4317	-0.5191
	Soil Mg				1	0.3849	0.5562	-0.0816	-0.3385	0.0814	0.0731	0.1264	-0.181	-0.126	0.114
	Soil Mn					1	0.6166	0.6554	-0.5385	-0.095	-0.4573	0.8197	0.0176	-0.5747	-0.542
	Soil Na						1	0.3451	-0.2168	-0.138	-0.0109	0.2761	-0.1458	-0.3813	-0.2187
	Foliar Al							1	-0.5348	-0.279	-0.5249	0.5692	0.0663	-0.5251	-0.7543
	Foliar Ca								1	0.312	0.4803	-0.4948	-0.1859	0.389	0.8133
	Foliar K									1	0.5292	-0.1931	0.335	0.6459	0.3114
	Foliar Mg										1	-0.3022	0.0894	0.6144	0.4104
	Foliar Mn											1	0.0083	-0.629	-0.5835
	Foliar Na												1	0.4506	-0.1634
	Foliar P													1	0.4317
	Fol. Ca/Al														1

Field Study

To evaluate the relationship between foliar elemental concentrations and stand growth we collected foliage from 10 FIA sites on the Monongahela National Forest. Periodic mean annual volume increment (PMAVI) between 1989 and 2000 ranged from 4.9 to 5.2 m³ha⁻¹yr⁻¹ on these plots. Elemental concentration varied widely between species (Table 6-5; Figure 6-2). Average sugar maple elemental concentration was 54 mg kg⁻¹ Al, 6553 mg kg⁻¹ Ca, 8460 mg kg⁻¹ K, 1365 mg kg⁻¹ Mg, 1323 mg kg⁻¹ P, 2.8% N, and 54% C. Average northern red oak elemental concentration was 58 mg kg⁻¹ Al, 6002 mg kg⁻¹ Ca, 8747 mg kg⁻¹ K, 1469 mg kg⁻¹ Mg, 1515 mg kg⁻¹ P, 3.0% N, and 54% C.

Table 6-5: Range of nutrient concentrations for two species on FIA plots. Values are minimum, maximum, mean, and standard error.

	Al	Ca	K	Mg	P	N	C
	------(ppm)-----						
N. red oak	39	4353	6893	1138	1303	25578	516082
	90	7635	10868	2113	1755	36284	549238
	58 ± 6	6002 ± 428	8747 ± 420	1469 ± 117	1515 ± 59	29164 ± 1515	537694 ± 4199
Sugar Maple	31	4023	7210	1030	1211	25646	523760
	124	11685	9768	2026	1433	30126	554302
	54 ± 23	6553 ± 1795	8460 ± 527	1365 ± 232	1323 ± 51	27650 ± 996	536029 ± 6711

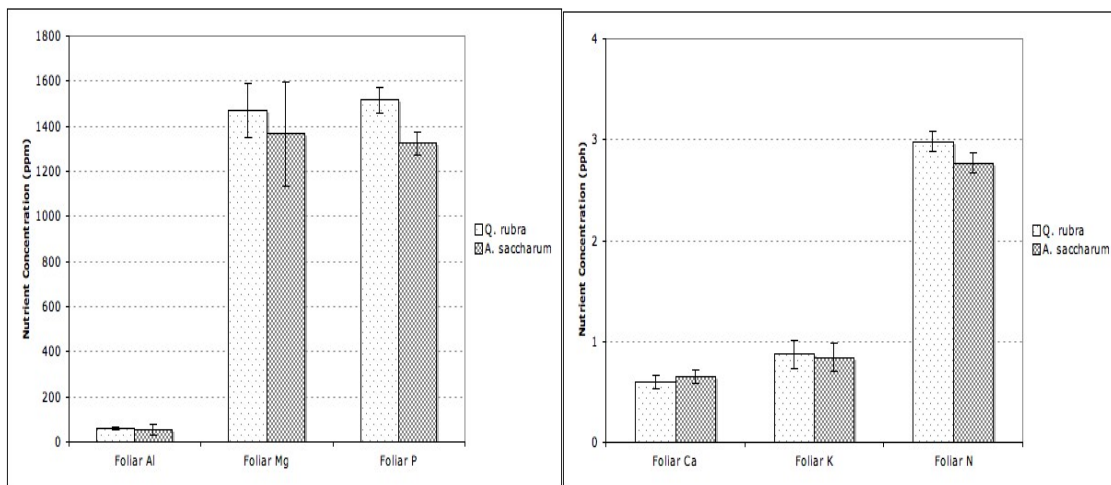


Figure 6-2: Range of foliar nutrients of northern red oak and sugar maple on FIA plots

Periodic mean annual volume increment for all trees on the FIA plots from where red oak and sugar maple were sampled was not significantly related to any elemental nutrient concentrations for sugar maple or red oak; however, there were some trends in the data (Table 6-6; Figure 6-3). Although not statistically significant, the lowest PMAVI was on sites with foliar Ca concentrations of 4000 ppm, which is below reference levels. Average sugar maple foliar K, Ca, and Mg were below reference levels (Table 6-6). Average northern red oak foliar N and K concentrations were higher than reference levels, and increased on plots with higher PMAVI. Average northern red oak P, Ca, and Mg concentrations were lower than reference levels, and increased on sites with higher PMAVI.

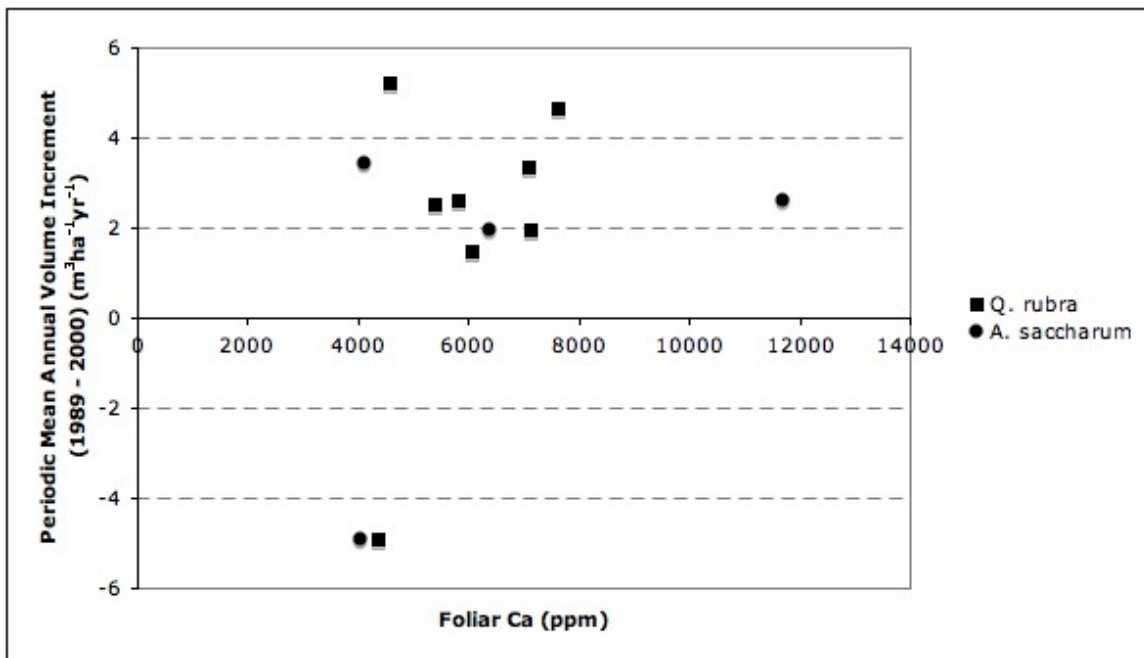


Figure 6-3: Relationship between periodic mean annual volume increment and foliar Ca concentration

Sugar maple foliar element levels were significantly correlated with soil elements. Foliar Al was positively correlated with surface horizon K concentration, and negatively correlated with surface Mg. Foliar Ca was positively correlated with surface pH and subsurface K. Foliar Mg was positively correlated with surface pH and subsurface K.

Northern red oak foliar element levels were significantly correlated with soil elements. Foliar Ca was positively correlated with surface horizon Ca/Al, and negatively correlated with surface Al concentration. Foliar K was positively correlated with surface pH and Ca/Al ratio, and negatively correlated with surface Al and K concentrations. Foliar Mg was positively correlated with surface Ca/Al and Mg/Al.

Table 6-6: Foliar elemental concentrations for red oak and sugar maple grouped by stand periodic mean annual volume increment (Red oak average values ^afrom non-declining stands (Auchmoody and Hammack, 1975; Johnson *et al.*, 1982b); Sugar maple values from ^bnon-declining sugar maple stands in PA (Drohan *et al.*, 2002) and ^cuntreated sugar maple stands in Maine (White *et al.*, 1999)

	Less than 0 m ³ ha ⁻¹ yr ⁻¹	Between 0 to 3 m ³ ha ⁻¹ yr ⁻¹	Over 3 m ³ ha ⁻¹ yr ⁻¹	Reference baseline concentration (ppm)
N. red oak	n = 1	n = 4	n = 3	
Al	40	64	55	
N	25991	28665	32642	22500 ^a
P	1349	1532	1547	1810 ^a
K	8345	8724	8924	7990 ^a
Ca	4353	6089	6435	7520 ^a
Mg	1185	1363	1707	2240 ^a
Sugar maple	n = 1	n = 2	n = 1	
Al	28	79	32	47 ^b
N	26502	29227	25647	15000 ^c
P	1433	1323	1211	907 ^c
K	9768	8322	7210	9412 ^b
Ca	4023	9032	4122	7528 ^b
Mg	1030	1690	1049	1260 ^b

Discussion

The potted seedling study showed that liming and further acidification changed soil acidity values to achieve an extreme gradient of seedling growth conditions. Although in this case the liming treatment probably raised pH above the alkalinity tolerance of northern red oak, sugar maple responded positively to increased pH levels. There were significant relationships between foliar and soil elemental concentrations. For both red oak and sugar maple, foliar Ca, Al and Mn all responded to differences in soil pH. No element was significantly correlated between its foliar and soil

concentrations. Based on other studies, we had expected to see more relationships between individual nutrient concentration in foliage and in soils (i.e. Drohan *et al.*, 2002; St.Clair and Lynch, 2005); however, these relationships may occur in second-year foliar growth. Treatment effects on foliar elemental concentration were less apparent in growth data, in which only sugar maple has begun to exhibit changes in growth due to differences in foliar elemental concentration. The second-year growth and foliage data may provide results that help further understand the relationship between growth, foliar nutrient concentration, and soil acidity.

Foliar nutrient concentrations of red oak and sugar maple on the Monongahela National Forest do not appear to be directly correlated to growth on FIA plots; however there are some trends in the data that suggest that foliar sampling may be possible for AD-related monitoring. Compared to baseline foliar data, red oak foliar concentration of N and K were elevated, while Ca and Mg concentrations were depressed. Red oak foliage on stands growing at less-than-expected rates had lower Ca, Mg, K, P and N concentrations. Sugar maple trends were less apparent, but N and P concentration were above baseline, while Ca and Mg concentrations were below it.

There were some correlations between foliar and soil nutrient levels. For northern red oak, foliar Ca concentration was negatively correlated with surface soil Al concentration, which could be developed as an indicator of AD-related toxicity effects. These trends suggest that further work on the relationship between foliar and soil nutrient levels could be used to create monitoring programs using foliage sampling. The wide range of nutrient levels among species suggests that a monitoring program would need to be limited to a few species, amongst which nutrient level relationships would need to be developed.

Conclusions

Forest managers are interested in using foliar elemental concentrations for AD-specific site monitoring. First-year growth data from an experiment designed to grow red oak and sugar maple in extreme soil pH conditions show that soil treatment can be identified with foliar nutrient concentrations. For both species, foliar Ca, Al, and Mn

were correlated with soil pH. The pot study data reported were preliminary. Second year data are being processed and analyzed for the completion of this experiment. Second-year data are expected to improve the relationships between foliar elemental concentrations and growth of the seedlings. Data from eight long-term monitoring plots on the Monongahela National Forest suggest that foliage had N concentrations elevated above baseline, and Ca and Mg concentrations depressed from baseline. Foliar elemental concentrations of northern red oak were related, although not significantly correlated, with trends in stand periodic mean annual volume increment. With further data it may be possible to develop a foliar monitoring program on the Monongahela National Forest.

VII. Soil Sampling and Lab Analysis Techniques for Acid Deposition Related Monitoring

Abstract

Forest managers in the Appalachian Mountains are concerned about the deleterious effects of acid deposition (AD) on forest health, which include losses in productivity and increased susceptibility to damage from secondary stresses. To meet forest management objectives and guidelines managers must monitor for the effects of acidification and adapt their prescriptions and practices to ensure sustainable productivity. The purpose of this study was to determine the best soil sampling and analysis protocols to monitor forest changes in response to AD. Soils adjacent to 30 Forest Inventory and Analysis sites were sampled using two different protocols and analyzed for a suite of soil chemical indicators, including the use of both SrCl₂ and NH₄Cl non-buffered cation exchange methods. Calcium/aluminum molar ratio of 0 – 10 cm samples was significantly different from A horizon values. Soil pH, effective sum of bases, and sum of bases of 10 – 20 cm samples were significantly different from B horizon samples. A relationship between SrCl₂ and NH₄Cl Ca/Al molar ratio was determined for the two sampling methods. This analysis of sampling and lab methods can be used to create a soils-based monitoring program that specifically addresses the effects of AD across the landscape.

Introduction

Acid deposition (AD) results mainly from fossil fuel combustion, which produces sulfuric acid and nitrous oxides. This pollutant alters elemental reactions with terrestrial and aquatic ecosystems (Driscoll *et al.*, 2001c). Early in AD research, scientists were concerned about the direct effect of acidity on foliage, but this focus has since shifted to the acidification of soils (Van Ranst *et al.*, 2002). The effects on soil include base cation leaching, Al mobilization, and sulfur and N accumulation (Driscoll *et al.*, 2001c), and

there is a growing body of evidence that AD has induced productivity losses (Likens *et al.*, 1996; Schaberg *et al.*, 1997; Adams, 1999; Horsley *et al.*, 2000).

Reductions in sulfate emissions in response to the 1990 Clean Air Act Amendments have reduced associated base cation leaching (Driscoll *et al.*, 2001c). Soils data show changes due to atmospheric deposition. In Pennsylvania soil pH, and Ca and Mg concentrations decreased between 1967 and 1997 (Bailey *et al.*, 2005). However, although ecosystems vary widely in their ability to absorb N, evidence of N saturation continues to be reported in both Europe and the United States (Fenn *et al.*, 1998; Houle, 2006).

Proposed monitoring methods for assessing the effects of AD are as varied as the publications reporting the problem; however, there is some consensus that a valuable monitoring program should include: 1) selection of indicators of change and damage with sufficient signal-to-noise ratio, 2) applicability over large areas, 3) ability to provide services with minimal environmental impact while being cost-effective (Adams *et al.*, 2000; Arp *et al.*, 2001; White, 2004). The standard monitoring program that uses only productivity measurements may not suffice to evaluate the impact of AD across the landscape (Foster *et al.*, 1997; Adams *et al.*, 2000). Instead, the use of soil sampling to characterize acidity and fertility is commonly used; however, there is considerable debate about sampling by depth versus sampling by horizon. Furthermore, there are some questions as to which genetic horizons to sample to adequately capture how AD and the soil system interact (Bailey *et al.*, 2004).

Arguments in support of sampling by genetic horizon are supported by the soil acidity studies that have found soils are highly variable spatially, but differences among horizons are readily detectable (Yanai *et al.*, 2005). These results imply that soil characterization results could be greatly different without careful sampling by horizon. Sampling by genetic horizon may be especially important in rocky soils, which are considered to be more heterogeneous (Bailey *et al.*, 2005). Additionally, the distinct chemical and biological differences among soil horizons will often create great differences in the rate of anion production, consumption, and leaching, all of which are concerns related to AD (Johnson, 1992a). However, because sampling by horizon is expensive and requires general soils knowledge, the Forest Service Forest Health

Monitoring (FHM) program has decided to sample by depth on their plots (Palmer *et al.*, 2002). In a study comparing FHM by-depth methods with by-horizon methods to measure changes in forest soil carbon, Palmer *et al.* (2002) suggest using the depth method at three sub-samples per plot because it can cut costs while still providing valid data for highly variable results.

Selection of soil lab analyses will also influence interpretation of results. Lawrence *et al.* (1997) compared NH_4OAc , KCl , NH_4Cl , and BaCl_2 extracts in removing soil Ca and found no significant differences; however, others argue that a buffered salt method (NH_4OAc at pH 7) overestimates cation exchange capacity and 1.0 M NH_4Cl is the optimum method for measuring CEC of forest soils (Amacher *et al.*, 1990; Skinner *et al.*, 2001). Additionally, because strontium-chloride is considered to be an analytical surrogate for Ca/Al ratio of soil solution, there is debate over which analytical methods are most useful for an AD monitoring program (Edmeades and Clinton, 1981).

Therefore, our objectives were to 1) develop a soil sampling and analysis protocol for monitoring the effects of acid deposition on changes in soil chemistry and forest growth, and 2) to compare the results with those using the FHM sampling protocols. We hypothesized that sampling by depth and by pedogenic horizon would produce the same interpretation for land managers on the Monongahela National Forest. Furthermore, we hypothesized that analysis of pH, Ca/Al molar ratio, effective sum of base, sum of exchangeable bases, and NO_3/NH_4 ratio would produce similar analytical results.

Methods

Sampling Protocols

Soils were sampled at thirty locations throughout the Monongahela National Forest. We used Forest Inventory and Analysis (FIA) plots as sampling locations so that we could relate soil chemical characterizations with growth values. The FIA program is a national monitoring network, with plots located across the country on all land usages (i.e. public, non-governmental, corporate, individual, Native American) (USDA Forest Service, 2007). Each plot is re-sampled every five years, so that within each state 20% of

the plots are measured each year. Ground-plot measurements are taken over three 0.017 ha plots arranged around another 0.017 ha center-plot.

Soils were sampled by two different methods. For the first procedure we followed Forest Service FHM protocols (USDA Forest Service, 2007), in which samples are obtained from 0 – 10 cm and 10 – 20 cm of the mineral soil. This process was repeated at three sub-sample locations adjacent to each FIA plot. This method will hereafter be referred to as the depth method. For the second procedure we dug one narrow soil pit (to 1 m or bedrock) to collect standard profile data for the site. Using the pedogenic data gathered from the pit we collected representative samples from the A and B master horizons from three sub-sample locations adjacent to each FIA plot. This method will hereafter be referred to as the horizon method. All soil samples were collected between July 2006 and August 2007, and were air-dried, sieved through 2-mm mesh and stored at room temperature until analysis.

Laboratory Protocols

Soils were analyzed for a suite of acidity indicators. Soil $\text{pH}_{(w)}$ was determined using 10 g of soil in 20 mL of distilled water (Thomas, 1996). Soil exchangeable cations were measured using three different extractants: 1 N NH_4OAc at pH 7, 0.01 M SrCl_2 , 1 N NH_4Cl . Total cations were determined by exchanging with 1 N NH_4OAc at pH 7 (Amacher *et al.*, 1990). Strontium chloride (0.01 M SrCl_2) (Joslin and Wolfe, 1989; Sharpe and Sunderland, 1995) was used for Ca/Al molar ratio. Thirty mL of SrCl_2 were added to 10 g of soil and shaken for 30 min. The mixture was centrifuged for 15 min and the supernatant was filtered through a #2 Whatman filter. Effective sum of bases was determined by extraction using 1 N NH_4Cl (Amacher *et al.*, 1990). For each of these procedures, filtrate was refrigerated at 4 deg until elemental concentrations were determined using an Inductively Coupled Plasma spectrometer (ICP) (Vista-MIX CCD Simultaneous ICP, Varian, Walnut Creek, CA). Nitrate/ammonium ratio was determined with 2 M KCl exchange (Mulvaney, 1996), and analyzed on an auto-analyzer (Traacs 2000 Analyzing System, Bran & Luebbe, Buffalo Grove, IL). For horizon and depth samples, values were averaged for the three sub-samples for each FIA plot. Total profile calculations used horizon or sample depth and bulk density values. For values

determined through analysis on ICP or auto-analyzer, values below detection limits were assigned a zero.

Method Comparisons

We tested for differences among sampling procedures using Student's t-tests for pH, Ca/Al molar ratio, effective sum of bases, sum of bases, and NO₃/NH₄ ratio. These soil properties are standard measurements and this range of properties provides indicators of soil acidity, toxicity, fertility, cation-buffering, and N-saturation. To further discern the relationship with AD, we compared the correlation strength between these indicators and periodic mean annual volume increment on FIA plots using the horizon and depth sampling methods. Within-sample variation was determined using a Student's t-test. All differences were considered to be significant at $p \leq 0.1$.

Results

Sampling Protocols

Statistical comparisons of pH, Ca/Al molar ratio, effective sum of bases, sum of bases, and NO₃/NH₄ ratio were used to determine differences between and within sampling methods. Average pH values were not significantly different between A horizon and 0 – 10 cm samples (Figure 7-1). Ten to twenty cm sample pH values were significantly lower than B horizon samples. Both sampling by horizon and by depth was effective at detecting significant differences between soil layers, and both followed similar trends in that the deeper soil layer had a higher pH. The relationship between horizon and depth samples for pH was the same for the 0 – 10 cm and A horizon, but the depth method underestimated pH disproportionately along the range of B horizon pH. Correlations between volume mean annual increment (PMAVI) and pH were only significant for B horizon samples ($p = 0.07$).

Average Ca/Al values were significantly higher for 0 – 10 cm samples compared to the A horizon samples, but 10 – 20 cm Ca/Al values were not different from B horizon values (Figure 7-2). Both sampling by horizon and by depth was effective at detecting

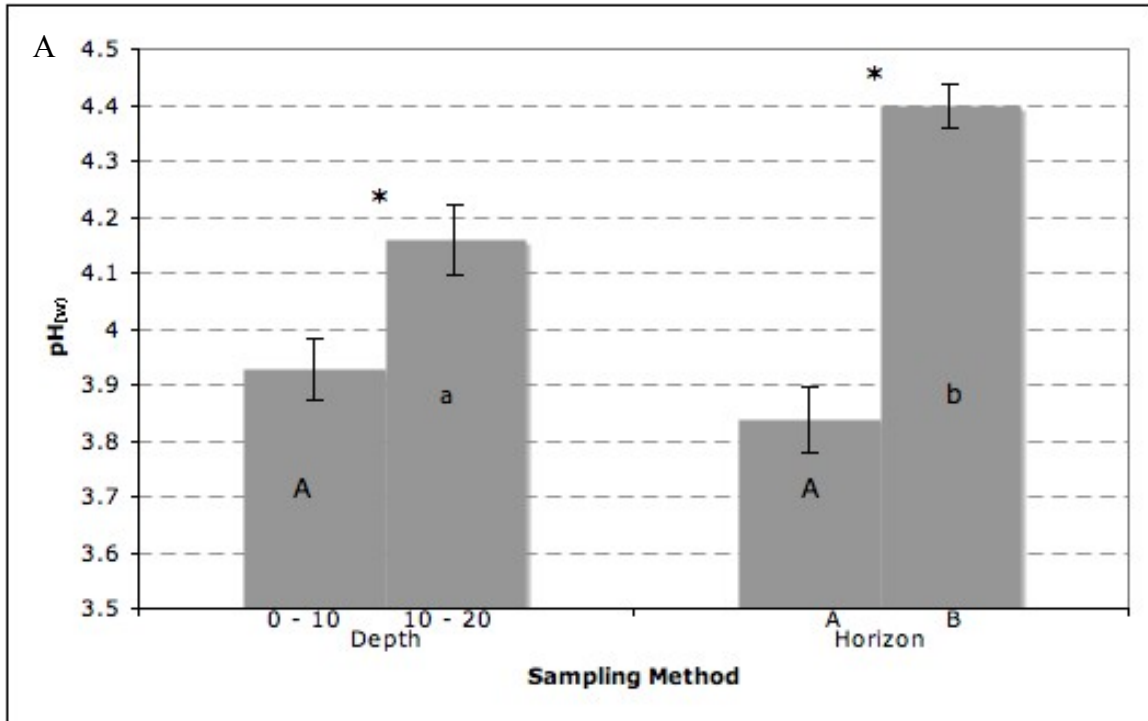
significant differences between soil layers, and the trends were similar between sampling methods in that Ca/Al decreased with depth. The relationship between horizon and depth samples was similar for the surface soil layers, but highly variable for the subsurface layers. Correlations between PMAVI and Ca/Al molar ratio were significant for 0 – 10 samples ($p = 0.02$) and A horizon samples ($p = 0.002$).

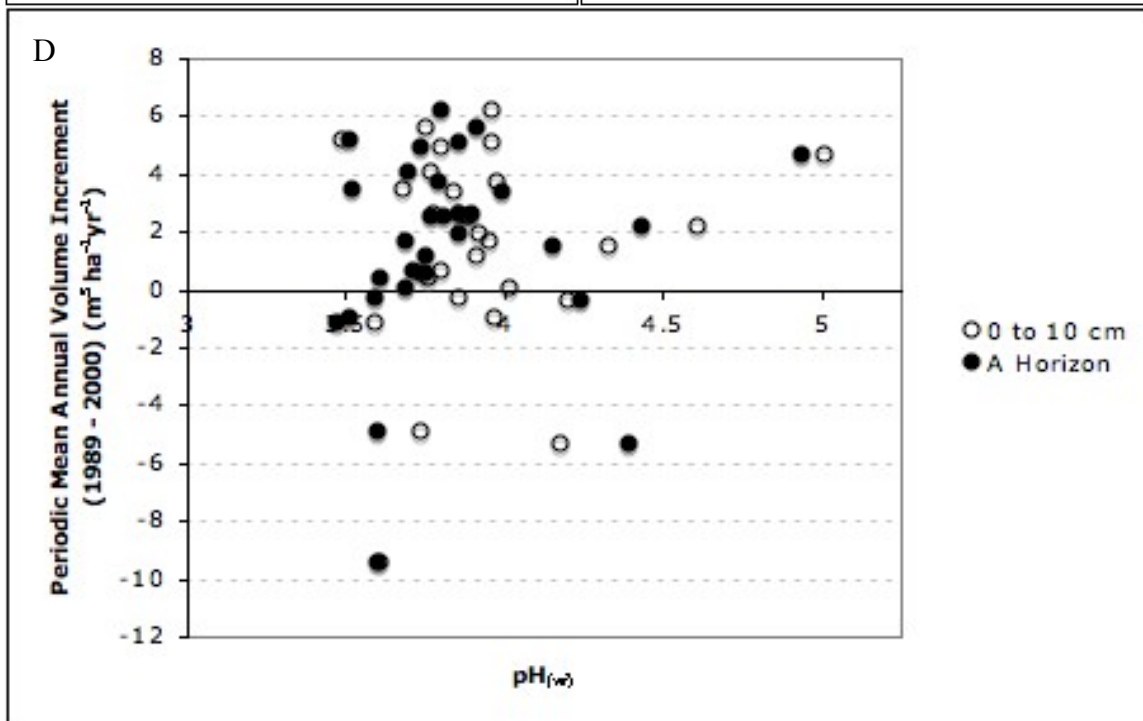
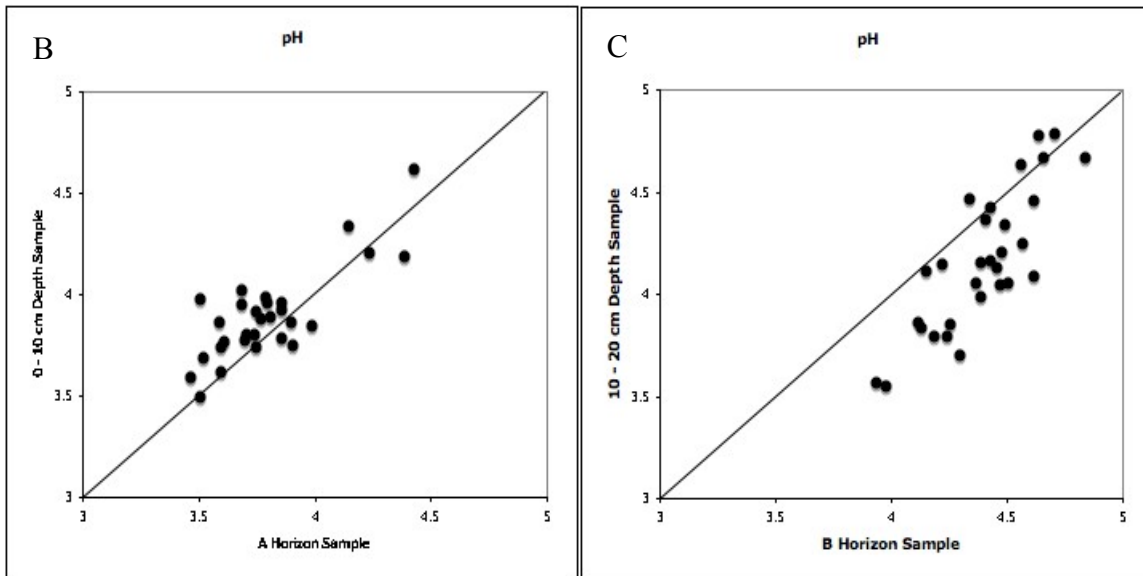
Effective sum of bases values were not significantly different between A horizon and 0 – 10 cm samples, and were significantly lower in 10 – 20 cm samples compared to B horizon samples (Figure 7-3). The relationship between horizon and depth samples for the surface horizons was comparable, but highly variable. The 10 – 20 cm depth sample greatly and disproportionately underestimated effective sum of bases as values increased. Correlations between PMAVI and effective sum of bases were significant for 0 – 10 samples ($p = 0.04$) only.

Sums of bases were not different between A horizon and 0 – 10 cm samples (Figure 7-4). Values for the 10 – 20 cm samples were significantly lower than the B horizon samples. Both horizon and depth sampling showed significant differences between soil layers; however, sum of bases trends were dissimilar between sampling methods. Sampling by depth did not show the same increase in sum of bases with soil depth as sampling by horizon did. The relationship between horizon and depth samples for the surface horizons was comparable, but highly variable. The 10 – 20 cm depth sample greatly and disproportionately underestimated sum of bases. There were no significant correlations between sum of bases and PMAVI.

There were no significant differences in NO_3/NH_4 values between sampling methods, but both showed similar trends of decreasing ratio with depth (Figure 7-5). There was a significant difference within sampling method by horizon, but not by depth. The relationship between horizon and depth samples was highly variable for both surface and subsurface horizon samples, but the 0 – 10 cm sample underestimated NO_3/NH_4 compared to the A horizon more than the 10 – 20 cm sample did compared to the B horizon. There were no significant correlations between NO_3/NH_4 and PMAVI.

Figure 7-1: The effect of different sampling methods on A) on pH values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between pH and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.





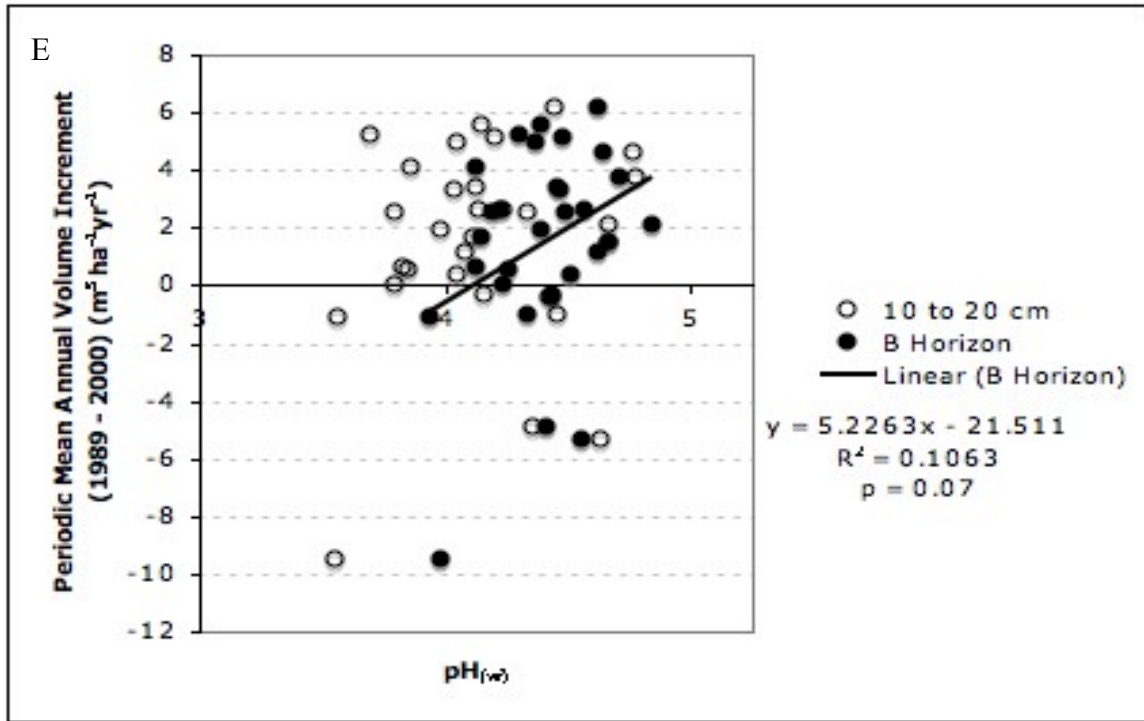
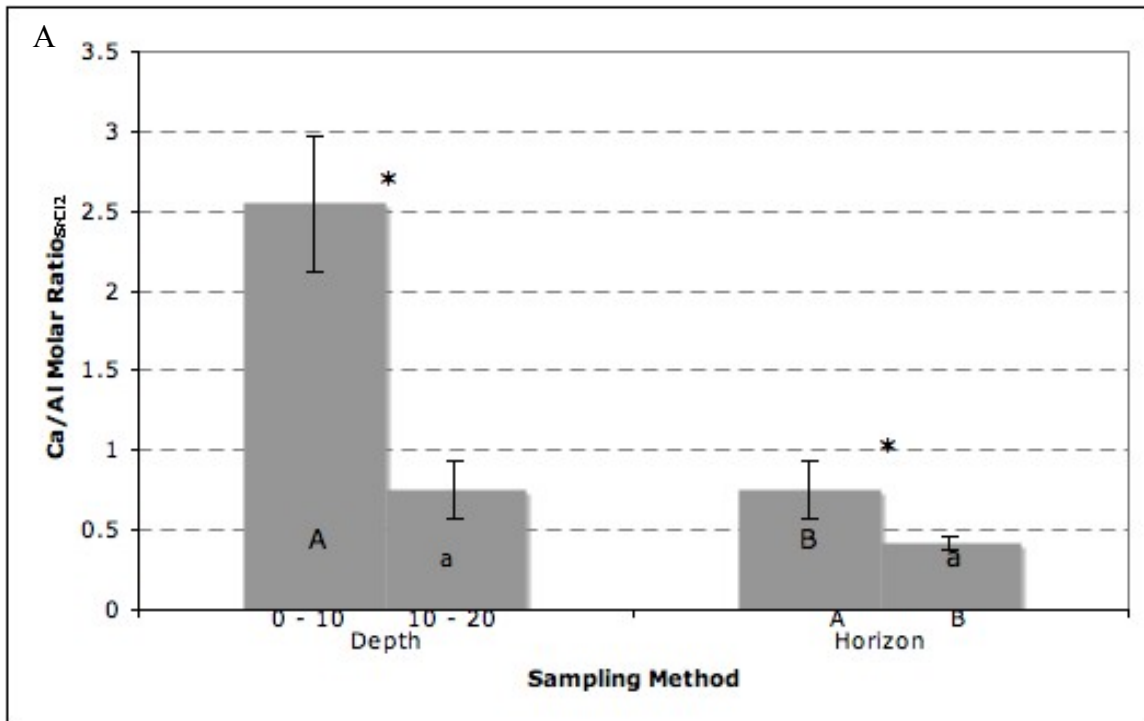
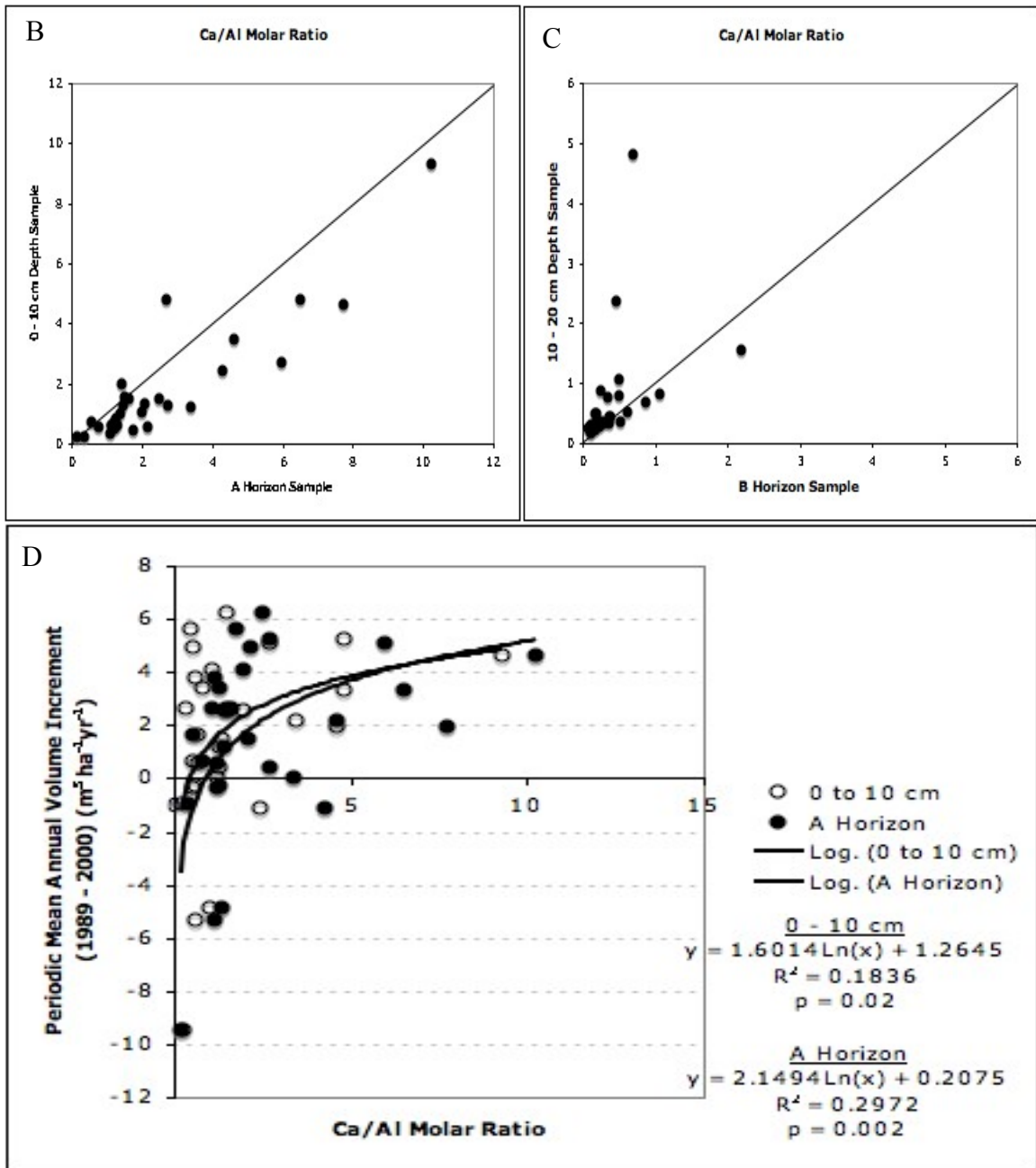


Figure 7-2: The effect of different sampling methods on A) on Ca/Al ratio. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between Ca/Al ratio and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.





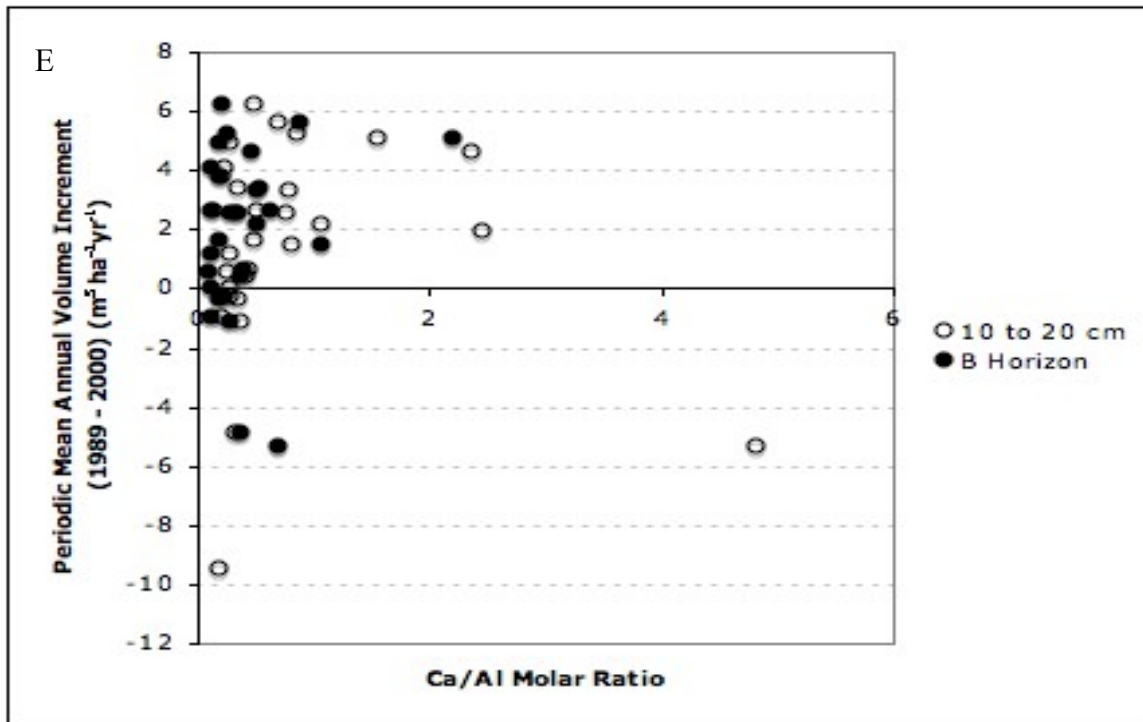
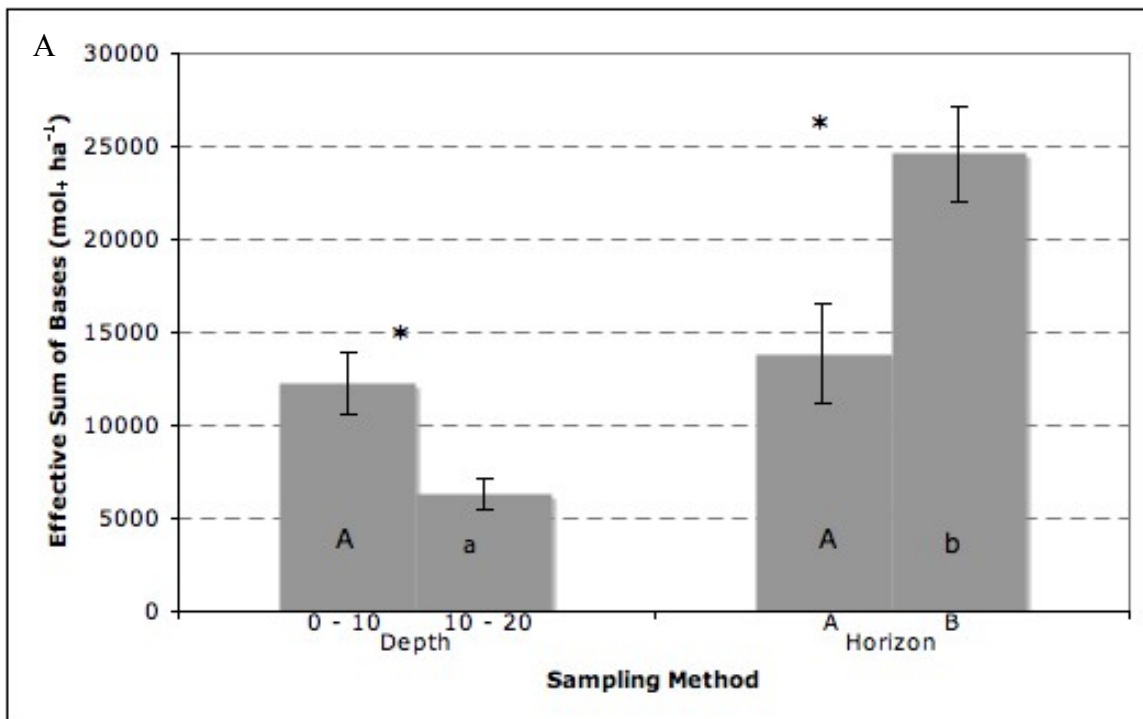
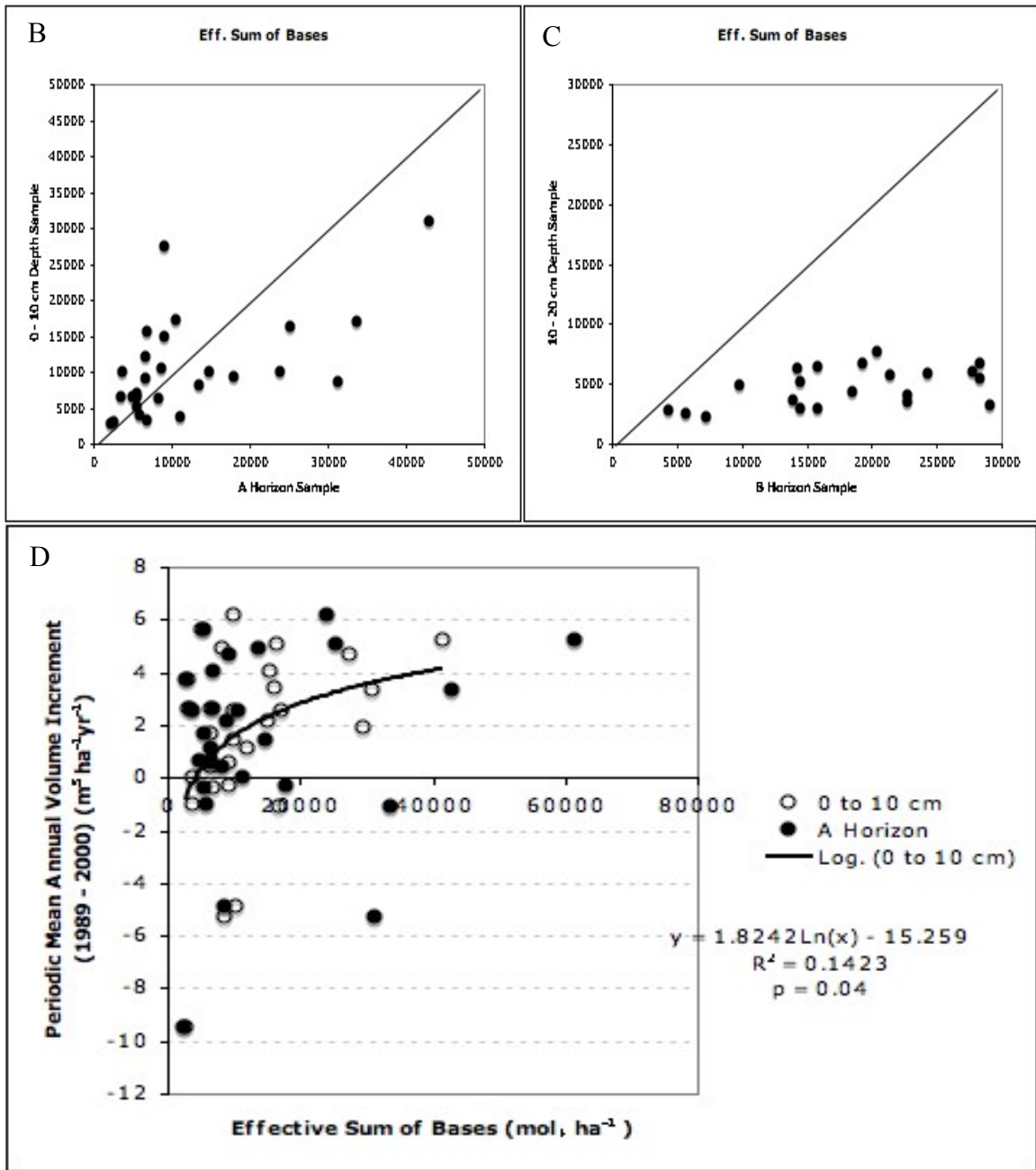


Figure 7-3: The effect of different sampling methods on A) on effective sum of bases values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between effective sum of bases and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.





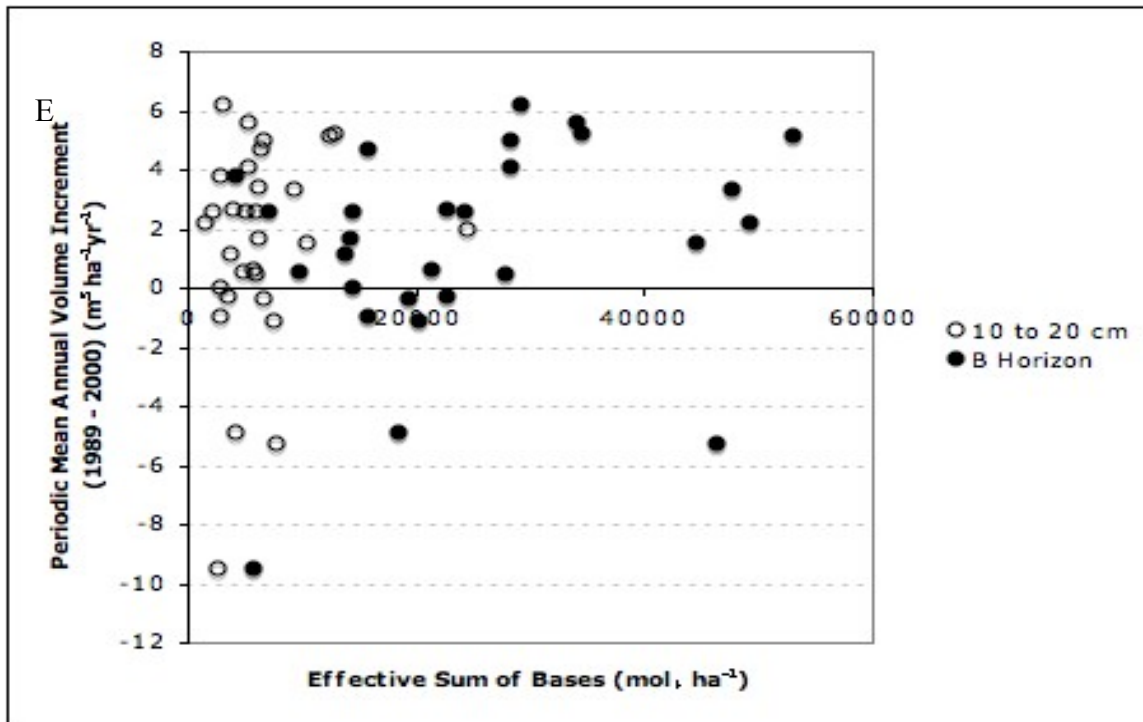
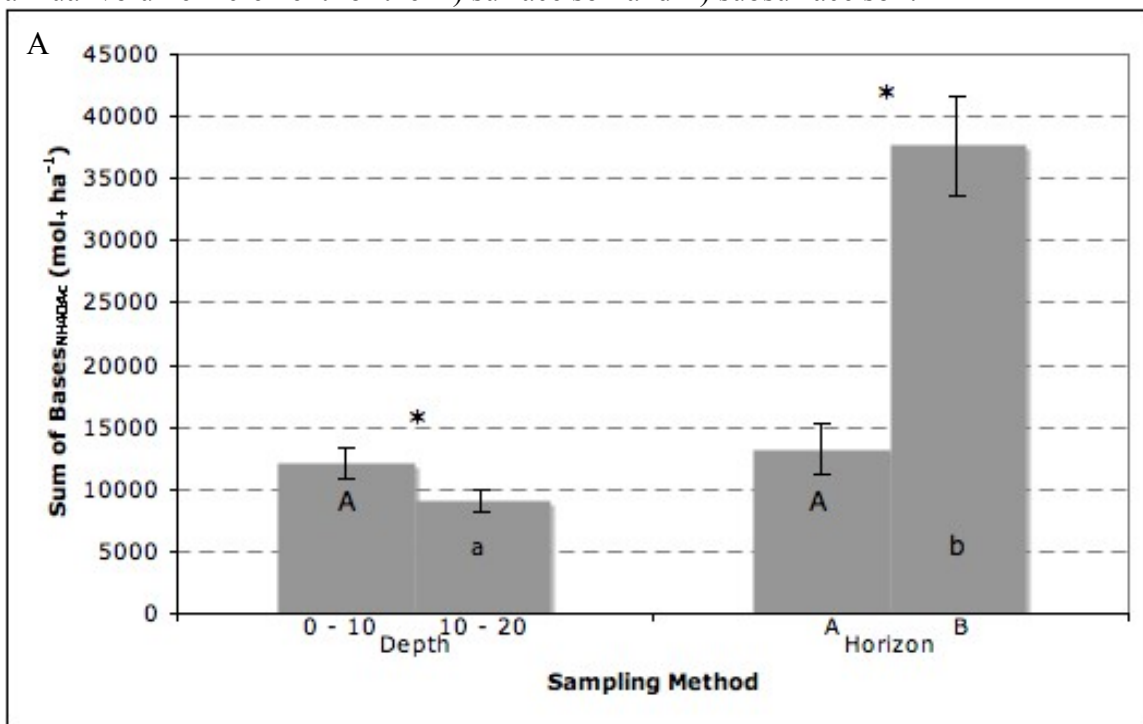
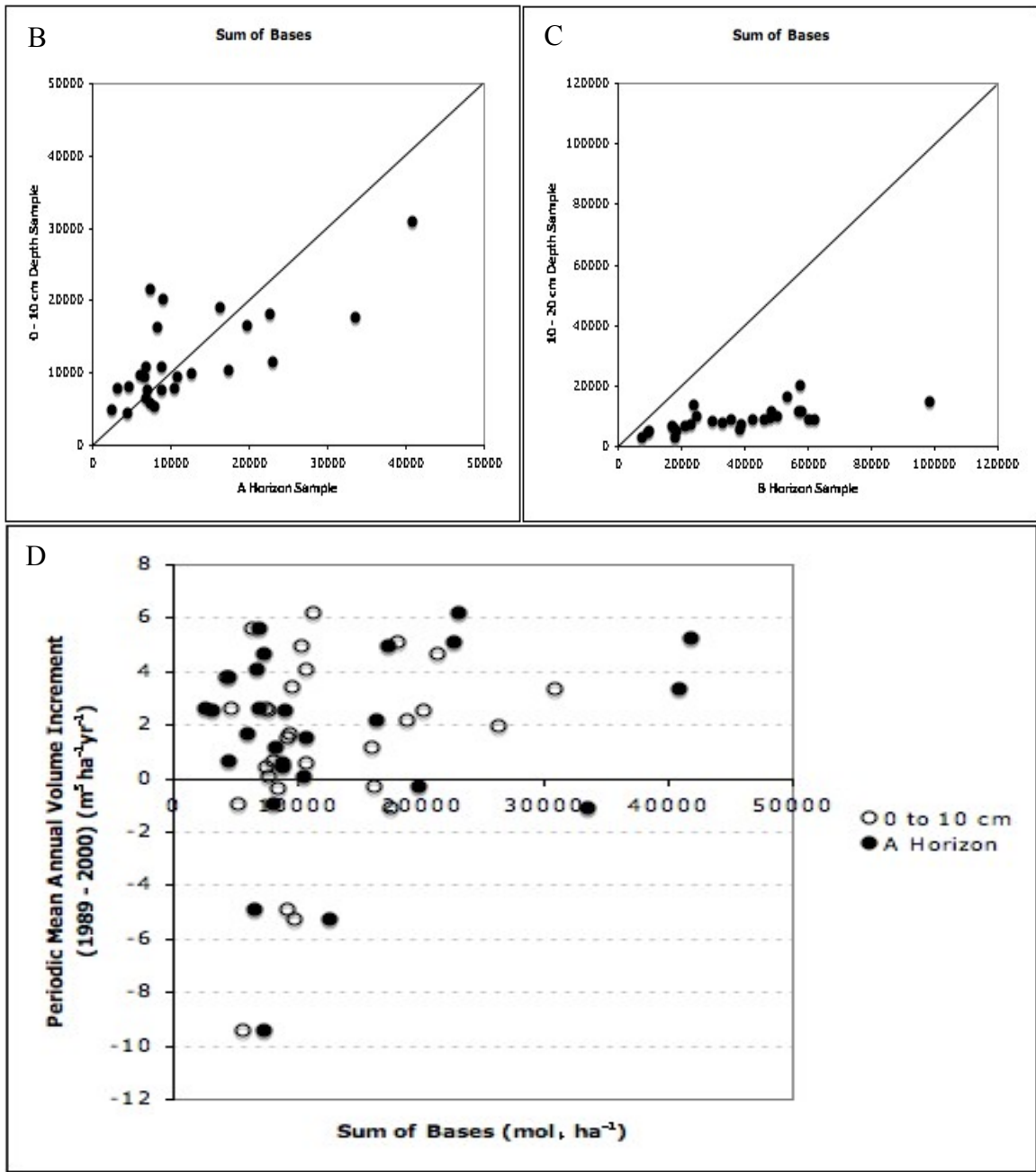


Figure 7-4: The effect of different sampling methods on A) on sum of bases values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between sum of bases and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.





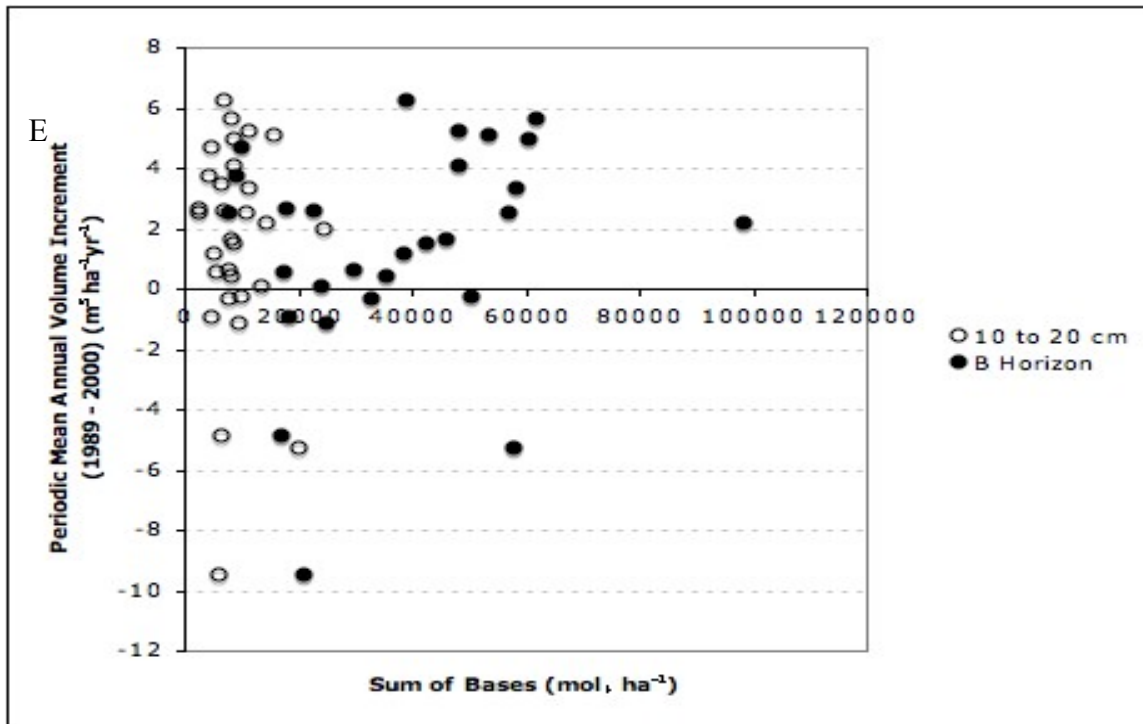
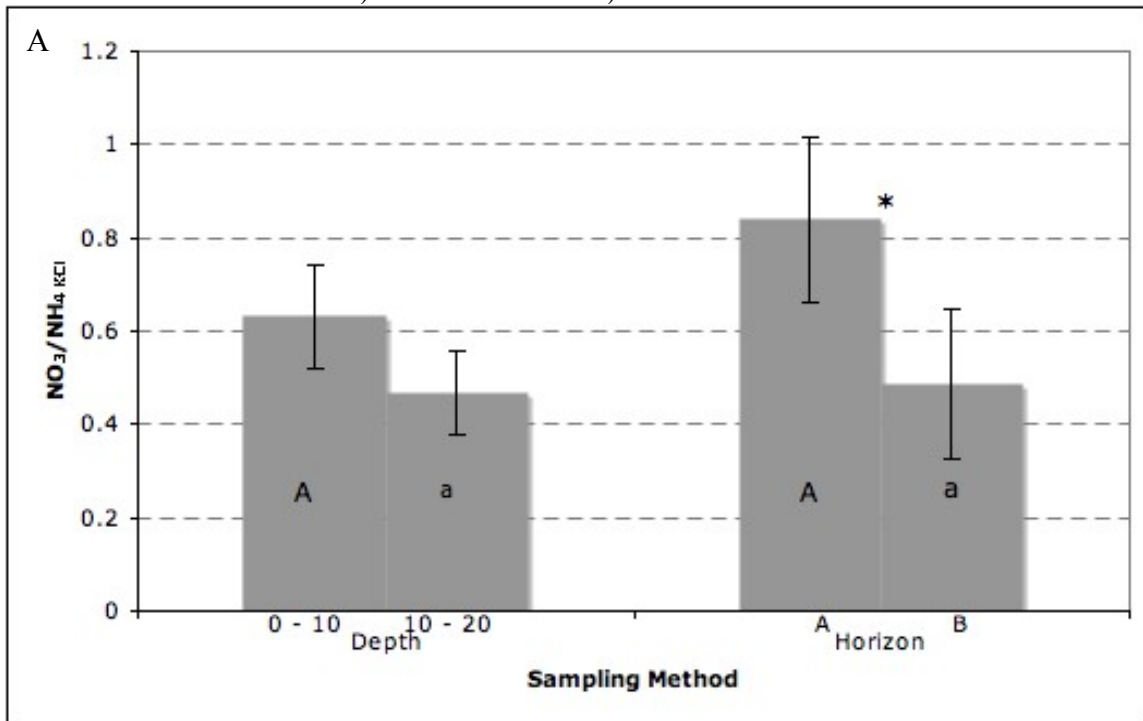
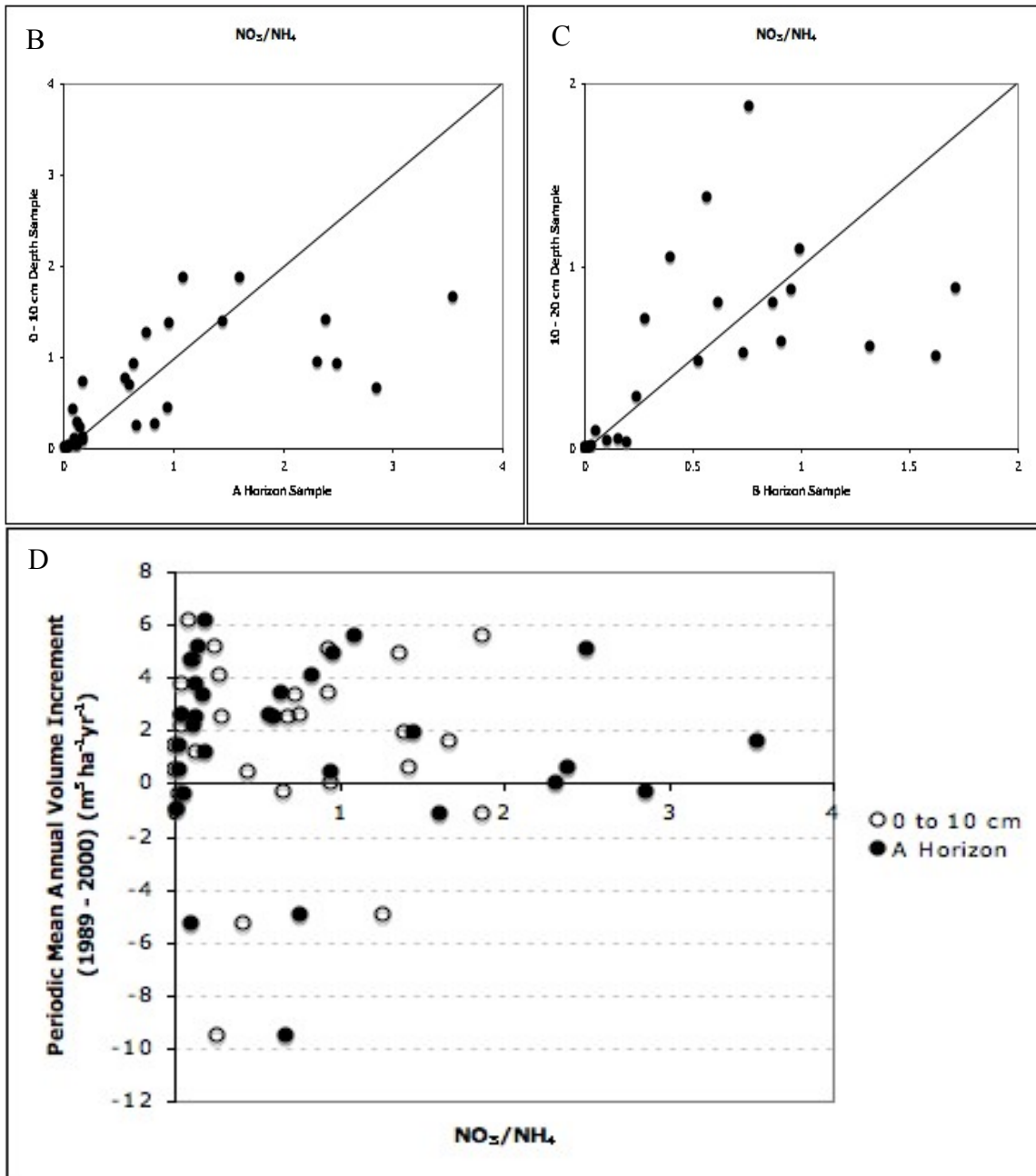
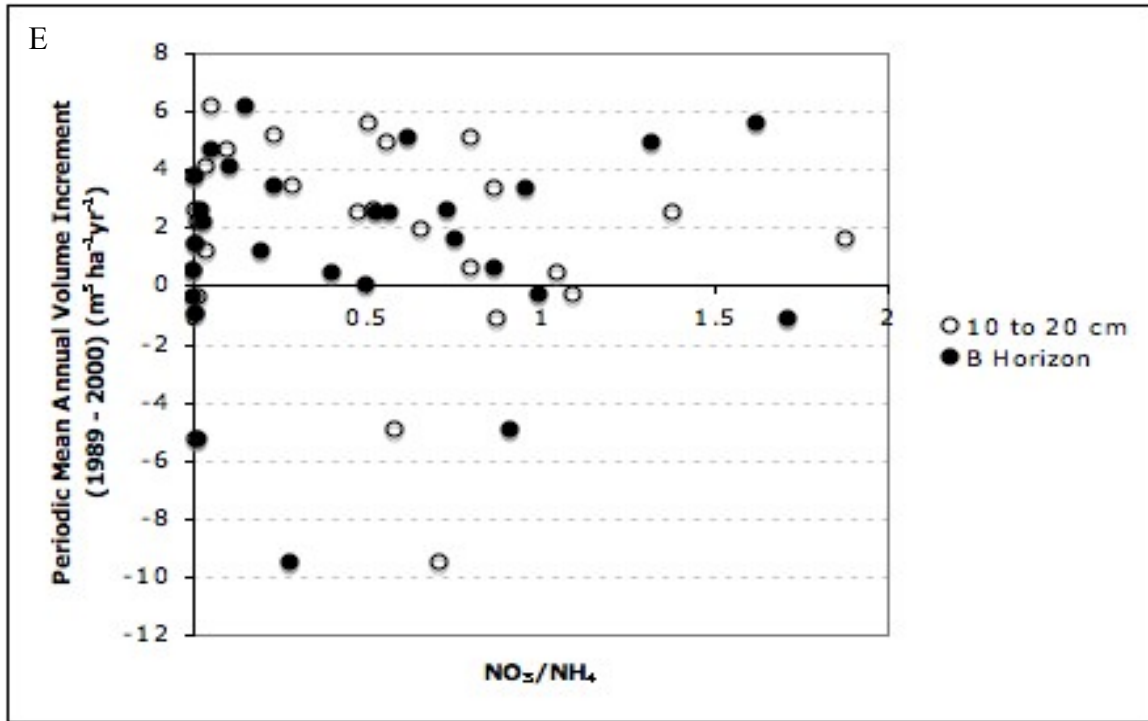


Figure 7-5: The effect of different sampling methods on A) on NO₃/NH₄ values. The one-to-one relationships between B) A horizon and 0 – 10 cm sampling and C) B horizon and 10 – 20 cm sampling. The relationship between NO₃/NH₄ and periodic mean annual volume increment for the D) surface soil and E) subsurface soil.







Applicability of Soil Survey Data for Determining Soil Depth

To further simplify soil sampling by horizon we evaluated the utility of using average soil depth data from the current soil survey for total profile contents in order to avoid digging a pit. To do this we compared the total profile content values of sum of the bases using horizon depths gathered with our narrow pit and horizon depths published in the soil survey. In the surface horizons, there was a significant relationship between sum of base values calculated using the pit versus the soil survey depth data, in which the survey data resulted in a significant overestimation of base levels ($p = 0.02$) (Figure 7-6). There was no significant difference when comparing the subsurface horizons.

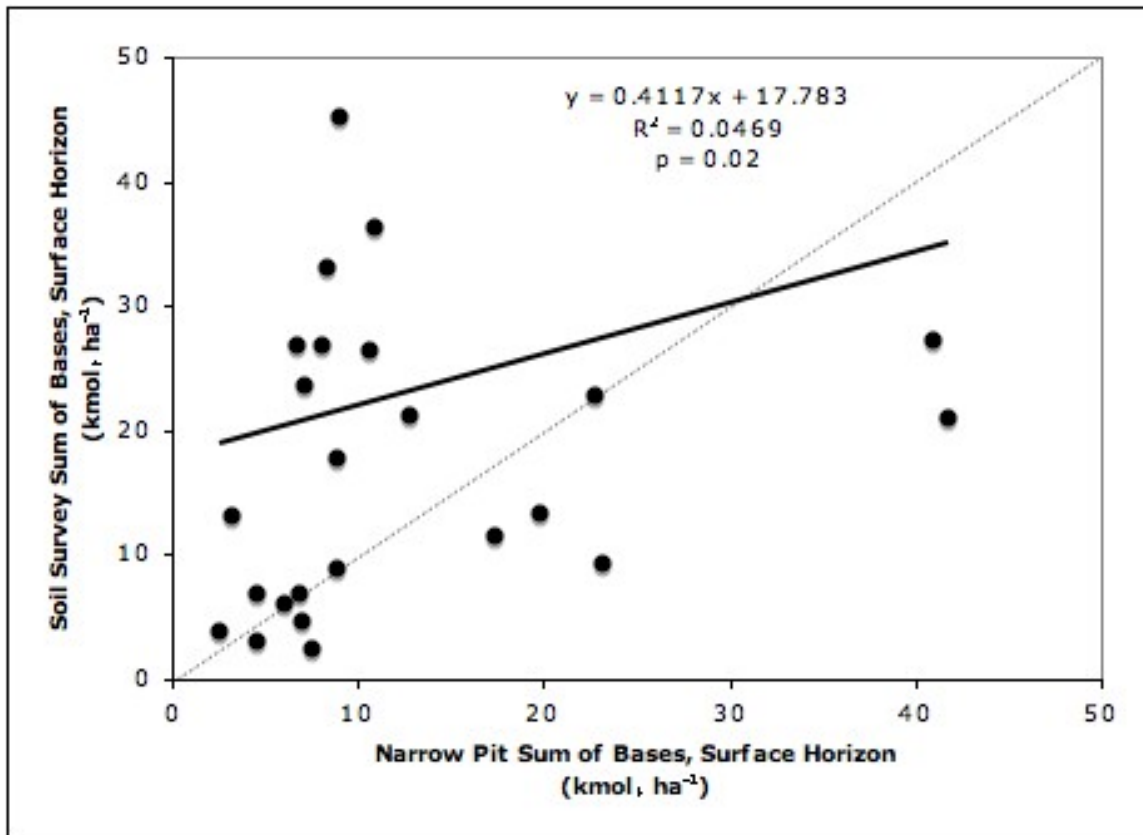


Figure 7-6: Relationship between sum of bases calculated using field-collected depth data and soil survey depth data

Laboratory Protocols

Calcium/aluminum molar ratio is a key soil indicator of acidity, and is often used as an index of site susceptibility to stress (Cronan and Grigal, 1995). Cronan and Grigal (1995) used soil solution values to develop this index; however, where lysimeter sampling is not possible, Ca and Al exchange with 0.01M SrCl₂ often serves as a surrogate (Edmeades and Clinton, 1981; Joslin and Wolfe, 1989). This method is not a standard lab procedure for the Forest Health Monitoring program (USDA Forest Service, 2007). Therefore, we analyzed differences between SrCl₂ and NH₄Cl lab analyses and found significant differences between SrCl₂ and NH₄Cl exchange of Al and Ca (Table 7-1). For horizon samples, NH₄Cl extracted 150 times more Al and 2.6 times more Ca than

SrCl₂. For depth samples, NH₄Cl extracted 20 times more Al and 2 times more Ca than SrCl₂.

Modeling the relationship between these two exchange procedures can be used to produce estimates of SrCl₂-Ca/Al molar ratio from the standard NH₄Cl procedure. Regression analyses between analysis procedures for the A and B horizons produced relationships of R² 0.84 and 0.91, respectively (Figure 7-7; Table 7-2). Regression analyses of 0 – 10 cm and 10 – 20 cm samples produced relationships of R² 0.88 and 0.43, respectively (Figure 7-7; Table 7-2). All regression analyses were significant. All relationships were linear and concentration did not influence the interpretation.

Table 7-1: Relative differences among cation concentrations extracted by NH₄Cl and SrCl₂

Average Relative Differences	Method	Al	Ca
Surface			
Mean (mg kg soil ⁻¹)	NH ₄ Cl:	462 ± 38.7	14.8 ± 1.27
	SrCl ₂ :	3.00 ± 0.36	5.80 ± 0.82
Difference between methods		154 times	2.6 times
Subsurface			
Mean (mg kg soil ⁻¹)	NH ₄ Cl:	431 ± 34.4	3.05 ± 0.31
	SrCl ₂ :	2.86 ± 0.28	1.42 ± 0.39
Difference between methods		150 times	2.1 times
0 to 10 cm			
Mean (mg kg soil ⁻¹)	NH ₄ Cl:	60.8 ± 5.0	10.1 ± 1.6
	SrCl ₂ :	3.0 ± 0.3	3.9 ± 0.7
Difference between methods		20 times	2.5 times
10 to 20 cm			
Mean (mg kg soil ⁻¹)	NH ₄ Cl:	60.0 ± 5.6	4.1 ± 0.7
	SrCl ₂ :	3.3 ± 0.3	1.9 ± 0.3
Difference between methods		20 times	2 times

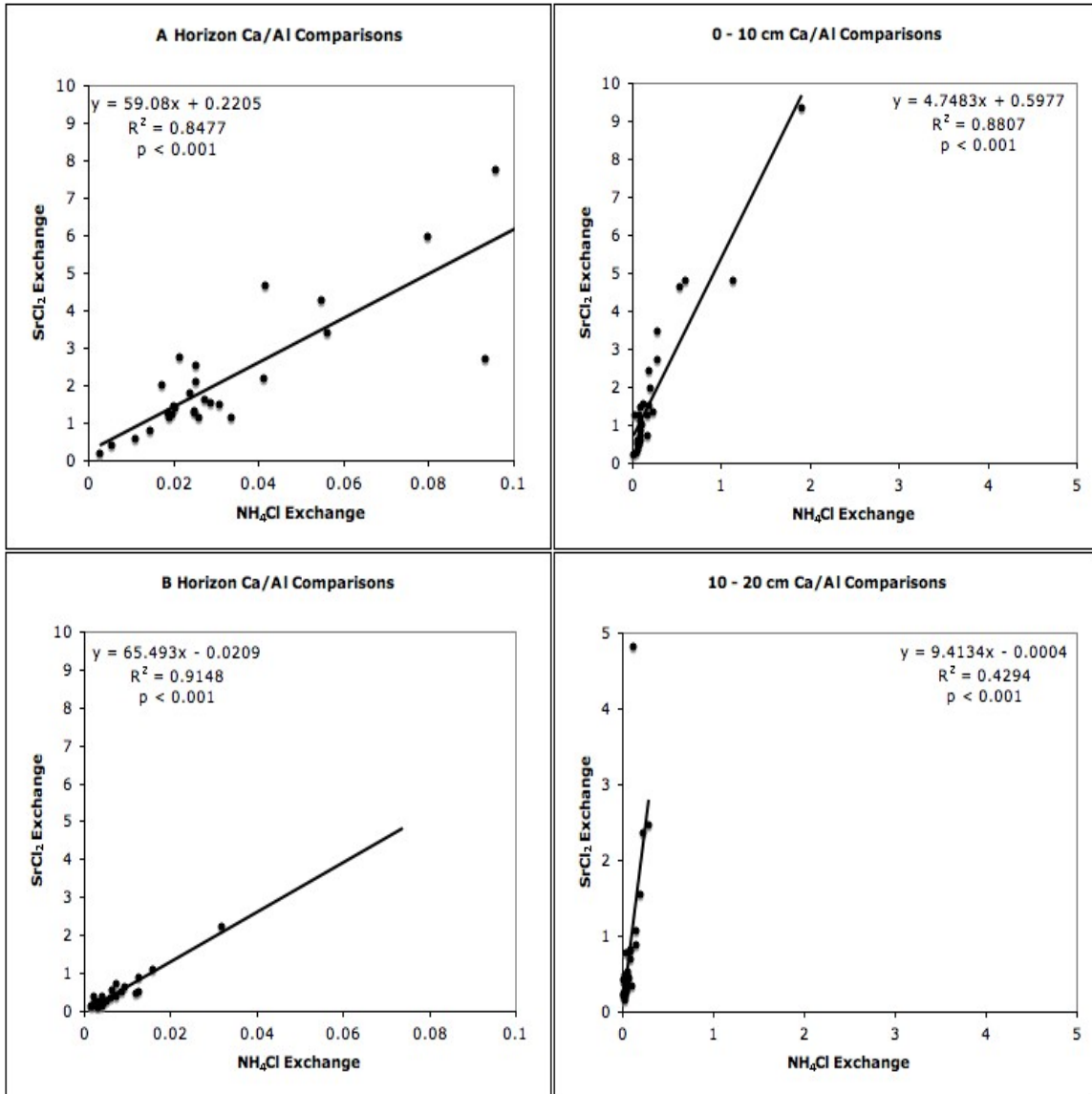


Figure 7-7: Relationship between Ca/Al molar ratio by two exchange procedures

Table 7-2: Models of Ca/Al by SrCl₂ as a function of Ca/Al by NH₄Cl

Sample	Model	R ²	p- value
Surface	$\text{Ca/Al}_{\text{SrCl}_2} = 0.22 + 59.07(\text{CaAl}_{\text{NH}_4\text{Cl}})$	0.84	< 0.001
Subsurface	$\text{Ca/Al}_{\text{SrCl}_2} = -0.021 + 65.49(\text{CaAl}_{\text{NH}_4\text{Cl}})$	0.91	< 0.001
0 – 10 cm	$\text{Ca/Al}_{\text{SrCl}_2} = 0.59 + 4.74(\text{CaAl}_{\text{NH}_4\text{Cl}})$	0.88	< 0.001
10 – 20 cm	$\text{Ca/Al}_{\text{SrCl}_2} = -0.0004 + 9.41(\text{CaAl}_{\text{NH}_4\text{Cl}})$	0.43	< 0.001

Discussion

Analysis of pH, Ca/Al ratio, effective base saturation, sum of bases, and NO_3/NH_4 ratio between sampling methods provided a comparison of the effectiveness of the two methods in capturing the same AD-related site effects. There were no differences between A horizon and 0 – 10 cm samples in pH, effective sum of bases, sum of bases, or NO_3/NH_4 . That there were few differences was expected because for these soils the surface horizon was generally around 10 cm deep. Ca/Al molar ratio was significantly different between 0 – 10 cm and A horizon samples. The one-to-one relationships between A horizon and 0 – 10 cm samples sometimes showed that there was variability between the methods. The relationship between PMAVI and Ca/Al molar ratio was stronger for A horizon than 0 – 10 cm samples, which may be important if Ca/Al molar ratio is used as a key indicator of soil acidity and stand vulnerability to decline (i.e. Connolly *et al.*, 2007). It is unclear as to why effective sum of bases of the 0 – 10 cm samples were significantly correlated with PMAVI, but A horizon values were not.

B horizon and 10 – 20 cm samples were significantly different in pH, effective base saturation, and sum of bases. These relationships are indicative of the influence of sampling deeper soil. Both effective sum of bases and sum of bases (total profile content calculations) increased with soil depth. Ca/Al ratio and NO_3/NH_4 were not significantly different. The one-to-one relationships between B horizon and 10 – 20 cm samples showed that there was variability in results between the two methods. B horizon pH values were significantly correlated with PMAVI. While none of these relationships explained as much variability in PMAVI data as the surface horizon, none of the 10 – 20 cm samples were correlated with PMAVI.

All analyses between soil layers were significantly different when sampling by horizon, and all but NO_3/NH_4 ratio were different when sampling by depth. The two sampling methods did not follow the same within-method trend for effective sum of bases or sum of bases. This is because the 0 – 10 cm sample had higher base levels than the 10 – 20 cm sample, and total profile content will not adjust for total soil volume when sampling only by depth. Therefore, sampling by horizon appears to capture more of the differences between pedogenic horizons. Also, by representatively sampling the B

horizon and knowing the entire depth of the horizon total profile content measurements such as sum of bases can be more accurately calculated. Overall, it appears that 0 – 10 cm sampling more adequately represents the A horizon than 10 – 20 cm sampling represents the B horizon; however, overall the depth method should not be used to replace sampling by horizon.

To verify the utility of the horizon method for use by field crews that were not trained in soil taxonomy, we mapped the soil series of each plot before field sampling and brought the official series description with us to the field. On all 30 plots subsurface horizons could be sampled at the depths identified on the soil survey. Comparing sums of bases calculated using our field-measured depths against soil survey depths, there was a significant disparity in surface horizon quantities, but the subsurface quantities were similar. Use of the soil survey depths caused an over-estimation because the surface horizons of some series in the soil survey are classified as Ap. Ap horizons are remnants from farm use, through which the top 8 to 10 cm of the soil surface were plowed. Therefore, we conclude that using the official soil series description will not adequately replace digging a pit.

There were significant differences between SrCl_2 - and NH_4Cl -exchangeable Al and Ca concentrations. The relationships between Ca/Al molar ratio calculated using the two analysis methods were linear for all sampling methods; therefore, it appears that once relationships between the two exchange methods have been established comparisons may be made across a wide range of concentrations. However, by not sampling consistently from the same horizon there will be greater variability in the results.

Regression relationships of Ca/Al molar ratio by SrCl_2 - and NH_4Cl -exchange were significant for all sampling methods. The difference between B horizon and 10 – 20 cm samples ($R^2 = 0.91$ and 0.43 , respectively) was comparatively much larger than the difference between A horizon and 0 – 10 cm samples ($R^2 = 0.84$ and 0.88 , respectively). This suggests that for lab analyses where NH_4Cl exchange results will be used to estimate The Ca/Al ratio, the best interpretations will be made if samples are collected by pedogenic horizon.

Conclusions

Two soil sampling techniques were evaluated for their efficacy at measuring the impacts of acid deposition on the Monongahela National Forest. In comparing pH, Ca/Al molar ratio, effective sum of bases, sum of bases, and NO₃/NH₄ ratio, there were significant differences in sampling by depth and by horizon. Samples from 0 – 10 cm were more similar to the A horizon than 10 – 20 cm samples were to the B horizon. Overall, sampling by depth cannot replace sampling by horizon, especially when calculating total profile content values. Sampling by horizon cannot be simplified by using horizon depths published by the soil survey. A comparison of lab analyses indicated that NH₄Cl results can be used to estimate SrCl₂-Ca/Al molar ratio. These results can be used to modify current AD-monitoring programs on the Monongahela National Forest.

VIII. Summary

The Monongahela National Forest (MNF) receives levels of acid deposition (AD) as high as 26 kg ha⁻¹yr⁻¹ SO₄²⁻ and 14 kg ha⁻¹yr⁻¹ NO₃⁻ (National Atmospheric Deposition Program (NRSP-3), 2006). Historical average growth rates for upland oak in West Virginia are as high as 4 m³ha⁻¹yr⁻¹ on excellent sites, and can exceed 5 m³ha⁻¹yr⁻¹ in managed stands (Schnur, 1937; Smith *et al.*, 1994). Although the MNF has been subject to AD since early in the 20th century, there have been no documented losses in productivity specifically as a result of this pollutant (Adams *et al.*, 2000). Still, surface water acidification and changes in soil chemistry have concerned managers, and the MNF has included assessing forest sites for susceptibility to acidification in the 2006 Forest Plan revision (USDA Forest Service, 2006). Therefore, it is necessary for the MNF to understand the effects of AD on forest growth and to develop an AD-specific monitoring program.

We used growth data from 30 Forest Inventory and Analysis (FIA) plots across the MNF to assess the impact of AD on forest productivity and to develop a monitoring program based on the following criteria of soil acidification: soil acidity, potential toxicity level, soil fertility, level of soil N-saturation, and potential neutralization of acidity. These criteria can be assessed using soil pH, Ca/Al molar ratio, effective base saturation, NO₃/NH₄ ratio, and sum of bases, respectively. Periodic mean annual volume increment (PMAVI) ranged from -9.5 to 11.8 m³ha⁻¹yr⁻¹ on the FIA plots, indicating that over two-thirds of the sites are experiences less-than-expected growth (3 m³ha⁻¹yr⁻¹).

Periodic mean annual volume increment was negatively correlated with stand age, and positively correlated with Ca/Al molar ratio and effective base saturation. Our model of PMAVI as a function of multiple indicators of soil acidification was:

$$PMAVI = 0.6 + 2.2(\ln Ca/Al_{surface}) + 0.18(-0.004 e^{0.09(Age)} + 4.9) - 0.73(NO_3/NH_4_{subsurface})$$

In this regression analysis model, Ca/Al ratio of the surface horizon accounted for over 30% of the variability in PMAVI. Additionally, Ca/Al ratio was correlated with many other soil chemistry characteristics. Acid Neutralization Potential on the FIA plots from

base cation-buffering ranged from 22 to 314 kmol₊ ha⁻¹. It is possible that this buffering mechanism will be depleted from the least buffered sites within 75 years.

A map of resistance to acidification across the MNF was produced by creating an resistance index (RI) based on parent material, elevation, aspect, soil texture, and soil depth. This index was positively correlated with PMAVI on the FIA sites, as well as pH, Al content and effective base saturation. Across the MNF, 14% of the forest was resistant, and 57% was moderately resistant, and 29% was slightly resistant to acidification. This resistance map can be used to develop site-specific management prescriptions where cation removal via harvesting is a concern.

We assessed dendrochronological and foliar monitoring methods on two sites with contrasting parent materials. Dendrochronologies of northern red oak on the two FIA sites showed that basal area increment was most different before and after the 50-year period of 1940 to 1990, when AD peaked on the forest. During this 50-year period when ring width and basal area increment on the two sites was most similar, growth rates plateaued, which may be due to the impacts of AD. Analyses on 10 FIA plots identified some relationships between foliar nutrients, growth and soil nutrients; however, these relationships would need to be developed for individual species to be applied to a forest-wide monitoring program.

To refine an AD-related soil monitoring program we compared the results of key indicators of soil acidity when sampling by depth versus sampling by pedogenic horizon. The Ca/Al molar ratio was significantly different between 0 – 10 cm and A horizon samples. Soil pH, effective sum of bases, and sum of bases were significantly different between 10 – 20 and B horizon samples. The improved relationships between PMAVI and sampling by horizon, as well as the inability to calculate total profile values suggests that sampling by horizon is the optimum method.

Periodic mean annual volume increment for the 10-yr period 1989 to 2000 on two-thirds of the FIA plots on the MNF was less-than-expected. These reductions in growth were correlated with key indicators of soil acidity. Monitoring programs applied across a range of site resistance to acidification can help evaluate the effectiveness of site-specific management for achieving sustainable forest management. While it is difficult to determine cause and effect relationships between forest changes and AD, it is

possible to draw a logical conclusion that the two are related if the data show consistency in time and space, if there are plausible mechanisms or linked processes, and if it is possible to replicate the symptoms in controlled environments (Johnson *et al.*, 1992). In this study, below-historical PMAVI is a symptom of a possible AD effect exhibited across the MNF to varying degrees. This symptom is consistently related to indicators of soil acidification, and not site quality or stocking. It is plausible that the influence of AD creates a scenario in which loss of bases and N-saturation either directly affect growth rates due to changes in nutrient resources, or leave the system susceptible to secondary stresses. Our soil criteria, acidity, potential toxicity, fertility, N-saturation, and potential neutralization addressed a wide range of possible soil mechanisms through which growth could be adversely affected. We determined that indicators representing these criteria were related to PMAVI. Studies in controlled environments as well as historical soil chemistry comparisons have shown that there are relationships between soil acidification and tree growth (i.e. Decker and Boerner, 1997; Bailey *et al.*, 2004).

We recommend that the MNF continue to address AD in their management guidelines, through the adaptive management scheme. AD-related management guidelines should be different developed for sites with varying resistance to acidification. To monitor effectiveness of management practices, the MNF should apply the acidification criteria and indicators examined throughout our work. The current MNF horizon soil sampling procedure should be continued, as well as the analyses techniques, which address all of our criteria and indicators. Furthermore, we recommend that the MNF continue to consider AD as a factor related to other environmental and management-related changes on the forest.

IX. Works Cited

- Aber, J.D., Goodale, C.L., Ollinger, S.V., Smith, M.L., Magill, A.H., Martin, M.E., Hallett, R.A., Stoddard, J.L., 2003. Is nitrogen deposition altering the nitrogen status of Northeastern forests? *Bioscience* 53, 375-389.
- Aber, J.D., Magill, A., Boone, R., Melillo, J.M., Steudler, P., 1993. Plant and soil responses to chronic nitrogen additions at the Harvard Forest, Massachusetts. *Ecological Applications* 3, 156-166.
- Aber, J.D., Nadelhoffer, K.J., Steudler, P., 1989. Nitrogen saturation in northern forest ecosystems. *Bioscience* 39, 378-386.
- Abrams, M., Orwig, D., Dockry, M., 1997. Dendroecology and successional status of two contrasting old-growth forests in the Blue Ridge Mountains, USA. *Canadian Journal of Forest Research* 27, 994-1002.
- Adams, M.B., 1999. Acidic deposition and sustainable forest management in the central Appalachians, USA. *Forest Ecology and Management*, 17-28.
- Adams, M.B., Angradi, T.R., Kochenderfer, J.N., 1997. Stream water and soil solution responses to 5 years of nitrogen and sulfur additions at the Fernow Experimental Forest, West Virginia. *Forest Ecology and Management* 95, 79-91.
- Adams, M.B., Burger, J.A., Jenkins, A.B., Zelazny, L., 2000. Impact of harvesting and atmospheric pollution on nutrient depletion of eastern US hardwood forests. *Forest Ecology and Management* 138, 301-319.
- Amacher, M.C., Henderson, R.E., Breithaupt, M.D., Seale, C.L., LaBauve, J.M., 1990. Unbuffered and buffered salt methods for exchangeable cations and effective cation-exchange capacity. *Soil Science Society of America Journal* 54, 1036-1042.
- Andrews, S., Karlen, D., Cambardella, C., 2004. The soil management assessment framework: A quantitative soil quality evaluation method. *Soil Science Society of America Journal* 68, 1945-1962.
- Arp, P., Leger, W., Moayeri, M., Hurley, J., 2001. Methods for mapping forest sensitivity to acid deposition for Northeastern North America. *Ecosystem Health* 7, 35-47.

- Auchmoody, L.R., Hammack, K., 1975. Foliar nutrient variation in four species of upland oaks. NE-331. Upper Darby, PA: US Dept of Agriculture, Forest Service, Northeastern Forest Experiment Station. 17 p.
- Auchmoody, L.R., Smith, H.C., 1979. Oak soil-site relationships in Northwestern West Virginia. NE-434. Broomball, PA: US Dept of Agriculture, Forest Service, Northeastern Forest Experiment Station. 27 p.
- Bache, B.W., 1980a. The acidification of soils. In: Hutchinson, T.C., Havas, M. (Eds.), *The Effects of Acid Precipitation on Terrestrial Ecosystems*. Plenum Press, New York, pp. 183-202.
- Bache, B.W., 1980b. The sensitivity of soils to acidification. In: Hutchinson, T.C., Havas, M. (Eds.), *The Effects of Acid Precipitation on Terrestrial Ecosystems*. Plenum Press, New York, pp. 569-572.
- Bailey, S.W., Horsley, S.B., Long, R.P., 2005. Thirty years of change in forest soils of the Allegheny Plateau, Pennsylvania. *Soil Science Society of America* 69, 681-690.
- Bailey, S.W., Horsley, S.B., Long, R.P., Hallett, R.A., 2004. Influence of edaphic factors on Sugar Maple nutrition and health on the Allegheny Plateau. *Soil Science Society of America* 68, 243-252.
- Bertsch, P.M., Bloom, P.R., 1996. Aluminum. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E., Bartels, J.M., Bigham, J.M. (Eds.), *Methods of Soil Analysis. Part 3. Chemical Methods*. Soil Science Society of America, Madison, WI, pp. 517-550.
- Boerner, R.E.J., 1984. Foliar nutrient dynamics and nutrient use efficiency of four deciduous tree species in relation to site fertility. *The Journal of Applied Ecology* 21, 1029-1040.
- Boggs, J.L., McNulty, S.G., Gavazzi, M.J., Moore Myers, J., 2005. Tree growth, foliar chemistry, and nitrogen cycling across a nitrogen deposition gradients in southern Appalachian deciduous forests. *Canadian Journal of Forest Research* 35, 1901-1913.

- Brahy, V., Deckers, J., Delvaux, B., 2000. Estimation of soil weathering stage and acid neutralizing capacity in a toposequence Luvisol-Cambisol on loess under deciduous forest in Belgium. *European Journal of Soil Science* 51, 1-13.
- Braun, E., 1950. *Deciduous Forests of Eastern North America*. The Blackburn Press, Caldwell, New Jersey.
- Bray, R., Kurtz, L., 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Science* 59, 39-45.
- Burger, J.A., Kelting, D., 1999. Using soil quality indicators to assess forest stand management. *Forest Ecology and Management* 122, 155-166.
- Burt, N., Villars, T., Stratton, D.A., 2005. Acid deposition and its potential effects on soil productivity and timber management in the Green Mountain National Forest, Vermont.
- Chadwick, M., Kuylenskierna, J., 1991. The relative sensitivity of ecosystems in Europe to acidic depositions. A preliminary assessment of the sensitivity of aquatic and terrestrial ecosystems. *Perspectives in Energy* 1, 71-93.
- Connolly, S., 2006. In, Elkins, WV.
- Connolly, S.J., Cain, T., Vestal, J., Edwards, P.J., 2007. The potential effects of acid deposition: What's a National Forest to do? In: Furniss, M., Clifton, C., Ronnenberg, K. (Eds.), *Advancing the Fundamental Sciences: Proceedings of the Forest Service National Earth Sciences Conference*. PNW-GTR-689, Portland, OR.
- Cronan, C.S., Grigal, D.F., 1995. Use of calcium/aluminum ratio as indicators of stress in forest ecosystems. *Journal of Environmental Quality* 24, 209-226.
- Cronan, C.S., Reiners, W.A., Reynolds, R.C.J., Gerald, L.E., 1978. Forest floor leaching: Contributions from mineral, organic, and carbonic acids in New Hampshire subalpine forests. *Science* 200, 309-311.
- Cronan, C.S., Schofield, C.L., 1979. Aluminum leaching response to acid precipitation: effects on high-elevation watersheds in the Northeast. *Science* 204, 304-306.
- Decker, K.L.M., Boerner, R.E.J., 1997. Ca:Al ratio effects on growth and competitive interactions of northern red oak (*Quercus rubra*) and yellow-poplar (*Liriodendron tulipifera*). *Journal of the Torrey Botanical Society* 124, 286-296.

- Demchik, M., Sharpe, W.E., 2000. The effect of soil nutrition, soil acidity, and drought on northern red oak (*Quercus rubra* L.) growth and nutrition on Pennsylvania sites with high and low red oak mortality. *Forest Ecology and Management* 136, 199-207.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001a. Acid rain revisited: advances in scientific understanding since the passage of the 1970 and 1990 Clean Air Act Amendments. Hubbard Brook Research Foundations Science Links Publication 1.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001b. Acid rain revisited: advances in scientific understanding since the passage of the 1970 and 1990 Clean Air Act Amendments. Hubbard Brook Research Foundation Science Links Publication 1, 1-24.
- Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., Weathers, K.C., 2001c. Acidic deposition in the Northeastern United States: sources and inputs, ecosystem effects, and management strategies. *BioScience* 51, 180-198.
- Drohan, P.J., Stout, S.L., Petersen, G.W., 2002. Sugar maple (*Acer saccharum* Marsh.) decline during 1979-1989 in northern Pennsylvania. *Forest Ecology and Management* 170, 1-17.
- Duchesne, L., Ouimet, R., Houle, D., 2002. Basal area growth of sugar maple in relation to acid deposition, stand health, and soil nutrients. *Journal of Environmental Quality* 31, 1676-1683.
- Duchesne, L., Ouimet, R., Morneau, C., 2003. Assessment of sugar maple health based on basal area growth pattern. *Canadian Journal of Forest Research* 33, 2074-2080.
- Edmeades, D.C., Clinton, O.E., 1981. A simple rapid method for the measurement of exchangeable cations and effective cation exchange capacity. *Communications in Soil Science and Plant Analysis* 12, 683-695.
- EPA, U.S., 2005. Acid Rain Program, 2005 Progress Report.

- Federer, C.A., Hornbeck, J.W., Tritton, L.M., Martin, C.W., Pierce, R.S., Smith, C.T., 1989. Long-term depletion of calcium and other nutrients in Eastern US forests. *Environmental Management* 13, 593-601.
- Feller, M.C., 1977. Nutrient movement through Western Hemlock-Western Redcedar ecosystems in Southwestern British Columbia. *Ecology* 58, 1269-1283.
- Fenn, M.E., Poth, M.A., Aber, J.D., Baron, J.S., Bormann, B.T., Johnson, D.W., Lemly, A.D., McNulty, S.G., Ryan, D.F., Stottlemeyer, R., 1998. Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies. *Ecological Applications* 8, 706-733.
- Fernandez, I.J., Rustad, L.E., Norton, S.A., Kalh, J.S., Cosby, B.J., 2003. Experimental acidification causes soil base-cation depletion at the Bear Brook Watershed in Maine. *Soil Science Society of America* 67, 1909-1919.
- Fisher, R.F., Binkley, D., 2000. *Ecology and Management of Forest Soils*. John Wiley & Sons, Inc., New York.
- Fitzhugh, R.D., Driscoll, C.T., Goffman, P.M., Tierney, G.L., Fahey, T.J., Hardy, J.P., 2003. Soil freezing and the acid-base chemistry of soil solutions in a northern hardwood forest. *Soil Science Society of America Journal* 67, 1897-1908.
- Foster, D.R., Aber, J.D., J.M., M., Bowden, R.D., Bazzaz, F.A., 1997. Forest response to disturbance and anthropogenic stress. *Bioscience* 47, 437-445.
- Fritts, H.C., 1976. *Tree Rings and Climate*. Academic Press Inc., New York.
- Godbold, D.L., Fritz, E., Huttermann, A., 1988. Aluminum toxicity and forest decline. *Ecology* 69, 3888-3892.
- Goodale, C.L., Aber, J.D., 2001. The long-term effects of land-use history on nitrogen cycling in northern hardwood forests. *Ecological Applications* 11, 253-267.
- Gress, S.E., Nichols, T.D., Northcraft, C.C., Peterjohn, W.T., 2007. Nutrient limitations in soils exhibiting differing nitrogen availabilities: What lies beyond nitrogen saturation? *Ecology* 88, 119-130.
- Hamburg, S.P., Yanai, R.D., Arthur, M.A., Blum, J.D., Siccama, T.G., 2003. Biotic control of calcium cycling in Northern hardwood forests: Acid rain and aging forests. *Ecosystems* 6, 399-406.

- Harrison, R.B., Johnson, D.W., 1992. Sulfur cycles: Inorganic sulfate dynamics. In: Johnson, D.W., Lindberg, S.E. (Eds.), *Atmospheric Deposition and Forest Nutrient Cycling*. Springer-Verlag, New York.
- Harrison, R.B., Johnson, D.W., Todd, D.E., 1989. Sulfate adsorption and desorption reversibility in a variety of forest soils. *Journal of Environmental Quality*, 419-426.
- Heninger, R., Terry, T., Dobkowski, A., Scott, W., 1997. Managing for sustainable site productivity: Weyerhaeuser's forestry perspective. *Biomass and Bioenergy* 13, 255-267.
- Hicks, R.R., 1998. *Ecology and Management of Central Hardwood Forests*. John Wiley & Sons, New York, NY.
- Holland, P.G., 1978. Species turnover in deciduous forest vegetation. *Vegetatio* 38, 113-118.
- Holmes, R., 1983. Computer-assisted quality control in tree-ring dating and measurement. *Tree Ring Bulletin* 43, 69-78.
- Horsley, S.B., Long, R.P., Bailey, S.W., Hallett, R.A., Hall, T.J., 2000. Factors associated with the decline disease of sugar maple on the Allegheny Plateau. *Canadian Journal of Forest Research* 30, 1365-1378.
- Horsley, S.B., Long, R.P., Bailey, S.W., Hallett, R.A., Wargo, P.M., 2002. Health of Eastern North American sugar maple forests and factors affecting decline. *Northern Journal of Applied Forestry* 19, 34-44.
- Houle, D., Ouimet, R., Couture, S., Gagnon, C., 2006. Base cation reservoirs in soil control the buffering capacity of lakes in forested catchments. *Canadian Journal of Fish and Aquatic Science* 63, 471-474.
- Huettl, R.F., Zoetl, H.W., 1993. Liming as a mitigation tool in Germany's declining forests - reviewing results from former and recent trials. *Forest Ecology and Management* 61, 325-338.
- Huntington, T.G., Hooper, R.P., Johnson, C.E., Aulenbach, B.T., Cappellato, R., Blum, A.E., 2000. Calcium depletion in a Southeastern United States forest ecosystem. *Soil Science Society of America* 64, 1845-1858.

- Husar, R.B., 1986. Emissions of Sulfur Dioxide and Nitrogen Oxides and Trends of Eastern North America. In, Committee on Monitoring and Assessment of Trends in Acid Deposition Environmental Studies Board and National Research Council (Eds), Acid Deposition: Long-Term Trends. National Academies Press, Washington, DC.
- Hutchinson, T.C., Watmough, S.A., Sager, E.P.S., Karagatzides, J.D., 1998. Effects of excess nitrogen deposition and soil acidification on Sugar Maple (*Acer saccharum*) in Ontario, Canada: an experimental study. Canadian Journal of Forest Research 28, 299-310.
- Johnson, A.H., McLaughlin, S.B., Adams, M.B., Cook, E.R., DeHayes, D.H., Eagar, C., Fernandez, I.J., Johnson, D.W., Kohut, R.J., Mohnen, V.A., Nicholas, N.S., Peart, D.R., Schier, G.A., White, P.S., 1992. Synthesis and conclusions from epidemiological and mechanistic studies of red spruce decline. In: Eagar, C., Adams, M.B. (Eds.), Ecology and decline of red spruce in the eastern United States. Springer-Verlag, New York.
- Johnson, C.E., 2002. Cation exchange properties of acid forest soils of the northeastern USA. European Journal of Soil Science 53, 271-282.
- Johnson, C.E., Ruiz-Mendez, J.J., Lawrence, G.B., 2000. Forest soil chemistry and terrain attributes in a Catskills watershed. Soil Science Society of America Journal 64, 1804-1814.
- Johnson, D.W., 1980. Site susceptibility to leaching by H₂SO₄ in acid rainfall. In: Hutchinson, T.C., Havas, M. (Eds.), The Effects of Acid Precipitation on Terrestrial Ecosystems. Plenum Press, New York, pp. 525-535.
- Johnson, D.W., 1992a. Base cation distribution and cycling. In: Johnson, D.W., Lindberg, S.E. (Eds.), Atmospheric Deposition and Forest Nutrient Cycling. Springer-Verlag, New York, pp. 275-333.
- Johnson, D.W., 1992b. Base cations. In: Johnson, D.W., Lindberg, S.E. (Eds.), Atmospheric Deposition and Forest Nutrient Cycling. Springer-Verlag, New York, pp. 233-235.

- Johnson, D.W., Swank, W.T., Vpse, J.M., 1995. Effects of liming on soils and streamwaters in a deciduous forest: Comparison of field results and simulations. *The Journal of Environmental Quality* 24, 1104-1117.
- Johnson, D.W., Turner, J., Kelly, J.M., 1982a. The Effects of Acid Rain on Forest Nutrient Status. *Water Resources Research* 18, 449-461.
- Johnson, D.W., West, D., Todd, D.E., Mann, L., 1982b. Effect of sawlog vs. whole-tree harvesting on the nitrogen, phosphorus, and calcium budgets of an upland mixed oak forest. *Soil Science Society of America Journal* 46, 1304-1309.
- Johnson, N., 1984. Acid rain neutralization by geologic materials. In: Bricker, O.P. (Ed.), *Geological Aspects of Acid Deposition*. Butterworth Publishers, Ann Arbor, MI.
- Joslin, J.D., Wolfe, M.H., 1989. Aluminum effects on Northern Red Oak seedling growth in six forest soil horizons. *Soil Science Society of America* 53, 274-281.
- Juergens, G.A., 2008. Data review. In, Blacksburg, VA.
- Juice, S.M., Fahey, T.J., Siccama, T.G., Driscoll, C.T., Denny, E.G., Eagar, C., Cleavitt, N.L., Minocha, R., Richardson, A.D., 2006. Response of sugar maple to calcium addition to northern hardwood forest. *Ecology* 85, 1267-1280.
- Juknys, R., 2004. Tree-ring analysis for environmental monitoring and assessment of anthropogenic changes. In: Wiersma, G.B. (Ed.), *Environmental Monitoring*. CRC Press, Boca Raton.
- Khanna, P.K., Ulrich, B., 1984. Soil Characteristics Influencing Nutrient Supply in Forest Soils. In: Bowen, G.D., Nambiar, E.K.S. (Eds.), *Nutrition of Plantation Forests*. Academic Press, London.
- Kobe, R.K., Likens, G.E., Eagar, C., 2002. Tree seedling growth and mortality responses to manipulations of calcium and aluminum in a northern hardwood forest. *Canadian Journal of Forest Research* 32, 954-966.
- Kogelmann, W.J., Sharpe, W.E., 2006. Soil acidity and manganese in declining and nondeclining sugar maple stands in Pennsylvania. *Journal of Environmental Quality* 35, 433-441.
- Kuylenstierna, J., Cambridge, H., Cinderby, S., Chadwick, M., 1995. Terrestrial ecosystem sensitivity to acidic deposition in developing countries. *Water, Air, and Soil Pollution* 85, 2319-2324.

- Lamson, N.I., 1987. Estimating North Red Oak site-index class from total height and diameter of dominant and codominant trees in Central Appalachian hardwood stands. NE-RP-605. Broomall, PA: US Dept of Agriculture, Forest Service, Northeastern Forest Experiment Station. 3 p.
- Langner, J., Persson, C., Robertson, L., 1995. Concentration and deposition of acidifying air pollutants over Sweden: Estimates for 1991 based on the MATCH model and observations. *Water, Air, and Soil Pollution* 85, 2021-2026.
- Lawrence, G.B., David, M.B., Bailey, S.W., Shortle, W.C., 1997. Assessment of soil calcium status in red spruce forests in the northeastern United States. *Biogeochemistry* 38, 19-39.
- Lawrence, G.B., David, M.B., Lovett, G.M., Murdoch, P.S., Burns, D.A., Stoddard, J.L., Baldigo, B.P., Porter, J.H., Thompson, A.W., 1999. Soil calcium status and the response of stream chemistry to changing acidic deposition rates. *Ecological Applications* 9, 1059-1072.
- Lawrence, G.B., David, M.B., Shortle, W.C., 1995. A new mechanisms for calcium loss in forest-floor soils. *Nature* 378, 162-165.
- LeBlanc, D.C., 1990. Relationships between breast-height and whole-stem growth indices for red spruce on Whiteface Mountain, New York. *Canadian Journal of Forest Research* 20, 1399-1407.
- Leininger, T.D., Winner, W.E., 1987. Throughfall chemistry beneath *Quercus rubra*: atmospheric, foliar, and soil chemistry considerations. *Canadian Journal of Forest Research* 18, 478-482.
- Likens, G.E., 1972. The chemistry of precipitation in the central Finger Lakes region. In: 50, T.R. (Ed.). *Water Resources and Marine Sciences Center*, Cornell University, Ithaca, New York.
- Likens, G.E., Driscoll, C.T., Buso, D.C., 1996. Long-term effects of acid rain: response and recovery of a forest ecosystem. *Science* 272, 244-246.
- Long, R.P., Horsley, S.B., Lilja, P.R., 1997. Impact of forest liming on growth and crown vigor of sugar maple and associated hardwoods. *Canadian Journal of Forest Research* 27, 1560-1573.

- Lucas, A., Cowell, D., 1984. Regional assessment of sensitivity to acidic deposition for Eastern Canada. In: Bricker, O.P. (Ed.), *Geological Aspects of Acid Deposition*. Butterworth Publishers, Ann Arbor, MI.
- Lyon, J., Sharpe, W.E., 1999. An assessment of the Ca:Al ratios of selected Pennsylvania forest soils. *Water, Air, and Soil Pollution* 109, 53-65.
- McNulty, S.G., Aber, J.D., Newman, S.D., 1996. Nitrogen saturation in a high elevation New England spruce-fir stand. *Forest Ecology and Management* 84, 109-121.
- McQuattie, C.J., Schier, G.A., 2000. Response of sugar maple (*Acer saccharum*) seedlings to manganese. *Canadian Journal of Forest Research* 30, 456-467.
- Moore, J.D., Ouimet, R., 2006. Ten-year effect of dolomitic lime on the nutrition, crown vigor, and growth of sugar maple. *Canadian Journal of Forest Research* 36, 1834-1841.
- Mulvaney, R.L., 1996. Nitrogen - Inorganic Forms. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E., Bartels, J.M., Bigham, J.M. (Eds.), *Methods of Soil Analysis. Part 3. Chemical Methods*. Soil Science Society of America, Madison, WI, pp. 1123-1184.
- National Atmospheric Deposition Program (NRSP-3), 2006. In. NADP Program Office, Illinois State Water Survey, 2204 Griffith Dr., Champaign, IL 61820.
- Nodvin, S.C., Driscoll, C.T., Likens, G.E., 1986. The effect of pH on sulfate adsorption by a forest soil. *Soil Science* 142, 69-75.
- Page-Dumroese, D., Jurgensen, D., Brown, M., Mroz, G., 1999. Comparison of methods for determining bulk densities of rocky forest soils. *Soil Science Society of America Journal* 63, 379-383.
- Palmer, C., Smith, W., Conkling, B., 2002. Development of a protocol for monitoring status and trends in forest soil carbon at a national level. *Environmental Pollution* 116, S209-S219.
- Pastor, J., Aber, J.D., McClaugherty, C.A., Melillo, J.M., 1984. Aboveground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk Island, Wisconsin. *Ecology* 65, 256-268.

- Patric, J.H., Smith, D.W., 1975. Forest management and nutrient cycling in Eastern Hardwoods. NE-324. Upper Darby, PA: US Dept of Agriculture, Forest Service, Northeastern Forest Experiment Station. 18 p.
- Reuss, J.O., 1983. Implications of the calcium-aluminum exchange system for the effect of acid precipitation on soils. *Journal of Environmental Quality* 12, 591-595.
- Reuss, J.O., Johnson, D.W., 1986. Acid deposition and the acidification of soils and waters. Springer-Verlag, New York, NY.
- Roach, B.A., Gingrich, S.F., 1968. Even-aged silviculture for upland central hardwoods. USDA Forest Service. Agricultural Handbook. 355. Washington, DC: US Department of Agriculture.
- Ruess, J.O., Johnson, D.W., 1986. Acid deposition and the acidification of soils and waters. Springer-Verlag New York, Inc., New York.
- Schaberg, P., Perkins, T., McNulty, S.G., 1997. Effects of chronic low-level N additions on foliar elemental concentrations, morphology, and gas exchange of mature montane red spruce. *Canadian Journal of Forest Research* 27, 1622-1629.
- Schnur, G., 1937. Yield, stand and volume tables for even-aged upland oak forests. USDA Forest Service Technical Bulletin. No. 560. 86 p.
- Schweingruber, F., 1983. Tree rings: basics and applications of dendrochronology. D. Reidel Publishing Company, Dordrecht, Holland.
- Scott, C.T., 1981. Northeastern forest survey revised cubic-foot volume equations. Res. Note NE-304. Broomall, PA: U.S. Department of Agriculture, Forest Service, Northeastern Forest Experiment Station. 3 p.
- Sharpe, W.E., 2007. Strontium Chloride Extraction Laboratory Procedures. In: Elias, P.E. (Ed.), State College, PA and Blacksburg, VA.
- Sharpe, W.E., Sunderland, T.L., 1995. Acid-base status of upper rooting zone soil in declining and non-declining sugar maple (*Acer saccharum* Marsh) stands in Pennsylvania. In: Gottshalk, K.W.a.F., S.L.C. (Ed.), 10th Central Hardwood Forest Conference, Morgantown, WV, pp. 172-178.
- Sims, J., 1996. Lime requirement. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E. (Eds.),

- Methods of Soil Analysis Part III: Chemical Methods. Soil Science Society of America, Madison, WI, pp. 508-510.
- Skinner, M.F., Zabowski, D., Harrison, R., Lowe, A., Xue, D., 2001. Measuring the cation exchange capacity of forest soils. *Communications in Soil Science and Plant Analysis* 32, 1751-1764.
- Smith, H.C., Miller, G.W., Lamson, N.I., 1994. Crop-tree release thinning in 65-year-old commercial cherry-maple stands (5-year results). NE-RP-694. Randor, PA: US Dept of Agriculture, Forest Service, Northeastern Forest Experiment Station. 11 p.
- St.Clair, S.B., Lynch, J.P., 2005. Base cation stimulation of mycorrhization and photosynthesis of sugar maple on acid soils are coupled by foliar nutrient dynamics. *New Phytologist* 165, 581-590.
- Tao, F., Feng, Z., 2000. Terrestrial ecosystem sensitivity to acid deposition in South China. *Water, Air, and Soil Pollution* 118, 231-243.
- Thomas, G.W., 1996. Soil pH and soil acidity. In: Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnston, C.T., Sumner, M.E., Bartels, J.M., Bigham, J.M. (Eds.), *Methods of Soil Analysis. Part 3. Chemical Methods*. Soil Science Society of America and American Society of Agronomy, Madison, WI, pp. 475-490.
- Ulrich, B., 1980. Production and consumption of hydrogen ions in the ecosphere. In: Hutchinson, T.C., Havas, M. (Eds.), *The Effects of Acid Precipitation on Terrestrial Ecosystems*. Plenum Press, New York, pp. 255-282.
- Ulrich, B., 1994. Nutrient and acid-base budget of Central European forest ecosystems. In: Godbold, D.L., Huttermann, A. (Eds.), *Effects of Acid Rain on Forest Processes*. Wiley-Liss, New York, pp. 1-50.
- USDAForestService, 2006. Monongahela National Forest Proposed Land and Resource Management Plan. USDA Forest Service. Northeastern Region.
- USDAForestService, 2007. The Forest Inventory and Analysis Database: Database Description and Users Guide Version 3.0. Forest Inventory and Analysis Program. US Dept of Agriculture, Forest Service. 230 p.

- Van Miegroet, H., Cole, D.W., Foster, N.W., 1992. Nitrogen distribution and cycling. In: Johnson, D.W., Lindberg, S.E. (Eds.), *Atmospheric Deposition and Forest Nutrient Cycling*. Springer-Verlag, New York, pp. 178-196.
- Van Ranst, E., De Coninck, F., Roskams, P., Vindevogel, N., 2002. Acid-neutralizing capacity of forest floor and mineral topsoil in Flemish forest (North Belgium). *Forest Ecology and Management* 166, 45-53.
- Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecological Applications* 7, 737-750.
- Watmough, S.A., 2002. A dendrochemical survey of sugar maple (*Acer saccharum* Marsh) in South-Central Ontario, Canada. *Water, Air, and Soil Pollution* 136, 165-187.
- Watmough, S.A., Dillon, P.J., 2003. Do critical load models adequately protect forests? A case study in south central Ontario. *Canadian Journal of Forest Research* 33, 1544-1556.
- Webb, R., 2004. Effects of acidic deposition on aquatic resource in the central Appalachian Mountains. In, *Shenandoah Watershed Study*.
- White, G., Fernandez, I., Wiersma, G., 1999. Impacts of ammonium sulfate treatment on the foliar chemistry of forest trees at the Bear Brook Watershed in Maine. *Environmental Monitoring and Assessment* 55.
- White, G.J., 2004. Selection of ecological indicators for monitoring terrestrial systems. In: Wiersma, G.B. (Ed.), *Environmental Monitoring*. CRC Press, Boca Raton.
- Widmann, R.H., Griffith, D.M., 2004. *Forest Resource Statistics for the Monongahela National Forest: 2000*. Resour. Bull. NE-161. Newtown Square, PA: US Dept. of Agriculture, Forest Service, Northeastern Research Station. 46 p.
- Williard, K.W.J., Dewalle, D.R., Edwards, P.J., 2005. Influence of bedrock geology and tree species composition on stream nitrate concentrations in Mid-Appalachian forested watersheds. *Water, Air, and Soil Pollution*, 55-76.
- Wilmot, T.R., Ellsworth, D.S., Tyree, M.T., 1996. Base cation fertilization and liming effects on nutrition and growth of Vermont sugar maple stands. *Forest Ecology and Management* 84, 123-134.

Yanai, R.D., Phillips, R.P., Arthur, M.A., Siccama, T.G., Hane, E.N., 2005. Spatial and temporal variation in calcium and aluminum in northern hardwood forest floors. *Water, Air, and Soil Pollution* 160, 109-118.

		1 M NH ₄ Cl					
		Al	Ca	K	Mg	Mn	Na
Plot	Sample	mmolc kg soil ⁻¹					
540251274	A Horizon	134.4556083	2.55170021	2.644748673	0.225488511	0.217190214	0.888866355
540251303	A Horizon	118.0050269	3.968743788	3.01080278	0.22058993	0.69038459	1.475535061
540251389	A Horizon	389.7557286	7.76460235	2.744070283	0.246433172	6.329898963	1.283286627
540252514	A Horizon	385.5483212	16.08472743	3.29496339	0.701113279	3.573080806	1.312057396
540711765	A Horizon	544.0669628	15.62836005	4.433888632	0.401637451	4.033160235	2.159457346
540750085	A Horizon	494.4366985	12.45513829	3.643248311	0.387426383	12.26012872	2.156980474
540750596	A Horizon	475.9754247	9.549671717	2.820463189	0.300455801	7.904660911	1.536205579
540750777	A Horizon	152.4395255	3.787314427	2.328743251	0.270829798	0.498814593	0.981118024
540751103	A Horizon	350.5704971	14.44749151	2.667564644	0.284139817	13.61663209	0.848370435
540751144	A Horizon	493.076953	1.314794543	0.798437436	0.081840702	0	0.690994055
540751341	A Horizon	199.935754	34.65700097	3.208128752	0.372258311	8.594634902	1.29762532
540751725	A Horizon	693.4674912	14.29188261	3.197002655	0.416693612	2.940244485	1.13588308
540751815	A Horizon	357.3110013	28.53469722	3.269771713	0.445360965	7.746237851	1.683300814
540751915	A Horizon	433.4975405	13.38436384	2.344706173	0.316943767	1.429462932	0.908084037
540751981	A Horizon	254.9833275	24.46301071	2.229000281	0.422446338	14.11964817	1.420478799
540752006	A Horizon	502.1374469	12.0466141	2.734206408	0.33119351	11.54871009	1.308496067
540752023	A Horizon	700.2272626	10.15647851	2.195786014	0.221328873	0.84256366	0.955327295
540752161	A Horizon	385.5419676	36.01352703	5.382820836	0.628719122	0.600581069	3.653208896
540830260	A Horizon	375.4823579	20.58052106	3.048096411	0.469691761	11.47590737	1.367382752
540830340	A Horizon	753.5889095	4.197001264	2.812218262	0.355706161	0.197806447	2.147492211
540830693	A Horizon	1030.773309	19.49798	2.855495022	0.437373308	0.860002368	4.107327652
540831421	A Horizon	593.0983283	10.38262824	1.558144882	0.155437081	0.522995549	1.700464599
540831918	A Horizon	651.6561084	17.01394638	3.996970596	0.41296187	2.794947259	3.445608773
540832067	A Horizon	679.6936573	16.89334317	3.660781444	0.384643417	8.119866364	1.648056384
540832115	A Horizon	571.7408061	14.5476789	2.9540899	0.360499414	3.738155975	1.448946841
540832222	A Horizon	788.7222979	17.03953994	2.875201728	0.411629634	1.878840876	2.913632928
540832392	A Horizon	325.1420916	18.28163485	2.55992041	0.349474522	6.232192443	1.703505933
541010517	A Horizon	269.9542628	7.413703604	0.950443348	0.165895834	0.992444012	1.203504529
541011823	A Horizon	420.5201147	4.724693423	2.323855353	0.203555575	2.478200188	1.475015035
541012463	A Horizon	327.067257	33.63540885	2.58783708	0.806268597	4.747828021	1.404004585

		1 M NH ₄ Cl					
		Al	Ca	K	Mg	Mn	Na
Plot	Sample	mmolc kg soil ⁻¹					
540251274	B Horizon	161.5973878	0.523184665	0.522921974	0.039043582	0	0.984479686
540251303	B Horizon	161.0046	0.674848453	0.515474662	0.043496575	0	1.099826364
540251389	B Horizon	388.7639789	1.772085601	1.580993731	0.078889868	0.266572472	1.698140039
540252514	B Horizon	341.7447537	4.365886004	2.003437805	0.936431115	0.41357982	2.358795732
540711765	B Horizon	513.1222879	2.132306744	1.183212048	0.066032678	0.716362011	1.559944764
540750085	B Horizon	260.8613624	4.146187285	1.320815448	0.267085713	1.777709508	1.802977293
540750596	B Horizon	248.3397255	1.509826229	0.972725535	0.067215727	0.363781679	1.966178605
540750777	B Horizon	314.7133966	0.981491192	0.562533946	0.0665687	0	1.071995147
540751103	B Horizon	299.4277177	1.097290307	0.749648685	0.046303569	1.06815428	1.033666052
540751144	B Horizon	856.6623611	0.82177203	0.48497571	0.055802438	0	0.589794544
540751341	B Horizon	152.2386062	1.833401791	0.967913796	0.075803261	0.845791565	2.261132071
540751725	B Horizon	415.4670522	1.75040884	1.619567578	0.085437492	1.483021659	1.30597011
540751815	B Horizon	312.5896802	9.928316766	1.073778893	0.152187544	1.730971782	1.608970199
540751915	B Horizon	612.1174843	1.225417974	1.158315582	0.061356274	0	0.666034819
540751981	B Horizon	293.9550605	21.74830441	1.56607732	0.548036957	10.67277024	2.365871745
540752006	B Horizon	472.9777238	6.059796888	1.023924043	0.066284561	0.514530446	1.081031242
540752023	B Horizon	382.4236576	2.859614737	0.75289052	0.065615069	0.630475004	1.28205553
540752161	B Horizon	614.2488143	3.190380483	0.718235608	0.092947881	0	1.951855782
540830260	B Horizon	848.7929717	2.327184086	1.635387598	0.10297051	5.70035877	1.808421466
540830340	B Horizon	435.3276005	0.847712254	1.285273214	0.063772156	0	1.892933171
540830693	B Horizon	561.7143883	3.696991965	1.015765796	0.141672012	0.804628301	2.112898427
540831421	B Horizon	838.4746726	1.423016414	0.662959745	0.064681681	0	1.543320609
540831918	B Horizon	397.3611529	2.934835982	1.841981707	0.205097645	0.26489309	4.131257313
540832067	B Horizon	374.294548	1.48085081	0.562631005	0.059557797	0.521475053	1.289798164
540832115	B Horizon	501.0364884	1.561864906	0.667709063	0.061690527	0.24105192	1.407548586
540832222	B Horizon	487.3487596	1.147392459	1.138880732	0.059074275	0.178131005	2.536021354
540832392	B Horizon	513.6628764	1.612324197	0.747512787	0.054713361	0.216104592	2.561941523
541010517	B Horizon	274.1988179	2.565721099	0.821589417	0.078421652	0.479301472	1.207893935
541011823	B Horizon	373.8928879	0.879271587	0.716905487	0.050640455	0.767913536	0.803550643
541012463	B Horizon	515.6007191	4.484344454	1.685759021	0.226642183	1.019491104	2.174640545

Plot	Sample	2 N KCI		C/N Analyzer		
		NH4	NO3	N	C	C/N
		ppm		%		
540251274	A Horizon	8.283881726	1.043063646	0.033066885	0.857549916	25.93379836
540251303	A Horizon	7.610924525	0.361726603	0.140888343	4.078039604	28.94518822
540251389	A Horizon	6.336062881	0.338033996	0.110282224	1.482067881	13.43886462
540252514	A Horizon	8.321129475	0.946128499	0.066160285	0.484486372	7.322918462
540711765	A Horizon	31.76770018	19.34411144	0.524659706	9.071090207	17.28947375
540750085	A Horizon	122.7073729	15.52500451	0.17467854	2.499897446	14.31141709
540750596	A Horizon	18.07757098	0.539448036	0.302728773	6.628273071	21.89508781
540750777	A Horizon	4.970585201	0.12100418	0.059029275	1.690169354	28.63273096
540751103	A Horizon	10.33995232	10.00696254	0.186252417	2.847496257	15.28837211
540751144	A Horizon	18.97795042	12.79235753	0.048499273	0.835553013	17.22815528
540751341	A Horizon	53.53427655	5.327098419	0.353763419	6.67835479	18.87802533
540751725	A Horizon	46.11555598	35.20586334	0.601324726	12.41296906	20.64270524
540751815	A Horizon	10.52192628	26.2789591	0.192514547	2.307658082	11.98692836
540751915	A Horizon	15.04444714	2.797903434	0.083656303	1.312861293	15.69351321
540751981	A Horizon	43.08092236	62.35149576	0.367250188	5.139150481	13.99359524
540752006	A Horizon	14.14132657	15.51105199	0.14961776	1.523958627	10.18567998
540752023	A Horizon	6.551215938	15.65999848	0.209550011	3.274144066	15.62464276
540752161	A Horizon	17.64775786	2.614659816	0.236498508	4.885840027	20.6590734
540830260	A Horizon	14.25832582	22.88573241	0.161868162	2.006594877	12.39647654
540830340	A Horizon	16.7907991	0.128058395	0.096407652	2.384856625	24.7372129
540830693	A Horizon	62.98365623	40.51531155	1.005423931	16.98392765	16.89230496
540831421	A Horizon	8.622700382	7.187672273	0.108057739	2.474875012	22.90326484
540831918	A Horizon	39.10551336	3.711129385	0.349593267	6.671606231	19.08390939
540832067	A Horizon	6.805793174	19.44128511	0.135893612	2.150771578	15.82687768
540832115	A Horizon	13.54794713	2.50745704	0.093320464	1.670162939	17.89707073
540832222	A Horizon	6.184950789	5.878034835	0.069735621	0.985103899	14.12626544
540832392	A Horizon	5.126869514	11.85341001	0.047459716	0.470866859	9.921400778
541010517	A Horizon	15.12102441	8.629459983	0.254190945	4.442594957	17.47739265
541011823	A Horizon	8.610958851	30.51918377	0.161202003	2.492303186	15.46074575
541012463	A Horizon	10.7055829	1.919133365	0.463194483	8.570240207	18.50246608

Plot	Sample	2 N KCl		C/N Analyzer		
		NH4	NO3	N	C	C/N
		ppm		%		
540251274	B Horizon	29.51396183	0.174735955	0.082958593	2.221208383	26.77490415
540251303	B Horizon	19.09836631	0.485251483	0.110535255	3.504872957	31.7081909
540251389	B Horizon	11.68032814	0.01185711	0.132157479	2.348143432	17.76776806
540252514	B Horizon	164.397895	5.510424393	0.235189926	4.419692511	18.79201457
540711765	B Horizon	82.90989306	47.08621983	0.080194998	1.320884158	16.4709046
540750085	B Horizon	4.54032216	0.044332672	0.413517466	5.810015542	14.05023008
540750596	B Horizon	6.20156056	3.279587827	0.060509152	0.849971158	14.04698517
540750777	B Horizon	26.42090124	0.091271976	0.146784944	5.08761051	34.66030211
540751103	B Horizon	31.14512405	41.08917051	0.5239979	3.266644535	6.234079439
540751144	B Horizon	46.20190792	12.94360333	0.279885358	4.647060272	16.60344185
540751341	B Horizon	5.902829128	0.319132966	0.033723057	0.626140134	18.56712239
540751725	B Horizon	10.9967463	10.00390143	0.277017846	4.314709977	15.57556684
540751815	B Horizon	170.3846745	105.0035267	0.385144066	4.568661105	11.86221341
540751915	B Horizon	58.63303909	11.4284577	0.123959748	1.982528945	15.9933283
540751981	B Horizon			0.387167026	7.237281113	18.69291707
540752006	B Horizon	69.19558868	112.2958674	0.318141721	3.656781925	11.49419167
540752023	B Horizon	43.52398119	37.77810452	0.256272675	3.898847757	15.21366943
540752161	B Horizon	55.73002027	22.43937758	1.007985253	19.05309362	18.90215512
540830260	B Horizon	36.74290308	63.03330607	0.365622914	5.83324683	15.95427041
540830340	B Horizon	34.61881658	0.239544992	0.24086704	6.468706868	26.85592378
540830693	B Horizon	11.82949566	2.808050177	0.164786464	2.474456809	15.01614116
540831421	B Horizon	75.56760448	7.939730641	0.267115617	5.328521106	19.94836981
540831918	B Horizon	102.2184055	1.878690915	0.161921699	2.656892295	16.40850056
540832067	B Horizon	83.15252213	82.61928588	0.509395465	7.644763372	15.00752145
540832115	B Horizon	130.7566481	20.02031111	0.33767268	5.820371947	17.23672742
540832222	B Horizon	76.28203132	30.44264011	0.233396661	3.655369092	15.6616169
540832392	B Horizon	96.95244445	48.56635683	0.207884241	2.937288619	14.12944344
541010517	B Horizon	7.815120869	5.745436578	0.123987306	2.110943876	17.02548388
541011823	B Horizon	96.90244545	73.34155555	0.337341926	5.172540688	15.33322805
541012463	B Horizon	31.25686621	29.8978989	0.125103529	2.178031122	17.40982961

		NH ₄ OAc					Bray 1	pH(w)
		Ca	K	Mg	Mn	Na	P	
Plot	Sample	mmolc kg soil ⁻¹					mg kg soil ⁻¹	
540251274	A Horizon	2.186309221	3.055687692	2.511101336	0.038981545	3.111317702	17.02844495	3.79
540251303	A Horizon	2.615321383	1.061141196	1.150384233	0.192626822	4.089446513	15.7327618	3.86
540251389	A Horizon	3.428841299	1.649589224	1.753865634	1.315255436	2.846403483	6.719665692	4.24
540252514	A Horizon	20.30090151	3.891114806	11.1375158	1.791039223	3.727029901	17.94061495	4.43
540711765	A Horizon	8.656729458	3.109866933	2.5659702	1.244783327	0.401192343	35.22671239	3.81
540750085	A Horizon	6.951456568	3.261142572	3.091144061	4.383191053	5.175043385	13.09422188	4.15
540750596	A Horizon	6.105403119	2.978946311	2.753186708	3.389336991	0.408954271	29.56619147	3.77
540750777	A Horizon	2.225608382	1.915684229	2.22468805	0.100533375	3.504895814	23.33951647	3.75
540751103	A Horizon	12.80387834	2.634193407	3.383019743	8.718997932	4.510359639	30.14722689	3.74
540751144	A Horizon	2.137104317	1.226116714	1.516305317	0	4.542992881	10.32185975	3.60
540751341	A Horizon	24.73227157	3.159940633	3.570999869	3.795040171	0.553038043	9.618932203	4.94
540751725	A Horizon	7.825173269	3.393503397	3.020147862	2.49380312	0.382141934	16.09315508	3.60
540751815	A Horizon	19.30143948	3.208286246	4.332342238	4.197640173	3.780118105	26.01368588	3.86
540751915	A Horizon	10.03074144	3.01069717	4.079867046	0.658636397	4.054327715	22.40025379	3.75
540751981	A Horizon	23.52182533	3.46681081	5.030973149	18.68209904	4.478139387	23.75121662	3.86
540752006	A Horizon	10.48362835	2.628001994	3.4822589	6.788075364	4.12915441	21.69474442	3.91
540752023	A Horizon	5.967686941	1.726320908	1.852218404	0.337728951	3.203299673	12.31277666	3.71
540752161	A Horizon	15.94217144	4.942907844	4.723453946	0.130466529	5.512860461	62.20454674	3.51
540830260	A Horizon	14.14882137	2.653501638	4.672390529	6.847800827	3.891391803	51.90807662	3.47
540830340	A Horizon	2.424291869	3.022741742	4.27113371	0.144487625	3.316843167	23.90067317	3.51
540830693	A Horizon	10.87589453	2.318500929	3.447328357	0.539947611	1.122899436	16.37542837	3.52
540831421	A Horizon	6.996223141	1.487279424	1.802026843	0.132522465	3.637680907	13.45266422	3.70
540831918	A Horizon	3.440603135	1.152044683	2.238666297	0.638962908	3.292265924	15.96067884	4.39
540832067	A Horizon	11.21170972	3.801592404	4.131893358	2.861916606	5.851067004	30.03743828	3.59
540832115	A Horizon	8.466201579	3.575428076	3.558494681	1.865817092	3.045369689	29.95911966	3.80
540832222	A Horizon	12.20709081	2.946310052	4.320034684	1.129589421	5.46402739	21.3248461	3.61
540832392	A Horizon	11.51062826	2.18989653	2.841711316	2.839538726	5.12260889	21.67014735	3.69
541010517	A Horizon	4.325053886	0.992610796	1.291024577	0.442162518	0.546030039	5.416093409	3.90
541011823	A Horizon	2.000851125	2.025531778	1.712744934	2.081258097	3.724584018	24.31285011	3.69
541012463	A Horizon	22.83744428	2.440987071	7.262180666	1.963221821	4.145181657	15.50222101	3.99

Plot	Sample	NH ₄ OAc					Bray 1	pH(w)
		Ca	K	Mg	Mn	Na	P	
		mmolc kg soil ⁻¹					mg kg soil ⁻¹	
540251274	B Horizon	0.701105367	0.434969061	0.460011621	0	2.889734771	5.430285344	4.71
540251303	B Horizon	0.88809693	1.010092173	1.290204785	0.010071651	4.26141274	6.257800563	4.57
540251389	B Horizon	1.867242378	2.103043504	1.390910114	0.772437265	3.40473081	4.604756075	4.43
540252514	B Horizon	3.93529338	1.589643767	10.15034173	0.075076182	3.665846732	0.990634543	4.84
540711765	B Horizon	2.267774961	1.733478154	2.058806506	2.029691255	0.068638238	22.2429995	4.19
540750085	B Horizon	3.05075577	1.363988533	2.482084158	0.825954001	5.556351373	5.366113227	4.66
540750596	B Horizon	0.95720521	0.939127257	0.456545401	0.20290787	0.354545855	28.20809379	4.49
540750777	B Horizon	0.778207794	0.662955523	0.744029274	0	2.699621039	15.21606137	4.26
540751103	B Horizon	1.29252375	0.803135968	0.669617698	0.551323967	3.490643418	3.118959568	4.37
540751144	B Horizon	1.507053425	0.53276592	0.9965138	0	4.233917982	1.218891004	3.98
540751341	B Horizon	1.338820436	1.120887705	0.486765124	0.452274511	0.282260383	2.191109432	4.64
540751725	B Horizon	1.424368979	1.888243059	0.936228749	1.221650157	0.207930658	4.234288902	4.41
540751815	B Horizon	6.621153981	0.834084643	1.46777319	0.702559162	3.907339388	8.951407418	4.48
540751915	B Horizon	2.248711891	1.201599704	1.26350045	0	3.985273637	1.970868573	4.62
540751981	B Horizon						5.063122861	4.39
540752006	B Horizon	8.15725546	1.209305854	1.183567155	0.252009921	4.420575279	3.769668418	4.39
540752023	B Horizon	2.104864813	0.642265413	0.729191194	0.366165663	3.436136915	9.055796538	4.13
540752161	B Horizon	1.759948954	0.693010493	0.828471252	0	5.051564489	19.12859254	4.30
540830260	B Horizon	1.988165466	1.112000945	1.118506013	3.012655786	3.022747126	3.485659885	3.94
540830340	B Horizon	0.643652929	1.259050073	0.767346527	0	2.122782138	6.318659619	4.34
540830693	B Horizon	2.575351313	1.064476752	1.14928538	0.565057601	0.644144874	2.282825001	4.46
540831421	B Horizon	1.477004246	0.571907938	0.897561066	0	3.351518538	5.723248273	4.12
540831918	B Horizon	3.232234173	1.88792326	1.873973679	0.890532689	4.372693785	5.971325809	4.56
540832067	B Horizon	1.649507569	0.656698971	0.861577462	0.131230421	4.378137591	7.586971272	4.43
540832115	B Horizon	0.85935116	0.796376149	0.701851561	0.097271048	2.616103159	1.796573116	4.62
540832222	B Horizon	1.277043258	0.757881877	0.768416961	0	3.467969355	2.003081609	4.51
540832392	B Horizon	2.098332919	0.731856443	0.949699993	0.040007586	4.500502447	1.098191243	4.24
541010517	B Horizon	1.87556367	0.824632778	0.600856908	0.190769792	0.435797151	2.529308056	4.22
541011823	B Horizon	2.341477172	0.866868957	1.22410037	0.403610158	3.543420802	8.080932225	4.15
541012463	B Horizon	3.198054865	1.277632423	1.963859047	0.681363238	4.055400421	1.727447931	4.47

		Mehlich III								
		P	K	Ca	Mg	Zn	Mn	Cu	Fe	B
Plot	Sample	ppm								
540251274	A Horizon	4	49	74	24	1.1	5.0	0.5	70.0	0.1
540251303	A Horizon	8	65	94	28	4.0	13.7	0.6	75.7	0.1
540251389	A Horizon	3	65	154	33	2.3	158.2	0.1	66.3	0.1
540252514	A Horizon	4	68	227	68	2.6	82.5	0.1	87.4	0.1
540711765	A Horizon	8	66	196	39	2.4	70.9	0.1	177.6	0.2
540750085	A Horizon	4	61	167	35	3.3	190.5	0.1	78.6	0.1
540750596	A Horizon	7	57	137	31	3.6	121.7	0.1	81.6	0.1
540750777	A Horizon	14	72	94	39	2.9	16.6	0.4	23.3	0.1
540751103	A Horizon	11	66	231	35	2.4	262.3	0.1	82.1	0.2
540751144	A Horizon	2	33	64	22	1.1	2.8	0.5	226.8	0.1
540751341	A Horizon	2	49	633	35	2.7	149.0	0.1	39.9	0.2
540751725	A Horizon	2	51	160	28	1.9	55.8	0.1	115.0	0.1
540751815	A Horizon	10	71	300	43	3.0	118.7	0.5	110.2	0.2
540751915	A Horizon	5	59	159	36	1.9	31.0	0.3	226.6	0.1
540751981	A Horizon	8	52	319	41	3.5	295.3	0.1	50.6	0.1
540752006	A Horizon	6	60	190	38	2.4	208.9	0.1	72.1	0.2
540752023	A Horizon	2	51	210	33	2.6	19.3	0.5	251.0	0.1
540752161	A Horizon	18	68	305	40	3.8	14.1	0.2	41.6	0.1
540830260	A Horizon	17	46	228	42	1.9	194.3	0.1	120.1	0.1
540830340	A Horizon	2	39	60	27	2.8	1.9	0.5	160.9	0.1
540830693	A Horizon	7	53	172	34	2.4	9.0	0.5	114.3	0.1
540831421	A Horizon	3	35	166	24	4.2	9.3	0.2	98.0	0.1
540831918	A Horizon	2	67	235	44	5.4	77.2	0.1	60.9	0.1
540832067	A Horizon	6	71	212	40	4.0	126.0	0.1	109.0	0.2
540832115	A Horizon	7	59	163	38	3.3	20.9	0.4	120.5	0.1
540832222	A Horizon	6	49	198	39	1.8	42.0	0.5	122.6	0.1
540832392	A Horizon	10	72	279	47	2.4	119.4	0.2	77.2	0.2
541010517	A Horizon	3	26	141	27	1.4	21.8	1.0	155.7	0.1
541011823	A Horizon	7	48	94	27	1.5	65.6	0.5	46.1	0.2
541012463	A Horizon	5	41	417	60	5.7	87.0	0.3	55.1	0.1

Plot	Sample	P	K	Ca	Mg	Zn	Mn	Cu	Fe	B
		ppm								
540251274	B Horizon	2	24	50	14	0.7	4.7	0.5	39.3	0.1
540251303	B Horizon	2	20	51	14	1.8	4.2	1.0	64.5	0.1
540251389	B Horizon	2	39	69	19	0.8	16.5	0.9	48.7	0.1
540252514	B Horizon	2	42	100	106	1.0	13.0	0.9	31.2	0.1
540711765	B Horizon	2	39	96	20	3.4	24.9	0.3	55.4	0.2
540750085	B Horizon	2	39	117	37	1.1	47.2	1.2	33.5	0.1
540750596	B Horizon	14	38	69	17	1.6	20.3	0.5	26.4	0.1
540750777	B Horizon	2	23	59	20	1.1	3.2	0.6	284.9	0.1
540751103	B Horizon	2	27	60	14	0.9	48.6	0.6	54.3	0.1
540751144	B Horizon	2	18	57	17	0.8	2.2	0.8	204.4	0.1
540751341	B Horizon	2	33	97	18	0.8	38.5	0.4	30.9	0.1
540751725	B Horizon	2	29	64	15	1.1	55.4	0.3	45.0	0.1
540751815	B Horizon	2	23	165	22	3.8	41.1	0.6	38.6	0.1
540751915	B Horizon	2	35	65	17	1.1	4.1	0.7	67.1	0.1
540751981	B Horizon	2	30	546	54	5.7	203.3	0.1	49.1	0.1
540752006	B Horizon	2	29	78	15	0.9	32.1	0.9	37.2	0.1
540752023	B Horizon	2	23	115	18	1.8	22.3	0.3	77.6	0.1
540752161	B Horizon	2	19	80	16	2.3	1.9	0.2	71.2	0.1
540830260	B Horizon	2	33	74	18	1.1	130.4	1.6	111.1	0.2
540830340	B Horizon	2	36	52	16	1.1	2.9	0.7	49.4	0.1
540830693	B Horizon	2	23	80	19	1.2	18.8	0.8	99.2	0.1
540831421	B Horizon	2	19	57	15	0.8	2.3	0.6	180.1	0.1
540831918	B Horizon	2	36	69	31	0.8	9.7	0.5	37.8	0.1
540832067	B Horizon	2	21	65	16	1.3	22.0	0.4	39.3	0.1
540832115	B Horizon	2	29	56	16	0.8	6.4	0.5	67.6	0.1
540832222	B Horizon	2	25	64	16	0.8	8.9	0.8	37.3	0.1
540832392	B Horizon	2	20	63	14	0.7	9.6	0.9	37.9	0.1
541010517	B Horizon	2	22	86	17	1.1	15.6	0.8	150.0	0.1
541011823	B Horizon	2	25	56	16	0.8	31.5	0.6	55.5	0.1
541012463	B Horizon	2	41	124	33	2.3	36.7	0.7	58.0	0.1

Plot	Sample	Ex. Acidity cmolc kg soil ⁻¹	0.01 M SrCl ₂		
			Ca mmolc kg soil ⁻¹	Al mmolc kg soil ⁻¹	Ca/Al
540251274	A Horizon	5.0324	1.6624	1.4746	1.127331562
540251303	A Horizon	1.4659	1.7033	1.5234	1.118147426
540251389	A Horizon	8.3953	2.5429	2.0927	1.215162014
540252514	A Horizon	2.7559	7.5627	1.6289	4.642939984
540711765	A Horizon	4.2699	6.2748	4.1659	1.506220949
540750085	A Horizon	8.8898	4.2600	2.0341	2.094262378
540750596	A Horizon	4.1243	4.2010	2.9624	1.418120838
540750777	A Horizon	4.2897	1.9671	1.5796	1.245315077
540751103	A Horizon	2.8246	5.6424	2.5873	2.18083743
540751144	A Horizon	5.6729	1.3653	8.0337	0.169951543
540751341	A Horizon	1.1786	10.3345	1.0101	10.23089596
540751725	A Horizon	16.0745	5.8120	4.1799	1.390461992
540751815	A Horizon	6.1657	10.0714	1.6879	5.966893853
540751915	A Horizon	4.8672	5.5102	3.7815	1.45712851
540751981	A Horizon	6.7591	12.8956	1.6700	7.721801523
540752006	A Horizon	4.1114	6.4025	3.6328	1.76243839
540752023	A Horizon	8.7751	3.4037	4.3167	0.788498233
540752161	A Horizon	12.8260	21.8145	8.0490	2.710197868
540830260	A Horizon	3.8979	4.0134	0.9375	4.281080389
540830340	A Horizon	11.7977	1.6252	4.2376	0.383521645
540830693	A Horizon	19.4758	9.7878	7.7597	1.261367934
540831421	A Horizon	6.6141	3.5609	1.7790	2.001653126
540831918	A Horizon	4.3745	3.7107	3.2368	1.146407741
540832067	A Horizon	5.5730	3.9747	3.0565	1.300398893
540832115	A Horizon	4.1370	3.0755	1.2284	2.503619487
540832222	A Horizon	7.4048	4.5588	1.6668	2.735081536
540832392	A Horizon	2.8246	8.8446	2.6053	3.394805254
541010517	A Horizon	4.9171	2.8990	1.7917	1.61802331
541011823	A Horizon	6.6141	1.9046	3.3657	0.565891919
541012463	A Horizon	5.7544	12.7181	1.9526	6.513430477

		Ex. Acidity	0.01 M SrCl ₂		
			Ca	Al	Ca/Al
Plot	Sample	cmolc kg soil ⁻¹	__mmolc kg soil ⁻¹ __		
540251274	B Horizon	2.4659	0.1820	0.990508446	0.183712853
540251303	B Horizon	1.2784	0.3136	2.590531464	0.121064765
540251389	B Horizon	7.6850	0.8722	4.461189198	0.195505526
540252514	B Horizon	2.9514	1.3080	2.606959299	0.501721744
540711765	B Horizon	4.6388	1.4157	4.926744043	0.287355513
540750085	B Horizon	4.0465	1.6699	1.556909584	1.072543211
540750596	B Horizon	2.0683	0.6490	1.835343872	0.353621243
540750777	B Horizon	6.6544	0.3179	3.676900827	0.086463194
540751103	B Horizon	2.6570	0.5039	2.755348592	0.182885371
540751144	B Horizon	8.5895	1.5272		
540751341	B Horizon	3.6584	0.7530	1.592880253	0.472754966
540751725	B Horizon	9.8903	0.6646	1.823737947	0.36439475
540751815	B Horizon	6.5050	3.6430	1.657062111	2.198456474
540751915	B Horizon	5.9095	0.8173	7.369106015	0.110905702
540751981	B Horizon	6.5934	11.9233	0.48708495	
540752006	B Horizon	3.8802	3.2774	3.713208016	0.882625251
540752023	B Horizon	4.2660	0.9182	2.33353719	0.393460935
540752161	B Horizon	12.3345	1.2297	4.737370343	0.259571501
540830260	B Horizon	8.3008	0.6280	2.331872839	0.269312278
540830340	B Horizon	4.7705	0.1926	1.796507794	0.107195073
540830693	B Horizon	10.5228	1.4845	2.809461589	0.528393316
540831421	B Horizon	8.4067	0.5656	4.650658985	0.121611586
540831918	B Horizon	2.4350	1.7789	2.561525546	0.694456369
540832067	B Horizon	3.4125	0.6433	2.709406416	0.237427809
540832115	B Horizon	4.5219	0.3116	1.562192623	0.199482238
540832222	B Horizon	3.3093	0.6351	1.708285261	0.371750735
540832392	B Horizon	4.8558	0.6170	4.934903835	0.125036808
541010517	B Horizon	5.2156	1.4374	2.305853266	0.623390666
541011823	B Horizon	3.1338	0.5354	2.94953552	0.18152343
541012463	B Horizon	9.7562	1.8351	3.647873377	0.503056276

