Sulfate Dynamics and Base Cation Release in a High Elevation Appalachian Forest Soil

by

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Thesis submitted to the Faculty of the

Virginia Polytechnic Institute and State University

In partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Crop and Soil Environmental Science

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May, 1998 Blacksburg, Virginia

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(ABSTRACT)

Two soils from the Fernow Experimental Forest near Parsons, West Virginia were characterized and evaluated in terms of their susceptibility to enhanced soil acidification via acidic atmospheric inputs. After initial physical, chemical, and mineralogical characterization, the soils were analyzed for their ability to adsorb and retain sulfate ($SO_4^{2^-}$) through a series of batch adsorption and desorption experiments. Reconstructed soil profiles were then subjected to water leaching as the preliminary step to a base release study in which each soil will be placed under simulated acid rain and evaluated for base cation release and subsequent changes in soil chemistry.

Experiments with $SO_4^{2^2}$ adsorption and desorption divide the soils into two categories: (i) shallow surface horizons with high organic matter and little Fe oxide content which had little ability to adsorb additional $SO_4^{2^2}$ and low capacity to retain $SO_4^{2^2}$; and (ii) deeper subsurface soils with low organic matter and high Fe oxide content which could adsorb $SO_4^{2^2}$ at solution concentrations above 0.5 mmol/L. All soil horizons desorbed $SO_4^{2^2}$ and had no ability for additional adsorption at solution concentrations below 0.5 mmol/L, which implies that the site may be saturated with respect to natural conditions. Initial mass (IM) and Langmiur modeling were used to illustrate $SO_4^{2^2}$ dynamics and make correlations with soil physical, chemical, and mineralogical properties. Fe oxides and Alsaturated organic matter were shown to be the preferential sites for $SO_4^{2^2}$ adsorption but may be already saturated or very near saturation.

Preliminary results from the base release study indicate that the two soils are dominated by different chemical processes and hence release ions into soil solution at different rates. Ion release is shown to be a function of both reactions on the exchange complex and the dissolution of mineral components.

Acknowledgements

Much appreciation and acknowledgement is given to Dr. L. W. Zelazny for his very valuable role in the development of this work. As both an academic advisor and a personal mentor, Dr. Zelazny has guided my graduate studies with tremendous wisdom, insight, and patience. His unique ability to combine outstanding academic leadership with a gracious and amicable personal character has been the foremost important factor in my graduate achievements on both a professional and personal level. He has taught me much about soil chemistry, and he has taught me perhaps even more about the love of learning and the roles of friendship and tolerance required in all notable pursuits.

Dr. James Burger is thanked for his valuable contributions in forest soil science. He has spent much time in advising me on the many opportunities of this research project. In so doing, he has shown great insight and the ability to develop an initial objective into a contributive and beneficial result. Dr. W. Lee Daniels has also been of great support in this project. He has provided invaluable wisdom in the planning and development stages and has helped me develop a greater knowledge of the science of the soil and the processes of academic achievement.

The department of Crop and Soil Environmental Sciences at Virginia Tech is greatly appreciated for many significant contributions. Members of the department have always been very willing to provide support in all of my work here. Hubert Walker is especially thanked for providing such an outstanding teaching role in my lab work and for his ability to locate absolutely anything I ever needed. The Soil Testing Lab has provided thousands of analytical results, and they are thanked for their time and efforts to provide quality data.

All research has been funded by the United States Forest Service, and staff members of the Northeastern Experimental Station in Parsons, West Virginia are thanked for their assistance in gathering data and collecting field samples. Mary Beth Adams, a forest soil scientist at Parsons, has been especially helpful in providing guidance and crucial background information throughout the project.

I am most grateful to my family for their support of this effort. My parents, Garland and Linda Gilchrist, have always been tremendous role-models in my life, and their love for me continues to guide me. Jenny Gilchrist, my sister and a talented musician, has always been there for me even though we have devoted our interests to entirely different things. My husband Craig is my greatest support and I am most thankful for his love and patience. He has taken such a sincere interest in my goals and pursuits that he may know this project as well as I do, and I love him for that.

I have devoted my life's work to a love for the land and devote this work to all those who have instilled that love within me.

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Chapter 1 Introduction

1.1 Anthropogenic Soil Acidification in Forest Ecosystems

The responses of forest ecosystems to large-scale anthropogenic soil disturbances are becoming increasingly documented in the literature (Kaiser, 1996; Likens, et al., 1996; Likens and Bormann, 1995; Flynn, 1994). One major source of soil disturbance is acid deposition; the atmospheric input of acidifying compounds derived from fossil fuel combustion. Decades of elevated atmospheric inputs of nitrogen (N) and sulfur (S) in industrialized regions of the world have led to localized areas characterized by a decrease in the soil's acid neutralizing capacity (ANC). Forest ecosystems have substantial capacity to neutralize acidic inputs, and one means of doing so is via base cation reserves in plant tissues and soils. Once acidic inputs exceed a threshold limit, however, base cation release by weathering and organic matter decomposition is no longer adequate to support sustainable forest productivity. In response, soils that support forest ecosystems in many acidified areas have become characterized by a decline in the soil's ability to replenish base cations after their removal by leaching, tree uptake, and harvesting. This decline in base saturation is associated with pH depression, AI mobilization and toxicity, and macronutrient deficiency. Furthermore, acid sensitivity may increase with time since the soil's (ANC) against further inputs decreases as the cation exchange complex becomes more saturated with Al.

Even though environmental regulations in many countries have led to recent declines in the input of acid forming materials to the soil, at present, there have been no corresponding observations of improvements in the base saturation or ANC of affected soils (Likens et al., 1996). Consequently, the effects of acid deposition on forest systems may be somewhat long-term and exceed the actual periods of acidic input. Already, nutrient imbalances that result in growth reduction and tree mortality are being observed in forested areas that are currently or have been historically disturbed by acid deposition (Johnson and Anderson, 1994; Smith et al., 1996; Shortle et al., 1997).

Aside from acid deposition, harvesting of trees is a second means of base cation removal. The loss of base cations through harvesting activities can be detrimental in itself, but it also intensifies the effects of acid deposition by reducing the ANC. Commercial harvesting in the eastern United States is expected to continue and become more intensive (Federer, et al., 1989).

In order to alleviate detrimental effects of soil disturbances and ensure longterm sustainability, we first need to characterize resistance mechanisms, which will be somewhat site specific. Inherent differences in the resistance mechanisms of soils result in degrees of sensitivity among forest ecosystems. However, the processes of resistance remain essentially the same and are based upon buffering processes inherent to the soil at hand.

1.2 Buffering Processes

Major impact processes of soil acidification and commercial harvesting involve the deposition of N and S and the depletion of base cations such as Ca, Mg, K, and Na. The buffering processes against soil disturbance, therefore, are those which contribute to (i) soil potential to absorb sulfate $(SO_4^{2^-})$, (ii) potential for biota to sequester N, (iii) the composition and stability of the soil's exchange complex, (iv) atmospheric and weathering inputs of base cations and (v) the soil's ability to serve as a sink for H ions.

For a forest ecosystem, the buffering processes are parts of a biogeochemical cycle that determines nutrient availability (Figure 1.1). Elevated inputs of atmospheric S can be attenuated through adsorption processes, which will be dependent on the mineralogy and pH of the soil. Atmospheric deposition of N is primarily buffered by microbial retention. Both $SO_4^{2^-}$ adsorption and microbial retention of N result in the release of alkalinity and the removal of mobile acid anions. When either the nature of the soil or excess atmospheric inputs limit these two buffering processes, base cations leach from the soil in association with the mobile anion. Furthermore, Cronan et al. (1990) have shown that mobilization of AI is increased when excess concentrations of $SO_4^{2^-}$ and NO_3^- anions are present. While AI is a common cation in forest soil systems, its increased mobility can be harmful for aquatic systems. The AI ion is toxic to aquatic life when present in large concentrations in receiving waters.





The extent and stability of the exchange complex determine the soil CEC. The nature of the exchange complex is a function of several variables, including, mineralogy, climate, and vegetation. Weathering of parent material is the major long-term source of base cation supply to the soil mineral pool and exchange complex. Although base cations may also be deposited to the soil through atmospheric input, this mode of transport is, overall, decreasing due to emissions restrictions. Likens et al. (1996) report that from 1955 to 1975, the demand for Ca met by bulk precipitation fell from 29% to 8% at the Hubbard Brook Experimental Forest. During the same time, soil depletion of Ca had increased 1.4 times due to soil acidification. The trend of decreasing input of base cations from atmospheric deposition continues today and establishes weathering inputs as one of the most crucial buffering processes against base depletion.

1.3 Research Overview and Objectives

The working hypothesis of this study is that soils of the high-elevation Appalachian forests are being adversely affected by chronic inputs of anthropogenic acidity. Consequently, forest sustainability will be hindered and productivity will decline unless mitigative actions are initiated.

Two major impact processes that may contribute to forest decline through enhanced acidic inputs are (i) SO₄ and NO₃ deposition, which can cause coleaching of important base cations (Ca, Mg, K) and result in their depletion from soil reserves; and (ii) harvesting removals of base cations that are supplied in the organic matter of either living tissue or decaying material on the forest floor.

The objective of this study is to characterize various properties of a forest soil to determine its sensitivity to the above impact processes. Specifically, the research is being conducted at the Fernow Experimental Forest near Parsons, West Virginia. Encompassed within a broader national study being conducted by the USDA Forest Service, this study is part of a national research effort to assess the long-term productivity of forests disturbed by human influence. By identifying the mechanisms by which the forest responds to anthropogenic disturbances, we can determine restrictive or mitigative actions which must be taken to ensure sustainability.

While other parts of the national effort are focusing on microbial and vegetative dynamics, this part of the study has focused only on the three buffering processes related to the nature of the soil at hand: (i) $SO_4^{2^2}$ adsorption capacity and $SO_4^{2^2}$ retention, (ii) the extent and nature of the cation exchange complex, and (iii) weathering inputs of base cations.

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Chapter 2. The Fernow Experimental Forest

2.1 Location and History

The Fernow Experimental Forest is located near Parsons in Tucker County, West Virginia (39°03'N and 79°41' W). Much of the site lies within the boundaries of the Elklick Run drainage (Figure 2.1). It is in the Allegheny Mountain section of the unglaciated Allegheny Plateau, and its topography is rugged. Elevations are from 533 to 1,112 m, and slopes are from 10 to 60%, with slopes of 20 to 30% being most common.

Established on May 28, 1934 from a portion of the Monongahela National Forest, the experimental site is named in honor of Bernard E. Fernow, a pioneer of scientific forestry in the United States. The site originally comprised 1,473 hectares (ha) and was expanded to 1,902 ha in 1974.

Because it has been recognized as representative of much of the timberland of West Virginia and adjacent states, the Fernow is utilized for research projects in the sustainability of central Appalachian forest ecosystems. Research projects are headquartered at the Northeastern Forest Experiment Station's Timber and Watershed Laboratory at Parsons.

In 1951, five watersheds within the Fernow were selected and instrumented for hydrologic research. The watersheds were monitored for six years to establish streamflow patterns and ambient stream chemistry. Then in 1957-58, various treatments of forest management practices were initiated on four of the



Figure 2.1. The Fernow Experimental Forest shown with research points 1 through 13. LTSP plots are located along Fork Mountain Road in the NW corner of the forest.

watersheds. The fifth watershed was established as a control, and monitoring and experimentation continues today at each of the watersheds. Research interests have included relationships between silvicultural practices and soil and water quality, precipitation chemistry, and streamflow modeling.

2.2 Parent Material and Soils

The soils of the Fernow Experimental Forest are predominantly derived from sandstone and shale parent material. A majority of the soils are of the Calvin, Berks, and Meckesville series. The Calvin (Loamy-skeletal, mixed, mesic Typic Dystrochrepts) soils are moderately deep and well drained. They have formed from noncalcareous shale, siltstone, and sandstone and have mostly loam or silt loam textures. Calvin soils range from moderately acid to strongly acid throughout the profile. Their mineralogy is dominated by illite, and there are also moderate amounts of vermiculite and chlorite.

Soils of the Berks (Loamy-skeletal, mixed, mesic Typic Dystrochrepts) series are also moderately deep and well drained. Their parent material is shale, siltstone, and sandstone residuum. Berks soils have loamy textures and from 30 to 70% rock fragments within the profile. They are slightly to moderately acid.

The Meckesville (Fine-loamy, mixed, mesic Typic Fragiudults) soils are very deep and well drained. The series is extensive throughout the states of Pennsylvania and West Virginia. In the more northern areas, soils of the Meckesville have formed from colluvium and glacial till from red acid sandstone, siltstone, and shale. The Fernow lies, however, within an unglaciated region. Thus, Meckesville soils within the Fernow are derived entirely from colluvium. The depth to bedrock is typically more than 150 cm, and depth to the fragipan ranges from 70 to 120 cm. These soils range from extremely through strongly acid.

A belt of Greenbriar limestone does run through one point of the Fernow, 91 m southwest of Big Springs Gap, and produces a zone of limestone soils of the Belmont series (fine-loamy, mixed, mesic, Typic Hapludalfs). The Belmont soils are deep and well drained with moderate permeability. Within the Fernow, these soils have rock fragments from 0 to 20% by volume in the A and B horizons and 20 to 60% in the C horizon. They typically range from strongly acid in the A horizon to mildly alkaline in the C horizon. Silt loam and silty clay loam textures predominate, and these soils have moderate shrink-swell potential. Limestone outcrops are common for the Belmont soils.

2.2.1 Characterization of experimental soils

Sixteen half-acre square research plots were established on Fork Mountain near Urus Spur Road within the Fernow Experimental Forest in 1995 (Figure 2.2). Research projects at the sixteen plots are each part of the integrated study being conducted by the USDA Forest Service to quantify the long-term productivity of forests that have been disturbed by elevated atmospheric inputs of N and S. The plots are commonly referred to as the Long Term Site Productivity (LTSP) Research plots.

Soils within the Fernow have been hypothesized as susceptible to such disturbances and, therefore, may be characterized by a decline in the soil's ability



Figure 2.2. LTSP Research Plots at the Fernow Experimental Forest to replenish base cations after their removal by leaching, tree uptake, and harvesting (Section 2.5.1). In response, the LTSP plots have been assigned treatment combinations in a completely randomized block design with three treatment factors. The treatments are harvest removal, N and S input, and enhanced base additions via liming activities. They will be maintained for rotation-age duration, or approximately 80 years.

Prior to experimental treatment, initial characterization of soil properties for each of the sixteen plots began in 1995. Bulk soil samples were collected in triplicate from three depths (0-15 cm; 15-30 cm; 30-46 cm) at each plot (a total of nine samples per plot). The soils were air-dried, passed through a 2-mm (# 10) sieve, and stored in plastic bags at room temperature. Coarse fragments and roots not passing through the sieve were washed and their presence recorded as a percent of total bulk mass. Each sample was then analyzed in duplicate for physical and chemical characteristics. In addition to the sixteen research plots. four soil pits were excavated within the research area for taxonomic classification (Figure 2.2). Selection of sites for the four pits was based upon visual differences in landscape or vegetation, so that each pit represented visual degrees of variability within the research area. From the four pits, two were later deemed to represent the most extreme variations in the overall research area. Bulk samples from each morphologic horizon of these two profiles were selected for mineralogical analysis in addition to physical and chemical characterization. (Full profile descriptions for the four pits are presented in the Appendix).

2.2.1a Physical soil properties

Methods and Materials. A particle size analysis was conducted for each bulk sample by the hydrometer method. A 50 g aliquot of air dry soil was dispersed with 100 ml of Calgon solution (50 g Calgon/1 L DI water) and 400 ml of distilled water. The soil-Calgon suspension was mixed for 5 minutes, transferred to a 1000 ml sedimentation cylinder, and brought to volume with distilled water. The suspension was then thoroughly mixed, the hydrometer was placed into the suspension, and readings were taken at 40 seconds and 2 hours. Readings were taken at lab temperature, which was recorded for each sample and reading so corrections could be made for hydrometer buoyancy at various temperatures.

The organic C content of each bulk sample was determined by dry combustion at approximately 2400°C in an oxygen atmosphere by a LECO CR-12 carbon analyzer. A conversion factor or 1.724 was used to calculate percent organic matter from measurements of organic C, since organic matter content is typically about 1.724 times as great as the organic C content of a soil. This conversion factor represents an average based on assumptions of the presence of various organic substances in the form (CHO)_x. Also, for Profile A, the O, A, and BA horizons were further analyzed for percent C by chemical oxidation and loss on ignition methods. The chemical oxidation method was after the method of Walkley and Black (1934). A 10 ml volume of 1 N K₂Cr₂O₇ was added to 1 g of soil and gently swirled for a few seconds to mix the suspension. Then 20 ml of concentrated H_2SO_4 was added and the suspension was allowed to stand for 30 minutes. No external heat was applied to the system. In preparation for titration, 200 ml of distilled water and 5 drops of orthophenanthroline-ferrous complex indicator were added after the reaction period. The solution was titrated with FeSO₄ to a red-brown endpoint. A blank was titrated in similar fashion except for the absence of the sample in order to standardize the $Cr_2O_7^{2^-}$. The loss on ignition method involved placing a known mass of soil in a 380 °C muffle furnace for 3 days and then re-weighing the sample to determine the mass loss by ignition. The difference was held to be due to loss of organic C.

Results and Discussion. For each plot within the LTSP research area, there are increases in clay content and decreases in sand content with depth. Overall, the soils have loam textures throughout the profile or they grade from loams in the surface (0-15 cm) to clay loams in the subsurface (31-46 cm) (Table 2.1). The profiles A and C have variable trends in their particle size distributions with depth (Table 2.2). The O horizon of Profile C actually contains 32% clay. Visual inspection of the bulk O horizon sample does reveal large aggregates of B horizon-like material. These aggregates of clay were not likely formed in place however. Root action and mass wasting from higher slopes are the two main sources of clay movement into the O horizon. Similar observations and conclusions can be made for Profile A.

Percent C values decrease with depth over the entire research area (Tables 2.1-2.2). Since Fernow soils contain visible traces of charcoal in the surface horizons due to historical forest fires, percent C values may not correlate well with reactive soil organic matter. Dry combustion methods such as that employed by the LECO Carbon Analyzer will recover all forms of organic C, but cannot often distinguish between reactive C and inert forms such as charcoal.

Plot	Depth. cm	% C	% Sand	% Silt	% Clav	USDA Texture
1	0-15	8.5	56	30	14	Sandy Loam
1	15-31	2.8	42	32	26	Loam
1	31-46	1.0	37	32	31	Clay Loam
2	0.45	C 4	20	47	47	1
2	0-15	6.4 2.4	36	47	17	Loam
2	10-01	3.4 13	31	43	20 36	Clay Loam
2	51-40	1.5	51	55	50	
3	0-15	7.4	44	43	14	Loam
3	15-31	3.8	54	34	12	Sandy Loam
3	31-46	1.6	46	30	24	Loam
4	0-15	6.5	49	42	10	Loam
4	15-31	2.5	46	33	21	Loam
4	31-40	1.0	43	20	29	Loam
5	0-15	63	48	43	9	Loam
5	15-31	2.7	51	33	16	Loam
5	31-46	1.3	46	28	26	Loam
6	0-15	7.2	45	44	12	Loam
6	15-31	2.4	41	39	20	Loam
6	31-46	0.9	36	33	31	Clay Loam
7	0.15	6.0	45	10	10	Loom
7	0-10 15-31	24	45	43	12	Loam
7	31-46	0.9	40	29	30	Clav Loam
	01 10	0.0		20	00	
8	0-15	9.1	48	39	12	Loam
8	15-31	2.9	48	34	17	Loam
8	31-46	1.2	41	31	28	Clay Loam
0	0.45	5.0	40	40	10	1
9	0-15	5.8	42	43	12	Loam
9	31-46	2.2	35	35	22	Clay Loam
J	01 40	1.0	00	00	00	olay Loann
10	0-15	6.8	45	42	13	Loam
10	15-31	2.7	44	39	17	Loam
10	31-46	1.1	42	33	25	Loam
	0.45	Г 4			40	1
11	0-15	5.4 2.2	44 25	44	12	Loam
11	31-46	2.3	30	40 33	20	Clay Loam
	01 40	1.2	64	00	00	oldy Louin
12	0-15	4.8	44	39	17	Loam
12	15-31	2.3	46	36	18	Loam
12	31-46	0.9	44	29	27	Clay Loam
1.0	a / =			~ .		
13	0-15	4.4	51	34	15	Loam
13	10-01	1.7	31 40	31 27	10	Loam
15	31-40	0.0	49	21	23	LUain
14	0-15	3.9	46	37	16	Loam
14	15-31	1.7	45	34	21	Loam
14	31-46	0.9	40	31	29	Clay Loam
15	0-15	6.1	44	42	13	Loam
15	15-31	2.8	45 40	37	17	Loam
CI	31-40	1.2	40	31	29	
16	0-15	9.8	44	42	13	loam
16	15-31	5.0	46	36	18	Loam
16	31-46	2.1	42	31	27	Clay Loam

Table 2.1. Percent C and Particle Size Analysis for LTSP Plots

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Profile A	Depth, cm	% C	% Sand	% Silt	% Clay	USDA Texture
O Horizon	2.5	8.00	28	37	35	Clay Loam
A Horizon	17.8	6.25	43	31	26	Loam
BA Horizon	12.7	0.53	41	35	24	Loam
Bw1 Horizon	27.9	0.50	41	33	26	Loam
Bw2 Horizon	30.5	0.38	39	36	25	Loam
2C Horizon	43.2	0.29	35	41	24	Loam
Profile C						
O Horizon	1.3	11.2	35	33	32	Clay Loam
A Horizon	6.4	8.60	38	31	31	Clay Loam
BA Horizon	10.2	1.09	35	38	27	Loam
Bw1 Horizon	25.4	0.64	35	40	25	Loam
Bw2 Horizon	7.6	0.59	39	34	27	Loam
BC Horizon	15.2	0.32	37	36	27	Loam
2C Horizon	27.9	0.28	38	38	24	Loam

Table 2.2. Percent C and Particle Size Analysis for Profiles A and C

For Profile A, the O, A, and BA horizons were further analyzed for C by chemical oxidation and loss on ignition.

The LECO carbon analyzer produced the highest estimates of organic matter for the O and A horizons, while C loss on ignition produced the highest organic matter estimate for the BA horizon (Table 2.3). Lower organic C estimates by chemical oxidation suggest that inert forms of C were present in all three samples. Furthermore, the trend of more C recovery by ignition increases with depth. Carbonized materials such as charcoal may not have been recovered by chemical oxidation. This observation may be highest for the BA horizon because it contained the most visible traces of charcoal. Walkley (1947) observed that chemical oxidation without external heating recovered as little as 11% of organic C in such materials.

Estimates of organic C by combustion in the LECO carbon analyzer were only slightly higher for the O horizon when compared to the chemical oxidation method. While non-oxidizable materials may have been present in the sample, they would only be in relatively small concentrations, and it is unlikely that they were carbonized materials such as charcoal. Carbon loss on ignition to 380°C actually produced the lowest estimate of organic matter for the O horizon. Heat treatment to only 380°C was probably inefficient for combustion of all organic matter in this sample because of leaf litter and only slightly decomposed plant material.

Sample	Treatment	% Organic C	% Organic Matter	C Fraction of CLECO
Oi	$K_2Cr_2O_7-H_2SO_4^a$	7.46	12.68	0.93
Oi	Loss on ignition ^b	6.87	11.68	0.86
Oi	LECO ^c	8.00	13.60	1.00
А	$K_2Cr_2O_7-H_2SO_4$	4.71	8.00	0.75
А	Loss on ignition	5.61	9.53	0.90
A	LECO	6.25	10.63	1.00
BA	$K_2Cr_2O_7-H_2SO_4$	0.40	0.68	0.75
BA	Loss on ignition	0.75	1.28	1.41
BA	LECO	0.53	0.91	1.00

 Table 2.3. Soil Organic C and Organic Matter Estimates in the Surface

 Horizons of Profile A

a=chemical oxidation by dichromate and addition of sulfuric acid; b=C loss on ignition to 380°C; c=combustion in LECO C-12 carbon analyzer to ≈2400°C

In general, the dichromate method used here was not as efficient in recovering non-oxidizable materials (charcoal) in the BA horizon of the soil profile. Dry combustion methods recovered more total organic C, but they did not distinguish between carbonized C and soil organic matter C. Chemical oxidation methods may, therefore, be less appropriate for determining total organic C in a soil sample. However, chemical oxidation would be more appropriate for estimating soil organic matter alone.

2.2.1b Chemical soil properties

Methods and Materials. Soil pH values were determined in distilled water, 1 N KCl and 0.01 M CaCl₂. For each measurement, soil to solution ratios of 1:2 were used by placing 5 g of soil into a 50-ml beaker and adding 10 ml of the extractant. After equilibration for approximately 1 h, the pH of the solution above the soil was measured with a pH meter and combined electrode which had been calibrated with standard buffers at pH 4.0 and 7.0.

Exchangeable base cations were measured by extraction with 1 N NH₄OAc at pH 7.0 (70 ml NH₄OH and 57 ml acetic acid per liter solution; adjusted to pH 7.0 with NH₄OH). A 5-g sample was placed into a 100-ml plastic centrifuge tube and extracted with 25 ml of the NH₄OAc solution. The suspension was stoppered and placed at low speed on a shaker tray for 30 minutes. At the completion of the extraction, the suspension was centrifuged at 2000 rpm for 10 min. The supernatant was then transferred to a 50-ml volumetric flask fitted with a funnel and #42 Whatman filter paper and allowed to filter by gravity. The soil remaining in the tube was washed once with a 25-ml aliquot of NH₄OAc, which was then transferred to the flask. Concentrations of Ca, Mg, K, and Na in the extract were determined by atomic adsorption spectophotometry (AAS).

Exchangeable acidity was determined by extraction with 1 *N* KCI. A 5.0 g sample of each bulk soil was placed into a 100-ml centrifuge tube with 75 ml of the KCI solution. The tube was stoppered and shaken periodically by hand for two days. The sample was then centrifuged and filtered through Whatman #42 filter paper, transferred to a 100-ml volumetric flask and washed three times with 10 ml aliquots of 1 *N* KCI. Potentiometric analysis of exchangeable acidity was performed by titrating with an automatic titration apparatus 40 ml of the extract to pH 8.0 with 0.04 *N* NaOH.

Total acidity was measured by the BaCl₂-triethanolamine (TEA) method, which involves placing a 5 g soil sample into an Erlenmeyer flask and adding 25 ml of Melich's reagent (0.5 N BaCl₂ and 0.01 N TEA adjusted to pH 8.2). The flask was stoppered and periodically shaken by hand for 1 h. The suspension was then filtered through a Whatman #42 filter paper with a vacuum pump. Subsequent to the initial leaching, each sample was washed with three 25-ml aliquots of the buffer solution and four 25-ml aliquots of a BaCl₂ replacing solution (0.5 N BaCl₂ with 0.4 ml buffer solution per liter). Between washings, all of the solution was allowed to leach through the soil before the next addition of solution. The leachate was titrated with approximately 0.8 *N* HCl to the endpoint of a bromocresol-green methyl red indicator solution.

Results and Discussion. The key objectives of the chemical characterization were (i) determine if significant soil differences exist among the LTSP plots and if there are individual land areas within the whole research area that have unique chemical nature; (ii) describe significant soil differences with depth; (iii) identify and describe any relationships between soil chemical properties; and (iv) describe the chemical status of the research soil in terms of its ability to buffer acidic inputs.

A multivariable analysis of variance (MANOVA) was conducted with the chemical properties data. Variables included in the analysis were total acidity, Ca, Mg, K, total base cations, CEC, BS, water pH, KCl pH, and CaCl₂ pH. The MANOVA test shows that significant differences (p=0.0001) do exist among the 16 research plots. In order to characterize the differences between plots and place the plots into similar groupings, a principal components analysis was utilized. The principal components analysis is a multivariate technique that allows examination of relationships among several variables. Since the chemical properties data set contains variables that may be influencing each other (e.g. base cations and CEC, or total acidity and CEC), the principal components analysis is helpful in that it allows the data to be grouped into different components that represent linear combinations of the original variables.

Organic C values were included in the principal components analysis of soil chemical properties. The principle components analysis shows that percent C values contribute to the most variance (46.5%) between plots. Eigenvectors show similar loadings on percent C, TEA acidity, Ca, Mg, K, total bases, and CEC (Tables 2.4a and 2.4b). There are also similar loadings on water pH, KCl pH, and CaCl₂ pH. The pH values contribute less than 1% to the total variance. When the 16 research plots were scored according to statistical loadings on the above chemical properties, groupings of similar plots could be developed at each of the three sampling depths. Plots # 1, 2, 3, 6, 7, 10, 11, 13, 14, and 15 are all grouped closely together. Plots # 4, 5, 9, 12, and 16 are all individually separated from each other. Therefore, for the entire research area, six distinct groups exist in terms of overall chemical characterization.

Carbon values appear to provide a high level of control on overall soil chemical characterization. It is certainly a major source of base cations and determines largely the variability between plots due to its influence on base cation supply and total acidity levels.

On a general basis, soil water pH values ranged from 3.88 to 5.02, with an average value of 4.44 (Figure 2.3). The surface samples generally had the lowest pH values, and the deepest samples had the highest pH values. Surface soils are expected to display lower pH values, mostly due to the presence of organic matter and the associated organic acids. Acid deposition may also

contribute to more acidity in the surface, although it is impossible to quantify its effects without a natural background level for comparison. Exceptions to the trend of lower pH values in the surface are plots 4, 5, and 16, which have the lowest pH values in their subsurface. Since plot 16 lies within a drainage-way,

Variable	Eigenvalue	Difference	Proportion	Cumulative
% C	5.11545	3.38537	0.465040	0.46504
TEA Acidity	1.73008	0.327676	0.157280	0.62232
Ca, cmol+/Kg	1.35332	0.41351	0.123029	0.74535
Mg, cmol+/Kg	0.93982	0.15798	0.085438	0.83079
K, cmol+/Kg	0.78184	0.32849	0.071076	0.90186
Total Bases	0.45335	0.11837	0.041213	0.94308
CEC	0.33497	0.19972	0.030452	0.97353
BS	0.13526	0.03137	0.012296	0.98583
pH _{water}	0.10389	0.05215	0.009444	0.99527
pH _{kcl}	0.05174	0.05145	0.004704	0.99997
pH _{cacl}	0.00029		0.000027	1.00000

Table 2.4a. Eigenvalues of the Correlation Matrix for Soil ChemicalProperties

Table 2.4b.	Eigenvectors	of the First	Two Principa	al Components
-------------	--------------	--------------	--------------	---------------

Variable	Principal 1	Principal 2
% C	0.392576	0.040347
TEA Acidity	0.341972	0.227669
Ca, cmol+/Kg	0.104786	073719
Mg, cmol+/Kg	0.405447	0.033468
K, cmol+/Kg	0.392222	058403
Total Bases	0.398590	0.102793
CEC	0.351982	0.225737
BS	0.283912	072254
pH _{water}	126614	0.536823
pH _{kcl}	089067	0.442597
pH _{cacl}	111347	0.621094

basic inputs are likely being washed into its surface. Plots 4 and 5 may have higher surface pH values due to mass wasting since they are at higher slopes, although there is no other existing evidence of this. Values for pH estimated in KCl and CaCl₂ were both averaged at 3.94 (Figures 2.4 – 2.5).

Calcium is the dominant base cation on the exchange complex of all plots. It is especially prevalent in the upper plots 1 through 4 (Figure 2.6). Mg and K are the next most prevalent bases on an equivalent basis and are somewhat constant throughout the plot area (Figures 2.7–2.8). For all plots, total base cation concentrations decrease with depth, usually dropping off most sharply at the boundary of the 0 to 15 cm sample and the 15 to 31 cm sample (Figure 2.9). Since geochemical sources of base cations may be low, this observation supports the hypothesis that organic matter is an important source of base cation supply in the surface of Fernow soils.



Figure 2.3. Water pH values for LTSP Plots



Figure 2.4. KCl pH values for LTSP Plots



Figure 2.5. CaCl₂ pH Values for LTSP Plots



Figure 2.6. Additive Ca Levels in LTSP Plots







Figure 2.8. Additive K Levels in LTSP Plots


Figure 2.9. Additive Base Cation Levels in LTSP Plots





Total acidity is high for all plots, especially in the surface samples (Figure 2.10). Hence, total CEC is high though BS is relatively low. These soils are all saturated with Al^{3+} . This observation will have important implications for $SO_4^{2^-}$ adsorption dynamics and base cation cycling (Section 3.4).

Chemical analyses of Profiles A and C reveal both important similarities and differences between the two (Table 2.4). Both profiles have similar levels of total acidity, which decreases with depth throughout the profiles. Profile A, however, has much higher base cation levels and more KCI exchangeable acidity in its subsurface horizons. The Profile A soil displays a higher CEC and BS values approximately twice those of Profile C. Profile A also contains more extractable Fe, which is assumed to be in the form Fe_2O_3 (hematite).

<u>Horizon</u>	Total	BaCI-TEA Acidity	KCI Exch. Acidity	Total CEC	Total BS	ECEC	<u>EBS</u>	<u>% Fe</u>	<u>% Fe₂O3</u>
	Bases <u>cmol+/kg</u> ^a	cmol+/Kg	cmol+/Kg	<u>cmol+/Kg</u>		<u>cmol+/Kg</u>			
0									
А	2.06	27.00	4.60	29.06	0.07	6.66	0.31	1.88	2.54
BA	0.64	13.00	3.75	13.64	0.05	4.39	0.15	1.49	2.09
Bw1	1.87	10.25	4.25	12.12	0.15	6.12	0.31	2.35	3.29
Bw2	3.57	12.50	7.70	16.07	0.22	11.27	0.32	3.35	4.66
2C	3.95	12.00	9.30	15.95	0.25	13.25	0.30	5.12	7.08
Cr	3.54	13.00	7.25	16.54	0.21	10.79	0.33	4.76	6.61
Profile C									
<u>Horizon</u>	Total	BaCI-TEA Acidity	KCI Exch. Acidity	Total CEC	Total BS	ECEC	<u>EBS</u>	<u>% Fe</u>	<u>% Fe₂O₃</u>
	cmol+/kg	cmol+/Kg	cmol+/Kg	<u>cmol+/Kg</u>		<u>cmol+/Kg</u>			
0									
А	1.01	31.00	5.30	32.01	0.03	6.31	0.16	1.38	1.86
BA	0.29	18.25	3.38	18.54	0.02	3.66	0.08	1.80	2.48
Bw1	0.15	10.75	4.98	10.90	0.01	5.12	0.03	1.92	2.68

11.83

10.16

9.17

0.03

0.06

0.07

5.45

5.26

4.27

0.06 2.08 2.91

0.13 2.08 2.94

2.47

0.16 1.75

5.13

4.60

3.60

 Table 2.5 Chemical Characterization of Profiles A and C

 Profile

Α

Bw2

BC

2C

0.33

0.66

0.67

11.50

9.50

8.50

2.2.1c Mineralogical soil analysis

Methods and Materials. Bulk samples from the selected two taxonomic soil pits were further analyzed for mineralogical characterization. The majority of the mineralogical characterization was achieved by analysis of the clay fraction of each sample. Inspection of sand and silt fractions provided supplemental data. Also, a total analysis on the sand and silt fractions was employed to provide further information about elemental reserves in each soil. Samples were collected in November 1996 and kept frozen in plastic buckets during storage. Sample preparation involved removing one sample at a time from the freezer and placing it in a 4°C refrigerator. The sample was allowed to sit at 4°C overnight to thaw. Once the sample was thawed, a subsample was removed from the bucket and wet sieved by pressing the soil through a 3-mm sieve. The sieving process was done in as little time as possible in order to keep loss of moisture to a minimum. The sieved portion was then stored in plastic bags and immediately returned to the freezer until time of analysis. Coarse fragments not passing through the sieve were discarded.

For analysis, sieved samples were removed from the freezer and again allowed to thaw in a refrigerator at 4°C. A 30-g aliguot of moist soil was then removed, and the remainder of the sample was returned to the freezer. The 30-g aliquot from O, A, and BA horizons was pretreated for organic removal by oxidation with 30% (wt./wt.) H_2O_2 . For organic matter removal, 30 g of 1 N NaOAc buffered at pH 5.0 was added to the 30 g of soil. Then 30 ml of H_2O_2 was added and the suspension was allowed to sit overnight. The suspension was then stirred and heated on a hot plate at low temperature setting for 10 minutes. Frothing was controlled with jets of distilled water and continuous stirring. After 10 minutes of heating, another aliquot of H_2O_2 was added and the suspension was again heated until frothing had subsided. Continuous additions of H₂O₂ and heating were continued until there was conspicuous loss of dark color. There was a maximum of four H_2O_2 additions for each sample. At completion of organic matter oxidation, the suspension was boiled on a hot plate for 10 minutes to remove excess H_2O_2 , then cooled, washed once with 1 N NaCl, and any clear supernatant was discarded.

Samples from all horizons were treated for Fe removal. For removal of free Fe oxides, the soil samples for O, A, and BA horizons were kept in the same beaker from the organic matter treatment. For other horizons, a 30-g sample of moist soil was placed in a new beaker. A volume of 400 ml of 0.3 *M* Na citrate plus 50 ml of 1 *M* NaHCO₃ and 10 g of Na dithionite was then added to the soil. The mixture was stirred and allowed to stand for 24 hours. Only one treatment was necessary for the samples; the sample color changed to gray within 24 hours, indicating that free Fe had been reduced. After the reaction period, an aliquot of saturated (approximately 1*N*) NaCl was added to the suspension to promote flocculation. The suspension pH was also lowered to about 4.0 with 6 *N* HCl. The supernatant was discarded and the soil was subsequently washed twice with water to remove any excess salts.

Since the soil was collected from an acid forest system, and the presence of silica cements and amorphous materials was not evident, no pretreatments were conducted for these materials.

Quantitative free Fe was determined by the same reaction as for Fe removal in the pretreatment process. However, a smaller sample of 0.5 g of soil was used with 40 ml of 0.3 *M* Na citrate, 5 ml of 1 *M* NaHCO₃, and 1 g of Na dithionite. The suspension was mixed in a 100 ml centrifuge tube for 24 hours, centrifuged, and filtered through a Whatman #42 filter paper. The supernatant was filtered into a 250 ml volumetric flask. The remaining soil was washed with 50 ml of saturated NaCl, centrifuged again, and the supernatant added to the volumetric. The solution in the flask was brought to volume with distilled water and analyzed for Fe by ICP.

Following pretreatments, the same soil subsample was separated into separate particle sizes. A particle size separation was conducted for each sample. Also, particle size separation allowed for determination of sample texture.

For particle size separation, the soil suspension was adjusted to pH 9.5 with 1 $N \operatorname{Na_2CO_3}$ and then transferred quantitatively to a 300 mesh sieve supported over a collection container. Jets of pH 10 water facilitated the transfer. The sand fraction, which remained within the sieve, was then washed with acetone to remove water and dried at 110°C for several minutes. After weighing to determine sand yield, the sand was saved for further fractionation and identification.

The material which passed through the sieve was silt and clay combined. For silt separation, the solution was quantitatively poured into several 250 ml centrifuge bottles. They were then centrifuged at 2000 rpm for 5 minutes and the supernatant decanted into a container labeled >2 μ clay. The bottles were refilled with pH 10 water, stirred, centrifuged at 1000 rpm for 2 minutes, and the supernatant decanted into the clay container up to 8 times or until the supernatant was clear. The silt, which remained in the bottles, was dried in an oven and weighed.

Sand fractionation was achieved by passing the sand fraction through a nest of sieves in the sequence 1000, 500, 250, 106, and 53 μ , reading from top to bottom. After 3 minutes of shaking the sieves, each separate was removed and weighed. Separates in the 1000, 500, 250, 106, and 53 μ sieves were recorded as very coarse, coarse, medium, fine, and very fine sand, respectively.

Adjusting the suspension pH to approximately 4.0 with 6 N HCl flocculated the clay fraction which had been obtained by centrifugation and decantation. If pH adjustment did not provide adequate flocculation, an aliquot of saturated NaCl was added to the suspension to increase electrolyte concentration and further enhance flocculation. The clear supernatant was then siphoned off and discarded. De-ionized water was added to the clay for a total volume of 250 ml. A sub-aliquot of the suspension was then removed with a pipet and dried at 110°C to determine the mass of clay per volume of suspension.

Ceramic tile mounts were used for x-ray analysis of the clay fractions. Tile preparation consisted of placing a clean, flat ceramic tile in a suction apparatus and adding a pre-determined volume of clay suspension so that 225-250 mg of clay were placed on the tile. The clay was added with a pipet in one application to prevent separation of fine and heavy clays. After all water was removed, the tile was saturated with either 5 ml of 1 *N* KCl or 5 ml of 1 *N* MgCl₂. Cation saturations were repeated a total of five times, waiting for the solution to be suctioned through the tile between washings. After cation saturation, the tiles were washed five times with 5 ml of distilled water. The MgCl₂ tile was then further saturated with 5 ml of a 20% glycerol solution. The tiles were stored in separate dessicators until analysis by x-ray.

X-ray analysis was conducted with a Scintag x-ray diffractometer equipped with a theta-theta goniometer and a Cu target. To aid in separating hydration effects, the K-saturated tile was analyzed at four treatments: room temperature (RT), 110, 300, and 550°C; the Mg-saturated tile was analyzed only for the first two heat treatments. A small sample of the K saturated tile at 110 was removed and saved for thermal analysis. The sand and silt fractions were run at room temperature only.

For thermal analysis, the clay removed from the K-saturated tile was lightly ground to uniform size, and approximately 5.0 mg was placed in the thermal unit of a DuPont Differential Scanning Calorimeter (DSC). The sample was heated from 50 to about 650°C. Percentages of kaolinite and gibbsite in the sample were determined by taking a ratio of sample heat loss (J/g) to that of a pure standard.

Sand and silt fractions were analyzed by x-ray diffraction via powder mount applications. The respective fractions were ground with a mortal and pestle until a fine powder of uniform distribution was achieved. The powder mounts was then analyzed for mineralogical identification as were the clay fractions.

As a final step in the mineralogical analysis, a total elemental analysis was conducted on the sand, silt, and clay fractions. Total elemental involved placing 100 mg of the respective fraction for each sample into a teflon container and digesting with a commercial hydrofluoric acid media (Spectrasol Inc, Reagent Z-A). The digestion process was facilitated by addition of 0.5 ml of concentrated HNO₃ and placement in a water bath at 95°C for 2 hours. At the completion of the 2 hour period, the samples were removed from the water bath and allowed to cool. They were then removed from the tefflon vessels and poured into 100-ml plastic volumetric flasks. The flasks each received 37.5 ml of a commercial boric acid solution (Spectrosol Inc., Reagent Z-B) and were then brought to volume with distilled deionized water. Digested samples were analyzed for Ca, Mg, K, Na, Mn, S, Al, and Fe by ICP.

Results and Discussion. X-ray diffraction patterns show that micaceous and vermiculitic mineralogy dominate the clay fractions of both profiles (Figures 2.11-2.12). For the two profiles, 10 Å mica peaks are strongest in the 2C horizon

and diminish moving upward through the profile. Vermiculite (14 Å RT), on the other hand, is most prevalent in the surface horizons and diminishes down the profile.

For profile C, mica peaks are almost completely absent from the O, A, and BA horizons, so that strong detection of a mica peak does not begin until the Bw1 horizon. Profile A has relatively larger amounts of mica still remaining in the O. A, and BA horizons. In either case, the general trend remains that the ratio of vermiculite to mica decreases with depth for both soil profiles. The only exception exists in the O horizon for profile A, where both vermiculite and mica have intermediate intensities. Since weathering is more extensive in the surface horizon, the decrease in mica from the 2C to the O horizon in both profiles is due to the weathering and subsequent alteration of mica to vermiculite. Since profile A is comprised of more primary materials due to its steeper slope and is derived from sandstone colluviuum over shale residue, this profile is somewhat less developed than profile C, which contains less colluvial material. (See Appendix A for complete profile descriptions). The less developed profile A still has mica from colluvial deposits being altered to vermiculite in the surface horizons. On the other hand, only trace amounts of mica in profile C indicate that it is in a further stage of development.



Figure 2.11. X-ray Diffraction Patterns for Profile C Mg-Gly RT



Figure 2.12. X-ray Diffraction Patterns for Profile A Mg-gly RT

The presence of a moderate 002 peak for mica at 5 Å indicates that mica in these samples is predominantly in the form of muscovite, $K(Si_3AI)AI_2O_{10}(OH)_2$, a dioctahedral mineral. Hence, vermiculite should exist largely in the dioctahedral form as well. Rich and Obenshain (1955) argue that dioctahedral vermiculite forms when K is removed from muscovite. The removal of K from mica occurs via diffusion processes in interlayer spaces and may occur somewhat slowly (Douglas, 1977).

In acid forest systems, vermiculite will often weather to intergrade materials such as hydroxy-interlayer-vermiculite (HIV). As growth of the interlayer becomes more complete, pedogenic chlorite formation may eventually occur. Both HIV and chlorite materials are identified by stability of the 14 Å peak with heat treatment. Vermiculite peaks will progressively collapse toward 10 Å as the sample is heated to 550°C. Chlorite peaks will remain between 13.8 and 14 Å upon heat treatment, and samples with HIV will exhibit peak sequences that progressively collapse from 11 to 13 Å.

Both profiles do contain small amounts of chlorite and HIV. When compared to true vermiculite, these materials are more prevalent in profile C than profile A, which is further evidence of greater weathering in profile C and the less developed nature of profile A.

For both profiles, the amount of chlorite decreases with depth; it is most prevalent in the O horizon and then gradually diminishes until it becomes completely absent in the 2C horizon. As the samples were heated from RT to 550°C, the 14 Å peak collapsed toward 10 Å, but a small peak from 14 to 11 Å was still present in the samples with chlorite and HIV (Figures 2.13-2.25). For example, in Profile A, the O horizon demonstrates a sharp 14 Å peak for the KCI RT run. At 110 and 300°C the 14 Å peak broadens and becomes progressively skewed toward around 11 Å. Then, at 550°C, only a small peak (chlorite) remains at 14 Å. A broad skewed peak (HIV) appears at 11-12 Å (Figure 2.16). By the time the 2C horizon is reached, only a 10 Å peak appears in the 550°C xray pattern (Figure 2.18). The complete collapse of the 14 Å peak in the 2C horizon results from the lack of interlayer filling by Al-hydroxy materials. However, in the surface horizons, interlayer filling is more extensive and the 14 Å peak only partially collapses. Also, the intensity of the 10 Å peak increases with heating in each horizon of Profile A. Only true vermiculite will collapse completely to 10 Å with heat treatment.

A similar trend develops in Profile C. However, HIV levels are slightly higher and chlorite is slightly lower. This would indicate a lower degree of interlayer filling by Al-hydroxy materials for Profile C. Both HIV and chlorite materials diminish down through the profile. Furthermore, the intensity of the 10 Å peak does not significantly increase with heating, as it does for Profile A. It follows, therefore, that Profile C contains less true vermiculite than Profile A. HIV is typically more prevalent in surface horizons where the weathering environment is more intense. For an Ultisol of the Appalachian region in South



Figure 2.13 X-ray Diffraction Patterns for Profile A O Horizon



Figure 2.14. X-ray Diffraction Patterns for Profile A A Horizon



Figure 2.15. X-ray Diffraction Patterns for Profile A BA Horizon



Figure 2.16. X-ray Diffraction Patterns for Profile A Bw1 Horizon



Figure 2.17. X-ray Diffraction Patterns for Profile A Bw2 Horizon



Figure 2.18. X-ray Diffraction Patterns for Profile A 2C Horizon



Figure 2.19. X-ray Diffraction Patterns for Profile C O Horizon



Figure 2.20. X-ray Diffraction Patterns for Profile C A Horizon



Figure 2.21. X-ray Diffraction Patterns for Profile C BA Horizon



Figure 2.22. X-ray Diffraction Patterns for Profile C Bw1 Horizon



Figure 2.23. X-ray Diffraction Patterns for Profile C Bw2 Horizon



Figure 2.24. X-ray Diffraction Patterns for Profile C BC Horizon



Figure 2.25. X-ray Diffraction Patterns for Profile C 2C Horizon

Carolina, HIV was the dominant clay mineral in surface horizons (Norfleet and Smith, 1989). It will also be more common in highly developed soils or relatively older soils that were formed in residuum of acid sandstones. It is a characteristic mineral of acidic environments where AI becomes mobile and is released fromsilicate structures (Robert and Tessier, 1992). Comparison of HIV and vermiculite levels in the two profiles provides insight on the weathering sequence of the Fernow Experimental Forest. As the soils at the Fernow continue to develop, the following weathering sequence will be maintained:

 $\label{eq:hill} Muscovite \Rightarrow Vermiculite \Rightarrow HIV \Rightarrow pedogenic Chlorite. \\ Rainfall is certainly not limiting at the Fernow; therefore, smectite minerals are not likely to form since dissolution products, particularly Si, are leached. \\ Furthermore, low soil pH values also limit smectite formation. \\ \end{array}$

Secondary minerals present in both profiles include kaolinite, quartz, and gibbsite. Kaolinite can be a further weathering product of HIV, or it can weather directly from feldspars, though no evidence of feldspar exists in the clay fractions of these soils. Feldspar can still occur in silt and sand fractions, however, and visual inspection of the sand fraction does reveal the presence of plagioclase feldspar. Kaolinite peak intensities (7 Å) are slightly higher in profile C, while clay-sized quartz is slightly higher in profile A. This is again due to the greater degree of development in profile C. Also, for both profiles, the kaolinite peak is broad and skewed. Treatment with formamide did not alter the 7 Å peak, so the possibility of hallyosite was ruled out. The most likely explanation for the skewed nature of the kaolinite peak is that several forms of kaolinite exist in these soils, with either slight differences in chemical composition, crystallinity, or stacking sequence. The complete absence of any 7 Å peak at 550°C may rule out the presence of kaolinite-chlorite interstratifications. The fact that kaolinite exists in smaller quantities than the 2:1 minerals at the Fernow is indicative of the cool climate and sloping topography which hinders soil genesis for both profiles. Furthermore, Norfleet and Smith (1989) have postulated that low amounts of kaolinite in Appalachian forest soils may be due to the rapid removal of silica under high leaching conditions. In such soils, low levels of kaolinite may be associated with higher levels of gibbsite.

Gibbsite is usually most prevalent in warm environments where leaching is intense and the soils are well developed. While the Fernow is characterized by cool temperatures, gibbsite has developed there due to the high amount of leaching. Also, Reynolds (1971) observed gibbsite formation in an arctic environment as long as the water infiltration from winter snowmelt was sufficient to create an intense weathering environment. For a North Carolina Appalachian forest soil, Velbel (1985) adds that gibbsite mineralogy is more a result of weathering intensity than the level of soil development. Daniels (1995) also observed gibbsite in Inceptisols in North Carolina. For such slightly weathered soils, gibbsite formation may be more due to low ion activities, which is the most likely case for forest soils of the Fernow.

	Chemical Composition					
Mineral	Interlayer ^a	Octahedron	Tetrahedron			
Dioctahedral Vermiculite	M _{1.8} H ₂ O	Al _{3.0} Fe ³⁺ 0.6	Si _{7.12} Al _{0.88}			
Muscovite	K ₂	Al ₄	Si ₆ Al ₂			
Dioctahedral Chlorite	Al _{4.0} OH ₁₂	Al _{4.0}	Si _{7.8} Al _{0.2}			
Kaolinite		Al ₄	Si ₄			

 Table 2.6.
 Cation Composition of Various Silicate Clay Minerals

^aM represents any metal cation satisfying interlayer charge.

Total elemental analyses provide insight on the ability of the geochemical pool to supply base cations to Fernow soils. Total elemental analyses show that Mg is not present in any soil fraction. The chlorite and vermiculite must be present in dioctahedral forms. Thus Al³⁺ is satisfying most if not all octahedral positions (Table 2.5). The presence of dioctahedral mineral and Al³⁺ in octahedral position is most likely attributed to conditions at the time of mineral formation and not to present environmental conditions. Analysis of the rock samples from each profile show that structural Ca and Al are present and that Mg is not. Therefore, there may be no geologic supply of Mg in Fernow soils since there are no identifiable sources of biotite, trioctahedral chlorite or ferromagnesian minerals. On a whole-soil basis, Ca is the most prevelant cation, especially in Profile A. There is much less Ca in Profile C; in fact, Ca appears only in the BC and 2C horizons of the sand fraction of Profile C. Calcium contents are attributed to the presence of Ca-feldspars such as plagioclase.

Both soil profiles formed under the same vegetation and climate. Parent materials are very similar, but Profile A contains more shale and more colluvial material, while Profile C is mostly non-calcareous sandstone residuum. The major mineralogical differences in these soils, however, is due to landscape position and the resultant differences in water dynamics. Profile A has a steeper slope (16% vs. 8% for Profile C), which facilitates the removal of silica from the soil (Cate and McCracken, 1972). LeGrand (1958) has demonstrated that the groundwaters of the Blue Ridge Mountains are highly siliceous, due to rapid removal of silica where slope is steep and the rate of water throughflow is heavy. Even for sloping sites, forested mountain soils often display negligible amounts of water runoff due to vegetative cover (Douglass and Goodwin, 1980).

In summary, the soils of the Fernow Experimental Forest are relatively young and poorly developed. However, comparisons of two excavated profiles show that the profile on a steeper slope and with more Ca-containing parent material is slightly less developed than a profile with a lower slope and more siliceous parent material. Mineralogical analyses of the two profiles are very similar in spite of differences in development, which indicates that the weathering sequence is essentially the same for the two soils; the steeper Profile A is only less developed than the lower Profile C due to more erosion from Profile A. Colluvial additions over Profile A may also contribute to its less developed mineralogy. Both soils are dominated by micaceous and vermiculitic clay mineralogy, which indicates that these soils are still undergoing pedogenesis. Clay minerals are present in the dioctahedral form and thus have only AI and no Mg in their octahedral positions. There are minor amounts of dioctahedral chlorite, HIV, gibbsite, and kaolinite. These are indicative of the intense leaching environment which favors the development of AI hydroxides and removal of silica.

Powder mount x-ray analysis of sand and silt fractions revealed very little difference between profiles or with depth for each profile (Figures 2.26-2.29). Examination of surface and subsurface horizons for each profile indicate that the

mineralogy of the sand and silt fractions are dominated by quartz. Trace amounts of plagioclase feldspar are also evident in some subsurface horizons.



Figure 2.26. Powder Mount X-ray Diffraction Patterns of the Sand Fraction Profile A



Figure 2.27. Powder Mount X-ray Diffraction Patterns of the Sand Fraction Profile C



Figure 2.28. Powder Mount X-ray Diffraction Patterns of the Silt Fraction Profile C



Figure 2.29. Powder Mount X-ray Diffraction Patterns of the Silt Fraction Profile C

	Table 2.7 Total Liemental Analysis of the Sand Traction							
Sample	Ca,ppm	K, ppm	Na, ppm	Mg, ppm	Mn, ppm	Fe, ppm	Al, ppm	S, ppm
Profile A								
0	15689	1588	249	0	1	40964	3221	22674
А	1974	639	232	0	0	7971	4007	19801
BA	640	456	186	0	0	4631	2991	22150
Bw1	19613	1052	173	0	0	50853	4698	22792
Bw2	2595	1251	105	0	0	2677	5251	19347
2C	279	1549	61	0	0	4034	5215	21662
Profile C								
0	0	0	120	0	0	1848	1626	20688
А	0	0	161	0	0	2721	1543	21725
BA	0	0	77	0	0	1548	1416	22411
Bw1	0	0	0	0	0	2031	1984	21489
Bw2	0	0	45	0	0	2947	2682	21235
BC	348	287	123	0	0	3715	2963	20081
2C	996	428	63	0	434	5978	3264	22127

Table 2.7 Total Elemental Analysis of The Sand Fraction

Sample	Ca,ppm	K, ppm	Na, ppm	Mg, ppm	Mn, ppm	Fe, ppm	AI, ppm	S, ppm
Profile A								
0	278	2523	567	0	0	3218	7505	21967
A	251	1594	522	0	0	2415	5289	20902
BA	294	1964	334	0	0	2984	6121	21456
Bw1	284	2657	644	0	0	3990	8647	22568
Bw2	985	2974	764	0	0	4987	9536	20585
2C	1577	5650	811	0	0	7584	8260	21326
Profile C								
0	0	1346	644	0	43	2936	4979	19674
A	0	1729	764	0	46	2434	5391	22042
BA	214	2120	718	0	41	2281	5186	21818
Bw1	250	2128	639	0	42	3468	6787	20065
Bw2	2141	1930	714	0	141	8793	6401	22076
BC	635	2188	582	0	46	4516	8178	22170
20	608	2241	495	0	44	4284	8642	20981

 Table 2.8 Total Elemental Analysis of the Silt Fraction

2.3 Climate at the Fernow Experimental Forest

Cool temperatures and high amounts of rain and snowfall characterize the climate for the Fernow Experimental Forest. Much of the precipitation occurs as snow in the winter and early spring months. Annual snowfall is heavy because of the high elevation, and winters are more severe on the Fernow than in lower surrounding areas. Precipitation monitoring has occurred on the Fernow since May 1951. On an annual basis, the site receives approximately 147 cm of precipitation, and approximately 14% of that is contributed by snow (Adams, et al., 1994). For the years 1951 to 1990, mean monthly precipitation was lowest from September to November and peaked from March to July (Figure 2.34). Precipitation is monitored weekly by catchment with 20-cm-diameter rain gages and weighing-type recording rain gages. The gages are located at an opening in the center of the forest, and each gage opening is clear from obstruction by a zenith angle of 45°.

Air temperature has also been monitored continuously on the Fernow since 1951. The mean annual air temperature is 9°C. Temperatures as low as -29°C have been periodically recorded. On average, daily variations in air temperature at the Fernow are more pronounced during the winter than the summer. The frost-free season runs for about 145 days, though frost may occur at the Fernow during any month of the year.



Figure 2.30. Average Monthly Precipitation, 1951 to 1990
2.4 Forestry

Most of the Fernow is covered with second and third growth stands of hardwoods. Virgin timber was first cut from 1905 to 1910 and was accomplished by horse and railroad. As with most of West Virginia, much of this early logging was heaviest along streams and more selective on the ridges. Fires often followed logging. Cutting was resumed in the 1950's when many timber stands were 40 to 50 years old. Today, timber within the Fernow is managed as uneven-aged and even-aged stands under various experimental treatments or controls. Oak-site indexes range from 60 to 80 feet for almost all of the Fernow, thus labeling most of the site as excellent, good, or fair.

Approximately 25 commercial tree species are found within the Fernow, with Northern Red Oak (*Quercus rubra* L.) being very common. Other common tree species include yellow poplar (*Liriodendron tulipifera* L.), black cherry (*Prunus serotina* Ehrh.), white ash (*Fraxinus americana* L.), hickory (*Carya* spp.), sourwood (*Oxydendrum arboreum* (L.) DC.), and sassafras (*Sassafras albidum* (Nutt.) Nees.). American Chestnut (*Castanea dentata* (Marsh.) Borkh.) was an abundant species within the Fernow until it was killed by the chestnut blight (*Endothia parasitica*) in the 1920's.

2.5 Acid Deposition at the Fernow Experimental Forest

Acid deposition occurs when emissions of SO_2 and NO_x react in the atmosphere with water and oxidants to form acidic compounds that are then deposited to the Earth's surface in precipitation or as particulates of SO_4 and NO_2 . The high elevation forests of the Appalachian region, such as the Fernow, receive some of the highest levels of acid deposition in the United States (Adams et al., 1993). This trend is due largely to geography and prevailing winds patterns which carry acid-forming compounds from industrial areas of the Ohio River Valley to the Appalachian region.

Under the Clean Air Act Amendments of 1977, eight wilderness areas within the Eastern Region, including the Ohio River Valley, of the United States were designated as Class I air quality areas. As such, these Class I areas became under federal mandate that air pollution levels increase there by only small increments above baseline levels and stay within national standards. Two of these areas, the Otter Creek and Dolly Sods Wilderness areas, lie adjacent to and nearby the Fernow Experimental Forest. The Otter Creek and Dolly Sods Wildernesses receive the highest annual rate of acid deposition among all Eastern Region Class I areas (Figures 2.35a and 2.35b). In 1991, high elevation points at these sites were listed as receiving 26 kg/ha/yr of total S and 19 kg/ha/yr of total N (Adams et al., 1991).

Amendments were again added to the Clean Air Act in 1990. The 1990 Clean Air Act Amendments (CAAA) require two phases for restricting the atmospheric input of acid-forming compounds. The first phase was initiated in 1995 and targeted emissions from 445 stacks located at 110 of the nation's most productive electric utility plants. Sixty-three of the targeted plants are located in



Figure 2.31a. 1990 S Deposition for Class I Areas



Figure 2.31b. 1990 N Deposition for Class I Areas

GGDR=Great Gulf/Pres. Range-Dry River; LBr= Lye Brook; DSOC= Dolly Sods/Otter Creek; RbL= Rainbow Lake; BWCAW= Boundary Waters Canoe Area; HG= Hercules Glade. (Source: Adams et al., 1991)

the Ohio River Valley (Lynch, et al., 1996). The second phase will begin in the year 2000 and will work to reduce SO_4 emissions for both large and small industrial plants. Also, the 1990 CAAA called for reductions in NO_x emissions beginning in 1996.

Reports released in 1997 from the U.S. EPA and the U.S. Geological Survey indicate that emissions began to significantly decline in 1995 (US EPA, 1997). Actual emissions at the 445 targeted units were measured at 5.3 million tons in 1995—almost half the 1990 level of 10.0 million tons and less than half of the 1980 level of 10.9 million tons. The 1995 emissions were 39% below the allowable emissions level of 8.7 million tons established under the CAA. Also, when 1995 precipitation data is compared with data from 1983 through 1994, most of the country shows a 10 to 25% decline for SO₄ levels in rainfall. The Fernow Experimental Forest lies within an area receiving 25% less sulfate for 1995 in the form of wet deposition. An extensive analysis of national air quality trends since implementation of the 1990 CAA amendments has been conducted by Lynch et al., 1996. Their work supports EPA and USGS data in stating that SO₄ levels were significantly lower in 1995 than the period 1983 through 1994. On the other hand, N levels remained unchanged or were actually higher in 1995 than predicted from 1983 through 1994 trends. Galloway et al. (1995) have also predicted that N deposition will increase 25% by the year 2020 despite present regulations.

2.5.1 Ecological impacts of acid deposition in forest systems

For a forest ecosystem, a number of buffering processes exist which give rise to a substantial capacity for the forest to neutralize acidic inputs. The buffering processes are part of a biogeochemical cycle that determines nutrient availability. Elevated inputs of S can be attenuated through adsorption processes on the soil complex. Atmospheric deposition of N is primarily buffered through microbial retention. Both SO₄ adsorption and microbial retention of N result in the release of alkalinity and the sequestering of the mobile acid anions (SO₄ and NO₃). Furthermore, processes such as weathering of parent material or organic matter decomposition contribute to pools of base cations (Ca, Mg, K, and Na) which can neutralize acidic inputs within the soil. The ability of these processes to counter anthropogenically increased acidity, however, is limited to a specific threshold for any given system, depending on the nature of such properties as its soil exchange complex, parent material, mineralogy, climate, and vegetation. Once atmospheric inputs exceed a threshold limit, base cation release by weathering and organic matter decomposition are no longer adequate to support sustainable forest productivity. In response, soils that support forest ecosystems in many acidified areas have become characterized by a decline in the soil's ability to replenish base cations after their removal by leaching, tree uptake, and harvesting. This decline in base saturation is associated with pH depression, AI mobilization and toxicity, and macronutrient deficiency. In essence, acid deposition alters soil chemistry (Lucier and Haines, 1990).

On a whole-ecosystem basis, the results of chronic changes in soil chemistry include nutrient imbalances, enhanced acidity and ionic strength in receiving waters, and the consequential damage to living organisms. For example, Cronan et al. (1990) have shown that mobilization of toxic Al is increased when excess concentrations of SO_4 and NO_2 are present. The mobile Al, which is often toxic to living tissues, is either taken up by plants or carried into ground and surface waters. Acid deposition and its impact on soil chemistry can thus affect both terrestrial and aquatic components of an ecosystem.

The USDA Forest Service reports that several streams within the Otter Creek Wilderness Area (part of the Monongahela National Forest; Figure 2.36) contain elevated concentrations of Al due to acid deposition (Adams et al., 1991). Pyritic parent materials at headwater regions contribute to a degree of natural acidity in the area's streams, and the combination of natural and depositionenhanced acidity place all but two area aquatic systems under chronic stress levels. Historical data do indicate that baseline or natural acidity is below the value of visible injury or ecosystem damage. In the presence of enhanced acidity, however, fish populations are not sustainable in the most highly affected streams. Two area streams, Yellow Creek and Devil's Gulch, have average pH values between 3.7 and 4.0 and total Al concentrations from 400 to 600 ppb. During high flow conditions, pH values have been measured as low as 3.3 and Al as high as 1,200 ppb (Adams et al., 1991). According to Overrein et al. (1981), fish populations may begin to experience stress at pH 4.3. In an experiment with



Figure 2.32. The Fernow Experimental Forest

brown trout, they report that mortality begins just 4 days after exposure to pH 4.0 and below. The detrimental effects of low pH are intensified in the presence of aqueous AI. The toxicity of AI in water is pH-dependent; maximum toxicity occurs around pH 5.0, so that even moderately acid systems can be harmful if AI levels are as high as only 200 ppb.

While substantial improvements are being made in controlling atmospheric inputs of acid forming compounds, at present, there have been no corresponding observations of improvements in the base saturation and buffer capacity of affected soils (Likens et al., 1996). Consequently, the effects of acid deposition on forest ecosystems may be somewhat long-term and exceed the actual periods of acidic inputs. Already, nutrient imbalances that result in growth reduction and tree mortality are being observed in forested areas that are currently or have been historically disturbed by acid deposition. Van Oene (1992) reports that base cation storage for a Swedish spruce forest soil had been reduced by 80% in a 60 year period and that 35% of that reduction may be explained by acid deposition. Likens et al. (1996) at the Hubbard Brook Experimental Forest in New Hampshire have estimated that Ca pools in the soil there have been reduced by more than 50% in the last 45 years. Calcium depletion at the Hubbard Brook site is attributed to acid deposition beyond the buffering capacity of the soil. One result has been that Ca concentrations in tree rings there decreased from more than 35 μ eg/g to 20 μ eg/g from 1960 to 1985 (Hedin and Likens, 1996). Foliar tissue analyses of V. rotundifolia, a herbaceous layer species, and several hardwood canopy species at the Fernow provide similar data (Gilliam et al., 1996). At the Fernow, an experimental watershed receiving treatments of enhanced $(NH_4)_2SO_4$ had significantly lower values for plant tissue Ca when compared to control watersheds. Stream NO₃ levels were also significantly higher for the treated watershed and were well correlated with stream Ca levels, which indicates co-leaching of Ca with the NO₃ anion. Rustad et al. (1996) demonstrated similar results for Mg in (NH₄)₂SO₄ treated spruce stands in Germany. Streamwater chemistry has been monitored at the Fernow since 1969. Chemical analyses show that Ca exports from the treated watershed have increased from 1.14 to 1.74 ppm; Mg exports have increased from 0.490 to 0.823 ppm (Peterjohn et al., 1996).

Furthermore, the same regulations which have served well to reduce acidic inputs via the atmosphere have also led to reductions in atmospheric base inputs. Hedin and Likens (1996) have reported a 49% decline in atmospheric bases since 1965 at Hubbard Brook and a 74% decline in southern Sweden since 1971. According to Lynch et al. (1996), national atmospheric contributions of K have decreased 23.5% since 1983, 27.9% for Ca, and 39.7% for Mg.

Forest soils that are inherently low in base cation supplies to start with due to either the parent material or nature of the weathering cycle—are particularly susceptible to declines in atmospheric base inputs. At Hubbard Brook, the demand for Ca met by bulk precipitation fell from 29% to 8% from 1955 to 1975 (Likens et al., 1996). During the same time, soil depletion of Ca had increased 1.4 times due to enhanced soil acidification and the subsequent co-leaching of Ca with SO_4 or NO_2 .

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Chapter 3. Sulfate Adsorption and Desorption Phenomena In a High-Elevation Appalachian Forest Soil

Abstract

Sulfate (SO₄²⁻) adsorption isotherms were developed for two Appalachian forest soils under both initial mass (IM) and Langmuir modeling. Experiments with SO₄²⁻ desorption were also conducted and, when coupled with adsorption data, provide quantitative insight on the ability of each soil to adsorb and retain atmospheric inputs of SO₄²⁻. Experimentation was conducted at four pH levels and two moisture contents in order to further establish the effects of different environmental conditions on SO₄²⁻ dynamics. The susceptibility of the soils to SO₄²⁻ leaching and the subsequent loss of counter base cations was then evaluated.

Both soils were shown to be desorbing SO_4^{2-} at solution concentrations up to 0.5 mmol/L and may already be saturated with respect to natural solution concentrations. Shallow surface horizons with high organic matter and low Feoxide content had little capacity to adsorb additional SO_4^{2-} . They also had lower capacity to retain SO_4^{2-} against desorption and were prone to SO_4^{2-} leaching. Deeper subsurface horizons with low organic matter and higher Fe-oxide contents would adsorb SO_4^{2-} at high input concentrations but also had little capacity for adsorption at lower input levels. The subsurface soils had greater retention of SO_4^{2} , but they are holding it with less energy than the surface horizons as demonstrated by high amounts of SO_4^{2-} that could be easily desorbed by 1 N KCI. Since these soils are taken from a high deposition environment, it is not surprising that surface horizons have had more time for SO_4^{2-} to become specifically adsorbed, and that in subsurface SO_4^{2-} has not had as much time to become organized and specifically adsorbed. Hence, both inner- and outer-sphere complexation models seem appropriate for both soils. Monolayer coverage under Langmuir modeling is positively correlated with Feoxide content and organic matter. It is proposed that Fe-oxides and Al-saturated organic matter provide the preferential sites for SO_4^2 adsorption and that these sites are already saturated or very near saturation since additional adorption is so low.

Experimentation with various pH treatements yielded inconsistent results but generally resulted in an adsorption maxima around pH 4.0. Above and below that level, adsorption was hindered by either the dissolution of Al-oxides or the lack of pH-dependent positive charge. Where an adsorption maxima was not observed, adsorption decreased with increasing pH and was attributed to more control by Fe-dominated systems than by Al-oxides which display different points of solubility.

Air-drying soil samples prior to analytical experimentation was shown to underestimate $SO_4^{2^-}$ adsorption in the O horizon due to masking effects of enhanced mineralization. Conversely, a 2C horizon sample was shown to have

enhanced adsorption when air-dried due to the formation of new solids of Fe and Al oxides.

3.1 Introduction

Sulfate $(SO_4^{2^-})$ has long been the predominant anion in precipitation in the Eastern United States (Nodvin, 1986; Xue and Harrison, 1991). As a component of precipitation, $SO_4^{2^-}$ is deposited to the earth as H_2SO_4 and enhances the acidity of terrestrial and aquatic ecosystems. The $SO_4^{2^-}$ anion may also be deposited via cloud and dry deposition with the same acidifying consequences. The effects of $SO_4^{2^-}$ deposition do not end with enhanced acidity, however. Further consequences include the co-leaching of plant macro-nutrients (Ca²⁺, Mg²⁺, K⁺, Na⁺) with the $SO_4^{2^-}$ anion, the subsequent depletion of these nutrients from soil reserves, and enhanced mobility of toxic Al³⁺ (Cronan et al., 1990). According to Cronan and Schofield (1990), the reaction of $SO_4^{2^-}$ with base cations on the soil exchange complex is a major fate of the anion.

The region of the U.S. with the highest levels of historic SO_4^{2} deposition has been the Ohio River Valley. That trend continues today in spite of reductions in SO_4^{2-} loading due to recent air guality improvements brought about by the 1990 amendments to the Clean Air Act (CAA). The U.S. Environmental Protection Agency (EPA) has stated this year that SO₄ levels in both wet and dry deposition are beginning to decline on a national basis (US EPA, 1997). Research indicates that $SO_4^{2^2}$ levels in 1995 had declined as much as 25% in the Ohio River Valley since implementation of the 1990 CAA amendments (Lynch et al., 1996). While trends for decreasing SO_4^2 deposition are encouraging, it still remains true that parts of the eastern U. S. are receiving remarkably high levels of SO_4^2 via atmospheric deposition. High elevations of the Appalachians are particularly susceptible to wet and dry deposition from industrial outputs of the Ohio River Valley, which are often carried to the Appalachians by prevailing winds. Consequently, soils of the high elevation Appalachian forests are significant sinks for SO_4^{2} deposition. Much research has thus focused on the dynamics of SO_4^{2} in soils in light of its high atmospheric inputs and detrimental environmental effects.

The primary means of natural $SO_4^{2^-}$ attenuation in terrestrial systems is via adsorption to soil solids. Once adsorbed to the soil solid, $SO_4^{2^-}$ can be sequestered and the co-leaching of cations consequently hindered. If the $SO_4^{2^-}$ is subsequently desorbed or has low adsorption initially , however, a spiraling effect of base cation depletion, enhanced AI mobilization as a function of $SO_4^{2^-}$ adsorption and concluded that AI concentrations in receiving watersheds increased when $SO_4^{2^-}$ retention was hindered. The concentration of labile AI was increased approximately 10-fold in an ecosystem with low $SO_4^{2^-}$ adsorption capacity when compared to a system with high adsorption capacity. With that in mind, the objectives of this study are to assess the capacity of a forest soil to adsorb $SO_4^{2^-}$, determine the ease of $SO_4^{2^-}$ desorption from the same soil, and characterize adsorption and desorption phenomena in relation to soil physical, chemical, and mineralogical properties.

3.2 Literature Review

Sulfate adsorption has been generally held to be achieved through inner sphere complexation in which the $SO_4^{2^-}$ ion displaces an OH⁻ group through ligand exchange (Kooner et al., 1995). Evidence of this is given by the increase in solution pH accompanied with $SO_4^{2^-}$ adsorption. Early researchers such as Hingston et al. (1968) suggested that $SO_4^{2^-}$ adsorption occurred via ligand exchange processes in which the OH⁻ ion is displaced after adsorption of HSO₄⁻. Under this assumption, $SO_4^{2^-}$ would accept a proton from the surface and the level of adsorption should equal the initial net positive charge. Rajan (1978) demonstrated that OH⁻ release does immediately follow $SO_4^{2^-}$ adsorption on hydrous alumina but believed that adsorption as HSO_4^- . This theory developed from the lack of evidence that $SO_4^{2^-}$ adsorption and net positive charge display a significant relationship.

More recently, Sposito (1989) and He et al. (1996a;1996b) have proposed that $SO_4^{2^-}$ adsorption on pure minerals and soils can also be achieved through outer sphere complexation, or the electrostatic attraction of $SO_4^{2^-}$ for positive sites. Under outer sphere complexation models, $SO_4^{2^-}$ adsorption should be a function of the ionic strength of the equilibrating solution.

A number of researchers have presented support for the outer sphere complexation model. Work by He et al. (1996a) was conducted with γ -Al₂O₃ and kaolinite and showed that SO₄²⁻ adsorption on those minerals was highly correlated with ionic strength. Increases in ionic strength would result in decreases in SO₄²⁻ adsorption. In a later paper, He et al. (1996b) presented evidence that SO₄²⁻ adsorption can occur on both the β -plane (outer sphere complex plane) and o-plane (inner sphere complex plane). Hence, SO₄²⁻ adsorption.

Support is also given for the outer sphere complexation model by reports of considerable amounts of $SO_4^{2^-}$ that can be desorbed by water and KCI solutions. Studies in $SO_4^{2^-}$ desorption have commonly employed KH₂PO₄ as the extracting agent. The fraction of $SO_4^{2^-}$ held by anion exchange or inner sphere complexation should be easily removed by a 1N KH₂PO₄ solution. Chao et al. (1964) observed that 85% of adsorbed $SO_4^{2^-}$ could be extracted from an Oregon silt loam soil after just 4 extractions with water. This implies that much of the adsorbed $SO_4^{2^-}$ was weakly held to the soil and provides support to a mechanism of charge attraction in $SO_4^{2^-}$ adsorption. Harrison et al. (1989) also analyzed the ability of water to extract adsorbed $SO_4^{2^-}$. They observed that water could successfully extract up to 64% the adsorbed $SO_4^{2^-}$ from a variety of forest soils. Curtin and Syers (1990) further showed that $SO_4^{2^-}$ could also be easily extracted by a 1 N KCI solution.

Ajwa and Tabatabai (1995) compared $SO_4^{2^-}$ adsorption on a variety of soil types with both 1 mmolar and 10 mmolar NaCl as a background electrolyte. All soils displayed higher adsorption capacities at the lower electrolyte concentration, and it was postulated that the decrease in $SO_4^{2^-}$ adsorption was a result of competition from Cl⁻. This theory is based on the diffuse double layer model in which decreases in double layer thickness with increasing ionic strength cause results in the preferential adsorption of Cl⁻ over $SO_4^{2^-}$ due to mass action. However, He et al. (1996b) demonstrated no empirical support for evidence of $SO_4^{2^-}$ adsorption on the diffuse layer plane. Bolan (1986) had earlier suggested that the effects of ionic strength on $SO_4^{2^-}$ adsorption were related to a plane of adsorption where electrostatic potential developed and not to the surface charge of the soil. One other postulate for the effects of increasing ionic strength on $SO_4^{2^-}$ adsorption is presented by Courchesne (1991), who suggested that aqueous complexes of $SO_4^{2^-}$ such as NaSO₄⁻ may form at high ionic strengths and compete with $SO_4^{2^-}$ for adsorption sites.

Not only is $SO_4^{2^-}$ adsorption related to the ionic strength of the soil, but it is also highly pH-dependent (Schindler, 1981; Nodvin et al., 1986). Adsorption is often shown to increase with decreasing pH. The most likely explanation for this is that adsorption is being enhanced by the presence of Fe and Al oxides which develop positive charge at low pH values (Chao et al., 1964). For a subsurface spodosol at the Hubbard Brook Experimental Forest in New Hampshire, Nodvin et al. (1986) observed large effects on $SO_4^{2^-}$ adsorption with only small changes in solution pH. An adsorption maxima was achieved at about pH 4.0; below and above this pH level, adsorption decreased.

Several groups of researchers have observed this adsorption maxima at pH values close to 4.0 (Chao et al., 1964; Khanna et al., 1987; Xue and Harrison, 1991). While decreases in pH will cause increases in pH-dependent charge on Fe and Al oxides, if pH is lowered below 4.0, Al oxides may begin to dissolve and lower the effective positive charge. In other words, at lower pH values, the oxyhydroxide surfaces can become protonated and serve as adsorption sites for $SO_4^{2^-}$, but once pH is lowered beyond 4.0, those surfaces begin to dissolve and $SO_4^{2^-}$ adsorption is hindered. According to Xue and Harrison (1991), the $SO_4^{2^-}$ adsorption maxima at pH 4.0 corresponds to the point at which Fe and Al begin to dissolve from soil solids and are released into solution. According to Chao et al. (1964), the adsorption maximum around pH 4.0 occurs only for Al dominated systems and not for Fe dominated ones. This is explained as a result of the lower isoelectric point for Fe than Al, which causes Fe to be more stable at low pH values.

For an acid forest soil, Khanna et al. (1987) demonstrated that $SO_4^{2^-}$ is adsorbed by the development of Al-hydroxy sulfate minerals such as jurbanite (AlOHSO₄). These minerals form as $SO_4^{2^-}$ additions become associated with Al(OH)₃ or Al-OH polymers in the interlayers of clay minerals such as secondary chlorites. After a series of acidification experiments, however, $SO_4^{2^-}$ and Al³⁺ levels in percolating water increased significantly due to dissolution of jurbanite. Furthermore, at low pH values, aqueous alumino-sulfate complexes can develop and may compete with $SO_4^{2^-}$ for adsorption sites (Sjostrom, 1994). The effects of pH on $SO_4^{2^-}$ adsorption and retention by soils has important

The effects of pH on $SO_4^{2^-}$ adsorption and retention by soils has important environmental implications. As soil acidity is increased by atmospheric inputs, $SO_4^{2^-}$ adsorption may increase for a while as positive charges develop on Fe and Al oxides. Hence, the $SO_4^{2^-}$ ion can be successfully sequestered for a time. However, acidification beyond about pH 4.0 will actually have the reverse effect on $SO_4^{2^-}$ retention as oxyhydroxides begin to dissolve and release $SO_4^{2^-}$ and AI^{3^+} back into soil solution. Lee and Weber (1981) conducted a large scale study of the effects of rain pH on soil solution chemistry within different regions of the soil profile. They concluded that rain at pH 4.0 and below can alter the chemistry of soil water within the root zone of a hardwood forest after only 1-2 years.

Soil mineralogy and the amounts of natural organic matter in a soil also influence SO_4^{2-} adsorption. With soil mineralogy in mind, the most important factor is repeatedly the level of Fe and Al oxides present in a soil. The percent clay in a soil has not been shown to be significantly correlated with SO_4^2 adsorption (Willimas and Steinbergs, 1962; Johnson and Todd, 1983). Early work by Chao et al. (1964) demonstrated the importance of Fe and Al coatings for SO_4^{2-} adsorption. Their experiments with SO_4^{2-} adsorption involved adding synthetic Fe and AI coatings to soils with low adsorption capacities. Additions of oxide coatings consistently resulted in higher SO₄² adsorption. Conversely, treatment for the removal of oxides resulted in decreases in adsorption. It was also observed that AI coatings were more effective at retaining $SO_4^{2^2}$ than were Fe coatings. A soil with an AI coating at 6.1% demonstrated retention of over 95% of added SO_4^{2-} at pH 4.0. The researchers further demonstrated that clay mineral type has no effect on SO₄² adsorption; a low adsorbing soil would significantly increase in adsorption capacity if it was covered with Fe or Al oxide coatings.

Later, Sjostrom (1993) investigated groundwater acidification in Sweden as a function of SO_4^{2-} adsorption. The Swedish experimental soil (Orthic Podzol) had SO_4^{2-} adsorption capacities most significantly correlated with the Fe oxide content. He concluded that for that soil, H₂SO₄ input from the atmosphere was causing the conversion of ferro-magnesian soil mineral to Fe-oxides and thus creating positive charge sites that attract SO_4^{2-} . Merino and Garcia-Rodeja (1994) acidified a series of mineralogically diverse soils from Spain with H₂SO₄. They observed no significant relationship between SO_4^{2-} adsorption on any soil and amorphous forms of Fe and Al. Only crystalline forms were significantly correlated with adsorption. Fuller et al. (1985) also observed greater correlations between crystalline Fe and SO_4^{2-} adsorption than for noncrystalline Fe.

Cronan et al. (1990) compared adsorption between a soil dominated by kaolinitic mineralogy and one dominated by vermiculitic mineralogy and observed significantly higher adsorption by the kaolinitic soil. Clay minerals such as kaolinite can develop significant positive charge under low pH conditions. While pure vermiculite will develop less positive charge than kaolinite, the interlayer hydroxy materials that develop in vermiculite and its secondary forms (chlorite and HIV) can be important sites for $SO_4^{2^-}$ adsorption (Sjostrom, 1993). For soils where $SO_4^{2^-}$ adsorption was highly pH-dependent, Kooner et al. (1995) concluded that Fe oxides and kaolinite were the major factors involved in adsorption processes. Conversely, soils that did not demonstrate pH-dependent adsorption were believed to be following an adsorption mechanism such as cation bridging.

Soil organic matter is usually held as an antagonistic factor for $SO_4^{2^-}$ adsorption (Inskeep, 1989; Jardine et al., 1990; Motavalli et al., 1991). Sorption capacities of $SO_4^{2^-}$ and organic acids are similar, and competition for adsorption sites may develop in the presence of natural organic matter (Ali and Dzombak, 1996). Bolan et al. (1993) observed a 12-fold decrease in $SO_4^{2^-}$ for soils dominated by organic matter as opposed to Fe and Al oxides. In their study, the decrease was attributed to the formation of Ca complexes with organic ligands. The Ca complexes do not develop positive charge sites. On the other hand, soils low in organic matter will specifically adsorb Ca on Fe and Al oxides and create positive charge sites, which results in enhanced $SO_4^{2^-}$ adsorption.

Furthermore, Johnson and Todd (1983) showed that even when Fe and Al oxide levels are high in a soil, the presence of organic matter can still inhibit adsorption. This is due not only to the formation of organic matter complexes, but also to the fact that organic matter can reduce the effective crystallinity of Fe, which was shown by Johnson and Todd (1983) to reduce adsorption capacity.

Exceptions to the inhibitory effect or organic matter are rarely presented in the literature. Fuller et al. (1985) do suggest that organic Al complexes can be as important for $SO_4^{2^-}$ adsorption as crystalline oxides. Their work with forested spodosols contradicts traditional beliefs that spodosols are poor adsorbers of $SO_4^{2^-}$ due to organic matter effects. Also, Ali and Dzombak (1996) demonstrated that $SO_4^{2^-}$ can successfully compete with organic acids for adsorption sites on pure geothite, especially at low pH values.

Very little work has been reported on the effects of temperature or air drying soil samples on $SO_4^{2^-}$ dynamics. Comfort et al. (1991), however, compared $SO_4^{2^-}$ adsorption on air-dry and field-moist samples. They observed up to 320% increases in $SO_4^{2^-}$ for the dried soils. It was postulated that air-drying the soil caused the formation of new solids due to transformations of Fe and Al to more insoluble forms. The new forms of Fe and Al were believed to provide greater surface for adsorption. Microbial transformations that led to $SO_4^{2^-}$ mineralization or the release of H⁺ were also considered as explanations for the increased adsorption on dry soils. The same researchers observed no significant effects of temperature on $SO_4^{2^-}$ adsorption. Shanley (1992) noticed a 100% increase in adsorption on air-dry Ultisols. Air-drying was also demonstrated to cause a decrease in subsequent $SO_4^{2^-}$ mineralization; a soil that is brought to a warmer temperature through laboratory experimentation than its natural field temperature will have increased mineralization rates. Laboratory induced

mineralization of organic S to inorganic forms may mask the effects of adsorption processes. In many soils, organic S may account for up to 80% of the total S fraction (Nodvin, 1986).

3.3 Methods and Materials

Samples were selected from the major taxonomic horizons of Profiles A and C on the LTSP sites within the Fernow Experimental Forest. Characterization of the soils is given in Chapter 2.

Sulfate Adsorption Isotherms. A SO₄ adsorption isotherm was developed for each major horizon of the two profiles. For each horizon, adsorption experiments were carried out at a constant ionic strength of 0.01 *N*. All adsorption experiments took place at room temperature (approximately 23°C). There were 4 pH treatments and 5 levels of SO₄ addition per horizon. The pH treatments consisted of: no adjustment (ambient) and adjustments to 3.2, 3.8, and 4.1. Concentrations of SO₄ progressively increased: 0.0, 0.05, 0.5, 1.0, and 2.0 mmol SO₄. Each sample was analyzed in duplicate so that there was a total of 40 subsamples per horizon (4 pH X 5 SO₄ X 2 duplicates).

A 5.0 g aliquot of the moist sieved soil was placed into a series of 100-ml plastic centrifuge tubes. Each tube then received 25 ml of a K_2SO_4 solution that ranged from 0 to 2 mmol SO₄. The K_2SO_4 solution was prepared in 0.01 *N* KCl. The samples were then stoppered and shaked by hand for approximately 1 minute. The first 10 tubes were not given any pH adjustment. Of the remaining 30 tubes, each set of 10 was treated for pH adjustment by additions of 0.1 *N* HCl or 0.1 *N* NaOH. The tubes were then stoppered again and allowed to shake at low speed on a shaker tray for 24 hours. For profile C, air-dry samples of the O and 2C horizons were also carried through each batch run. The air-dry samples were identical to the moist samples.

After the 24-hour period, a measurement of suspension pH was taken with a combined electrode and pH meter. The soil suspensions were then filtered through Whatman # 42 filter paper. The leachate was collected and analyzed for S by inductively coupled plasma spectroscopy (ICP).

Sulfate Desorption. Sulfate desorption experiments were conducted on each horizon of profile C. The experimental method involved packing a plastic soil column with an aliquot of the moist sieved soil. The columns were fitted at both ends with a small amount of glass wool, capped and connected via Tygon tubing to pumping and collection devices. Each column was attached to a peristaltic pump and leached with various extracting solutions via upward flow. (See Table 3.1 for column dimensions and flow parameters). Three separate columns of each sample were respectively leached with distilled-deionized water, 1 *N* KH₂PO₄, or 1 *N* KCI. Effluent was collected dropwise with a fraction collector into approximately 12-ml fractions. Collection tubes had been preweighed, and after collection, the filled tubes were weighed again to determine the exact mass of

column effluent in each tube. The effluent collections were then transferred to plastic storage bottles and analyzed for S by ICP.

Parameter	Dimensions		
Length	20 cm		
Cross-sectional area	1.77 cm ²		
Volume	35.4 cm ³		
Flow rate	9 ml/hr		
Flux	5 cm/hr		
Experimental temperature	23°C		

Table 3.1. Experimental Parameters ofSulfate Desorption Columns

3.4 Results and Discussion

3.4.1 Sulfate adsorption

For $SO_4^{2^-}$ adsorption, initial mass (IM) isotherms were constructed for each sample by plotting $SO_4^{2^-}$ retained as a function of $SO_4^{2^-}$ added to the soil. The IM isotherm is a linear partitioning model that has been successfully used by a number of researchers (Nodvin et al., 1986; Shanley, 1992). If a linear relationship can be successfully applied to the adsorption data, the slope of the IM isotherm is directly related to the $SO_4^{2^-}$ adsorption capacity; a slope of 0.0 or a negative slope indicates no further adsorption may occur on the soil, and a slope of 1.0 occurs when there is complete $SO_4^{2^-}$ adsorption by the soil. Also, the intercept of the isotherm can be used to make inferences about the native $SO_4^{2^-}$.

For Profile C, SO₄²⁻ adsorption isotherms were also constructed by conventional Langmuir-type models. Langmuir isotherms can be expressed by the linear equation:

C/(x/m) = 1/Kb + C/b

where C is the equilibrium concentration of adsorbate (SO_4^{2-}) , x/m is the mass of adsorbate per mass of adsorbent (soil), K is a constant that relates to the binding strength, and b is the maximum amount of adsorbate that can be adsorbed (Bohn et al., 1985). If a linear form can be successfully constructed from the adsorption data, plotting C/(x/m) vs. C will yield a straight line. From the linear form of the Langmuir isotherm, an adsorption maximum, b, can be determined from the slope (1/b) and the intercept (1/Kb).

A key assumption of the Langmuir equation is that adsorption occurs independent of the amount of surface already covered by the adsorbate. Since separate analysis had shown that Fernow soils contain high amounts of native $SO_4^{2^-}$, the preceding assumption cannot hold true. Therefore, the amount of KH_2PO_4 -extractable $SO_4^{2^-}$, as determined from desorption experiments, was added to the x/m value when constructing Langmuir isotherms. The POextractable $SO_4^{2^-}$ was held as the total native $SO_4^{2^-}$ naturally adsorbed on the soil surface under field conditions. Corrections for native $SO_4^{2^-}$ in this manner yielded linear plots of C vs. C/(x/m), whereas, linear plots could not be established without the correction.

Profile A was fitted only to the IM isotherm model (Table 3.2). Profile C was successfully fitted to the IM isotherm model and to the linear form of the Langmuir equation. (Table 3.3) Under IM modeling alone, Profile C was more successfully fitted to the IM isotherm model than Profile A.

Initial Mass (IM) Isotherms. The slope of the IM isotherm is a convenient tool for establishing comparisons between experimental soils. For this study, slope was calculated at the lowest three input concentrations, since a departure from linearity was observed at the higher concentrations. At ambient pH conditions, use of the IM isotherm shows that all soils are desorbing $SO_4^{2^2}$ at the two lower

input concentrations, 0.0 and 0.05 mmol/L solution (0.0 and 0.3 mmol/kg soil) (Figures 3.1 and 3.2). Natural waters at the FEF contain approximately 0.05 mmol/L $SO_4^{2^-}$ in solution. Hence, soils of the FEF may already be saturated with respect to natural solution concentrations. Almost all experimental soil horizons begin to adsorb $SO_4^{2^-}$ at the input range of 0.5 to 2.0 mmol/L. Only three exceptions exist. Two exceptions are the O and A horizons of Profile C, which do not begin to adsorb $SO_4^{2^-}$ until within the 1.0 to 2.0 mmol/L input range. The third exception is the O horizon of Profile A, which is desorbing $SO_4^{2^-}$ at all input concentrations (0.0 to 2.0 mmol/L). The inability of this horizon to adsorb additional $SO_4^{2^-}$ implies that it is presently $SO_4^{2^-}$ saturated with respect to solution concentrations up to 2.0 mmol/L.

Because all soil horizons except the O horizon of Profile A do display some zone of $SO_4^{2^-}$ adsorption, the slope of the IM isotherm, which is directly related to the net adsorption capacity, is positive with only the one exception. There are no significant correlations between $SO_4^{2^-}$ adsorption and soil depth, though a few notable trends develop from the data. In general, two families of curves can be shown for each profile. The first comprises low adsorbing members, which are the O and A horizons. The lower horizons have higher adsorption capacities and comprise the second family of curves. Net adsorption increases with depth for both profiles, though there is little difference among soils of the subsurface. The most significant change in net adsorption occurs at the boundary of the A and BA horizons. For Profile C, net adsorption actually increases from 1% to 54% between the A and BA horizons. This is strong evidence of $SO_4^{2^-}$ saturation in the surface of the soils.

Several researchers have observed that a SO_4^{2-} front develops in soils of high deposition environments (Reuss and Johnson, 1986; Mitchell, 1992). In such a front, SO_4^{2-} saturation is highest in the surface horizons because of high atmospheric input. The SO_4^{2-} does not begin to leach down through the profile until each progressive horizon becomes saturated. For the surface horizons of Fernow soils, historical increases in SO₄²⁻ inputs may have resulted in immediate increases in solution concentrations and the subsequent leaching of SO₄² to lower horizons. Certainly this is the case for the saturated O horizon of Profile A. The surface horizons of Profile C are approaching this point. The strong boundary in the net adsorption between the A and BA horizons may indicate the current position of the SO_4^{2-} front in these soils. The resulting increases in SO_4^{2-} solution concentration in the lower horizons may be attenuated for a time by adsorption processes in upper horizons until the soil reaches a new equilibrium with the solution. At that point, $SO_4^{2^-}$ leaching may begin again. Since none of the Fernow soils are adsorbing $SO_4^{2^-}$ under ambient input conditions, leaching of SO_4^{2-} and its associated cations may be presently occurring throughout the entire depth of these soils. Furthermore, SO_4^{2-} leaching may be accelerated by future expected decreases in atmospheric input. This accelerated leaching will occur until new equilibrium conditions are attained. Therefore, environmental regulations which serve to decrease atmospheric input will certainly be positive

but will not be paralleled with immediate positive responses in the soil. Positive responses such as decreased leaching will occur after a lag time during which the new equilibrium is attained. The degree of leaching depends on the amount of adsorption that is reversible (Harrison et al., 1989).

The intercept of the IM isotherm, which relates the binding strength of the native $SO_4^{2^-}$ pool, is negative down to the BA horizon of Profile A and to the Bw1 horizon of Profile C (Table 3.3). The results imply that $SO_4^{2^-}$ adsorption may be highly reversible in these upper horizons. As a result, a decrease in atmospheric input may not be simultaneously paralleled with decreases in solution $SO_4^{2^-}$ concentrations. This is because $SO_4^{2^-}$ will begin to desorb from the soil until the solution concentration is at equilibrium with the new input level. The result will be that soil solutions from the surface horizons will display a lag time in response to decreased inputs.

In Profile A, there is no significant trend between the IM intercept and soil depth, though the intercept generally increases with depth (Table 3.2). However, in Profile C, the intercept does statistically increase in a linear fashion with depth (r=0.96). Hence, native $SO_4^{2^-}$ is more tightly held against release to the equilibrating solution in the lower horizons. Under ambient conditions, the 2C horizons of both profiles have the highest capacity to retain $SO_4^{2^-}$ once it has been adsorbed by the soil. This can be an important source of protection for receiving waters. Also, if $SO_4^{2^-}$ readily enters solution from surface soils to maintain equilibrium conditions under reduced atmospheric inputs, it may be more readily removed from solution in lower horizons for the same reason.

Langmuir Isotherms. The Langmuir isotherms express a relationship between the equilibrium $SO_4^{2^-}$ in solution and the volume of the monolayer coverage of $SO_4^{2^-}$ on the soil surface. The Langmuir isotherms, unlike IM isotherms, were developed by accounting for native $SO_4^{2^-}$ and adjusting the equilibrium mass of adsorbate per mass of soil accordingly. Therefore, since each soil had high amounts of native $SO_4^{2^-}$ on its exchange complex, all soils display a positive slope and intercept under the Langmuir model. Isotherms developed for Profile C show that monolayer coverage (b) is currently highest in the A horizon. (Figure 3.3) This is the same horizon with the lowest adsorption capacity under the IM model, which supports the implication that this soil is approaching $SO_4^{2^-}$ saturation. Below the A horizon, $SO_4^{2^-}$ coverage decreases linearly (r=0.96) with soil depth (Table 3.3). The O horizon has a $SO_4^{2^-}$ maximum similar to the BC horizon.

Langmuir modeling indicates that under ambient pH conditions, monolayer coverage is directly related to both DCB-extractable Fe_2O_3 and soil organic matter (r=0.99 and 0.91, respectively). The presence of Fe and Al oxides is the most common soil property shown to correlate with $SO_4^{2^-}$ adsorption (Chao et al., 1962; Rajan, 1978; Johnson and Henderson, 1979; Neary et al., 1987). While many researchers have noted inverse relationships between soil organic matter and $SO_4^{2^-}$ adsorption, others have postulated that organic matter-Al surface

complexes create relatively stable sites for $SO_4^{2^-}$ adsorption (Singh, 1984; Harrison et al., 1989). Thus, a positive relationship may develop between $SO_4^{2^-}$ adsorption and organic matter content.

Differing from Langmuir modeling, extractable Fe and soil organic matter are poorly correlated with current net adsorption under the IM models. Such an observation implies that Fe-oxides and organic matter may have once been the primary agents of $SO_4^{2^-}$ adsorption but are now of secondary importance for these soils. Adsorption sites on Fe-oxides and organic matter may be approaching their maximum capacity, and sites such as those associated with mica edges or Al-hydroxy polymers are becoming the primary means of $SO_4^{2^-}$ adsorption.

Table	Table 3.2 IM Adsorption Parameters for Profile A					
	Slope	Intercept	R^2			
рН 3.6						
Ō	-0.99	-2.5874	0.79			
A	0.28	0.3364	0.73			
BA	0.66	0.3372	0.90			
Bw1	0.79	-0.2170	0.78			
Bw2	0.58	0.2547	0.79			
2C	0.39	-3.9827	0.87			
pH 3.8						
Ō	-0.63	-5.8538	0.77			
A	0.33	-3.2229	0.64			
BA	0.29	-0.8157	0.56			
Bw1	0.45	0.0524	0.87			
Bw2	0.50	0.2743	0.80			
2C	0.71	-1.5419	0.85			
pH 4.2						
O	-0.54	-7.2623	0.63			
A	0.39	-5.2659	0.78			
BA	0.35	-2.9595	0.65			
Bw1	0.30	-0.1545	0.74			
Bw2	0.61	0.2842	0.86			
2C	0.63	-0.8670	0.94			
pH 4.6						
• (ambient)						
Ò Í	-1.06	-2.1698	0.89			
A	0.34	-0.2125	0.82			
BA	0.45	-0.2430	0.75			
Bw1	0.38	0.1150	0.73			
Bw2	0.37	0.5643	0.66			
2C	0.35	0.1865	0.54			

 Table 3.2 IM Adsorption Parameters for Profile A

Horizon	Initial Mass Isotherm			Langmuir Isotherm				
рН 3.6	Slope	Intercept	R ²	Slope	Intercept	R ²	К	b,
0	0.16	-0.50	0.99	0.15	0.0119	0.99	13	6.67
А	0.20	-0.43	0.98	0.09	0.0052	0.99	17	11.11
BA	0.51	-0.01	0.95	0.12	0.0080	1.00	15	8.33
Bw1	0.65	0.07	0.96	0.17	0.0039	0.96	44	5.88
Bw2	0.65	0.09	0.90	0.15	0.0105	1.00	14	6.67
BC	0.68	0.17	0.94	0.15	0.0123	0.99	12	6.67
2C	0.70	0.36	0.77	0.17	0.0048	1.00	35	5.88
pH 3.8 O	0.13	-0.54	0.94	0.16	0.0116	0.99	14	6.25
A	0.19	-0.41	0.94	0.09	0.0046	1.00	20	11 11
BA	0.51	-0.04	0.95	0.12	0.0083	1.00	14	8.33
Bw1	0.52	-0.06	0.96	0.14	0.0147	0.99	10	7.14
Bw2	0.70	0.20	0.82	0.16	0.0088	1.00	18	6.25
BC	0.69	0.24	0.92	0.15	0.0105	0.99	14	6.67
2C	0.71	0.36	0.73	0.18	0.0040	1.00	45	5.56
рН 3.9								
0	0.15	-0.52	0.96	0.16	0.0114	1.00	14	6.25
А	0.01	-0.57	0.90	0.10	0.0044	1.00	23	10.00
BA	0.54	-0.19	0.96	0.12	0.0106	0.99	11	8.33
Bw1	0.55	-0.14	0.97	0.13	0.0147	0.98	9	7.69
Bw2	0.56	0.17	0.88	0.15	0.0088	1.00	17	6.67
BC	0.56	0.22	0.92	0.16	0.0110	1.00	15	6.25
2C	0.57	0.37	0.72	0.18	0.0038	1.00	47	5.56
pH 4.4	0.04	0.55	0.04	0.40	0.0040	1.00	44	5.00
0	0.04	-0.55	0.91	0.19	0.0046	1.00	41	5.26
A	0.10	-0.78	0.94	0.11	0.0049	1.00	-	9.09
BA	0.23	-0.84	0.99	0.14	0.0189	0.99	7	7.14
Bw1	0.37	-0.40	0.86	0.27	-0.0098	0.99	0	3.70
Bw2	0.48	-0.17	0.78	0.20	0.0098	1.00	20	5.00
BC	0.52	-0.02	0.93	0.18	0.0164	0.99	11	5.56
20	0.55	0.14	0.69	0.22	0.0049	1.00	45	4.55

Table 3.3. Adsorption Parameters for Profile C



Sulfate Added, mmol/Kg

Figure 3.1. IM Isotherms for Profile A pH Conditions Ambient



Sulfate Added, mmol/Kg



Figure 3.3. Langmuir Isotherms for Profile C pH Conditions Ambient

pH Treatments. The ambient solution pH of Profile A was around 4.6. Additions of HCl at varying concentrations were used to lower the solution pH to 3.6, 3.8 or 4.2. By use of the IM isotherm, soils of Profile A seem to be divided into two categories in relation to their adsorption capacities under different pH treatments. (Table 3.2) The first category includes the BA and Bw1, horizons, which have a maximum $SO_4^{2^-}$ adsorption under the lowest treatment of pH 3.6. Adsorption then decreases with increasing pH so that a minimum amount of adsorption corresponds to the ambient conditions at pH 4.6 (Figure 3.4). The second category includes the O, A, Bw2 and 2C horizons which have a maximum zone of adsorption somewhere between pH 3.8 and 4.2. Above and below that level, adsorption decreases (Figure 3.5). For example, the Bw2 horizon has a net adsorption of 58% under pH 3.6; it decreases to 50% at pH 3.8, goes up to 61% at pH 4.2, and then decreases again to 37% at pH 4.6 (ambient).

The division of the soil profile into these distinct categories suggests that important changes may occur in $SO_4^{2^-}$ dynamics if soil acidification is prolonged. First of all, the surface horizons (O and A) will actually adsorb more $SO_4^{2^-}$ up to acidity levels close to pH 4.2. However, further acidification to pH 3.8 or 3.6 will result in progressively less adsorption. The same observation will hold true in the Bw2 and 2C horizons. There is a zone, however, in the middle of the profile (BA and Bw1 horizons), where adsorption will increase with acidity increases down to pH 3.6.



Sulfate Added, mmol/Kg

Figure 3.4. IM Isotherms for Profile A Under Four pH Treatments Bw1 Horizon



Sulfate Added, mmol/Kg

Figure 3.5. IM Isotherms for Profile A Under Four pH Treatments 2C Horizon

In Profile A, $SO_4^{2^{\circ}}$ adsorption at pH 3.6 is poorly correlated with DCBextractable Fe₂O₃ (r=0.25). Since hydrolysis species of Fe³⁺ should be stable at pH values down to 3.0, Fe oxides must still be stable and present in the system. Their poor correlation with $SO_4^{2^{\circ}}$ adsorption may indicate that they are already saturated. Also, at pH values close to 3.5-3.6, there is a shift from FeOH²⁺ to FeOH⁺, so that there may be a loss of positive charge and a decrease in $SO_4^{2^{\circ}}$ adsorption (Lindsay, 1979). The most likely explanation for decreased adsorption at the lower pH value, however, is that Al species may begin to dissolve at pH values close to 3.6. Thus, there may be loss of reactive sites from Al-oxides at the lower pH value. At the higher pH values (3.8 and 4.2), adsorption is more strongly correlated with DCB-extractable Fe₂O₃ (r=0.93 and 0.90, respectively).

Current net adsorption is weakly or only moderately correlated with percent organic matter at all pH levels under IM modeling. Furthermore, correlation with organic matter decreases with increasing pH. This observation suggests that organic matter plays a less significant role in $SO_4^{2^-}$ adsorption at higher pH values where there is less development of positive charge sites. Hence, the most significant factor influencing $SO_4^{2^-}$ adsorption under the higher pH conditions is the presence and form of extractable Fe- and Al-oxides. At ambient pH, edge charges and hydroxy-Al polymers may also influence adsorption.

A notable observation for these soils is the degree of adsorption change which accompanies only small changes in solution pH. Nodvin et al. (1986) also observed large changes in adsorption with small incremental changes in pH. They further observed that minimum amounts of labile $SO_4^{2^2}$ correspond with the maximum adsorption pH. As pH increases, so does the concentration of labile soil $SO_4^{2^2}$.

The $SO_4^{2^2}$ adsorption dynamics of Profile C display a few notable differences from those discussed above for Profile A. The ambient solution pH of Profile C was around 3.9. Solutions of dilute HCI were used to lower two treatments to 3.8 or 3.6. Dilute NaOH was used to raise the final treatment to pH 4.4. These soils display little change in adsorption within the range of pH 3.6 to 3.9. Adsorption remains fairly constant as pH is increased within this range. However, a sharp decrease in adsorption is observed between pH 3.9 and pH 4.4. For example the Bw2 horizon has a net adsorption between 56-70% at the lower pH values but drops to 48% at pH 4.4 (Figure 3.6). The adsorption decrease at pH 4.4 is most likely attributable to decreases in positive charge development on Fe and AI oxides and organic matter. Profile C does not display the adsorption maximum around pH 4.0. This observation may indicate that Profile C is more Fe dominated and that at lower pH values there are still stable oxides for the adsorption of $SO_4^{2^2}$. Chemical characterization of the Profile supports this theory by showing that the profile does contain more Fe than Profile A

Prolonged acidification down to pH 3.6 would have little effect on the SO₄²⁻ adsorption capacity of Profile C. However, anthropogenic liming—which may be one means of replenishing vital base cations—would result in sharp decreases in

 SO_4^{2-} adsorption. The decreased adsorption may counteract the positive effects of base cation replenishment, since the SO_4^{2-} anion co-leaches with associated cations.

Moisture Treatments. Use of the IM isotherm shows that SO_4^{2-} retention by the O horizon of Profile C decreases by a factor of 23 times when the soil is allowed to air-dry before experimentation (Table 3.4). In fact, the air-dry sample is desorbing SO_4^2 within the input range of 0.0 to 2.0 mmol/L (Figure 3.7). This is contrary to the observations of Comfort et al. (1991), who postulated that H⁺ release during organic matter mineralization resulted in increased adsorption when surface soils were air-dried. However, if organic S is being converted to inorganic SO_4^{2-} during the drying process, release of mineralized SO_4^{2-} may mask adsorption trends. When S mineralization occurs in a soil, there are three possible pathways for removal of the resulting SO_4^{2-} ion: plant uptake. adsorption on soil solids, or leaching. In such a case, net S mineralization can actually exceed immobilization (uptake plus adsorption) so that leaching occurs and there appears to be a net loss of SO_4^2 . Since surface soils of forest systems may contain up to 85% organic S and the soil in guestion here is already approaching $SO_4^{2^-}$ saturation, it is not surprising that leaching is the dominant mechanism for SO_4^{2} removal once enhanced mineralization takes place. Fitzgerald and Autry (1992) observed that for a range of forest soils, organic S greatly exceeded adsorbed SO_4^2 . Specifically, for an Appalachian hardwood forest in Coweeta, North Carolina, organic S levels were more than 5 times the



Sulfate Added, mmol/Kg

Figure 3.6. IM Isotherms for Profile C Under Four pH Treatments Bw2 Horizon

	IM			Langmiur				
Ambient pH	Slope	Intercept	R ²	Slope	Intercept	R ²	к	b
O (Moist)	0.14	-0.52	0.96	0.16	0.0114	1.00	14	6.25
O (Air-dry)	-0.08	-0.96	0.74	0.45	-0.0698	0.99	0	2.22
2C (Moist)	0.21	0.37	0.72	0.18	0.0038	1.00	47	5.56
2C (Air-dry)	0.52	0.01	0.96	0.15	0.0021	1.00	71	6.67

 Table 3.4 Moisture Content Effects on Adsorption Parameters



Figure 3.7. IM Isotherms for the O Horizon Under Two Moisture Treatments

adsorbed $SO_4^{2^{-}}$ levels. A slight decrease in equilibrium solution pH (3.93 to 3.83) for the air-dry samples is evidence that mineralization may have taken place when the soil was brought to laboratory temperature and allowed to air-dry, resulting in the release of H⁺ to solution. Fasth et al. (1991) demonstrated that when mineralization was removed from the total $SO_4^{2^{-}}$ release, trends in $SO_4^{2^{-}}$ retention were better indicators of adsorption. Langmuir modeling shows that the air-dry soil has a potential monolayer coverage that is 36% less than that of the moist soil (Figure 3.8).

Unlike the O horizon, the 2C horizon of Profile C adsorbed 2.5 times more $SO_4^{2^-}$ when air-dried (Figure 3.9). Since S mineralization should be inconsequential in the 2C horizon, increases in adsorption with air-drying may develop for this soil and should not be masked by $SO_4^{2^-}$ losses via transformations from organic S. In the 2C horizon, the most likely cause for enhanced adsorption under dry conditions is that new solids have been precipitated from Fe and Al oxides. These solids result in the development of new sites for $SO_4^{2^-}$ adsorption.

These data suggest that air-drying soil samples may severely underestimate $SO_4^{2^2}$ adsorption in surface horizons where mineralization effects can mask total $SO_4^{2^2}$ retention. For the natural system at the FEF, though, mineralization processes are kept to a minimum due to cool temperatures and high soil moisture contents. Adsorption may be overestimated in lower horizons where precipitates of Fe and Al oxides form during the drying process and are more


Figure 3.8. Langmuir Isotherms for the O Horizon Under Two Moisture Treatments



Figure 3.9. IM Isotherms for the 2C Horizon Under Two Moisture Treatments

consequential in $SO_4^{2^-}$ adsorption dynamics. For the FEF, soils are unlikely to become air-dry during any time of the year, so it is crucial that analytical procedures utilize field moist samples. If surface horizons do become dry, enhanced leaching of mineralized S has potential to be adsorbed by lower horizons. However, it is difficult to determine $SO_4^{2^-}$ adsorption from atmospheric inputs for the dry surface horizons since mineralization losses augment the equilibrium solution concentration of $SO_4^{2^-}$.

3.4.2 Sulfate desorption

Sulfate desorption experiments were conducted for all horizons of Profile C. Continuous leaching with solutions of 1 *N* KCl, 1 *N* KH₂PO₄, and distilleddeionized water demonstrated that desorbable SO₄²⁻ varied greatly between the uppermost horizons and the lower horizons (Figure 3.10). Total specificallyadsorbed SO₄²⁻ (S_p) was taken to be represented by that which was extractable by 1 *N* KH₂PO₄ and was highest in the A horizon. Below the A horizon, S_p decreased with depth. The sharpest decrease occurred between the A and the BA horizon. Decreased desorption of S_p was then more gradual down to the 2C horizon. Release of water-soluble SO₄²⁻ (S_w) followed the same trend as S_p, except that total desorption values were much less for S_w. KCI-extractable SO₄²⁻ (S_k) was actually highest in the Bw2 horizon, and values in the BC and 2C horizons were higher than expected. In the surface horizons, S_k showed desorption trends similar to S_p and S_w.



Figure 3.10. Extractable Sulfate

The high presence of S_p in the A horizon is indicative of the area's high levels of atmospheric input and supports adsorption data that this soil is approaching SO_4^2 saturation in the surface. Furthermore, the maximum capacity of the monolayer for the A horizon soil is 10 mmol/Kg; desorption data show that this soil is currently holding 9.9 mmol/Kg S_p . Much of the SO_4^{2-} that reaches the litter layer in the O horizon is probably rapidly leached to the A horizon. This is because of the relatively unreactive nature of the less decomposed organic matter in the O horizon. Once the $SO_4^{2^-}$ reaches the A horizon, where organic matter is more reactive and clay content increases, there is more opportunity for adsorption. Hence, more native SO_4^2 can be observed on the A horizon soil. As the profile continues with depth below the A horizon, decreases in S_p are attributable to the $SO_4^{2^2}$ front phenomena discussed in Section 3.4.1. As each horizon receives SO_4^{2-} from the overlying horizon, it may retain SO_4^{2-} until equilibrium conditions are obtained, at which point the soil becomes saturated with respect to incoming solutions and initiation of leaching then moves the front down to the next lower horizon. The data here suggest that the $SO_4^{2^2}$ front has proceeded in Profile C to the boundary of the A-BA horizons. The sharp decrease in S_p at that point is a result of the lower binding strength for $SO_4^{2^2}$ in the BA horizon (K=11) when compared to that of the A horizon (K=23). While the BA horizon does have this lower binding strength, though, it has not yet reached its maximum monolayer capacity (b=8.3 mmol/Kg; Sp=5.2 mmol/Kg). Hence, only gradual decreases in Sp are observed below the BA horizon due to the fact that this horizon may still be coming to equilibrium with incoming solutions from the near-saturated A horizon. As the BA horizon becomes more saturated, the $SO_4^{2^2}$ front will proceed to the Bw1 horizon boundary.

Comparisons of SO₄²⁻ desorbed with different extractants divides the soil profile into two sections: surface horizons where organic matter reactions are of primary importance, and lower horizons where the mineral fraction is more consequential in determining SO₄²⁻ desorption. The first section comprises the surface horizons (O, A, and BA), which have high organic matter contents and low Fe oxide contents. For these soils, SO₄²⁻ is held with less energy and desorption is more related to the organic fraction than to the mineral fraction. Water-soluble SO₄²⁻ is considerable, but some evidence of specific adsorption arises from the fact that not all S_p can be extracted by KCI. Also, there may be a larger pool of organically-bound SO₄²⁻ in the surface horizons, which is replacable only by PO₄³⁻. The second group comprises the lower horizons (Bw1, Bw2, BC, and 2C), which are holding SO₄²⁻ more tightly in correspondence with higher Fe oxide contents. Unlike the first group, soil of the lower profile have considerably more S_k, which implies a mechanism of more reversible SO₄²⁻ retention. Although, very little of the SO₄²⁻ on the lower soils is water-soluble. The amount of water soluble SO₄²⁻ decreases with depth, corresponding with

The amount of water soluble $SO_4^{2^-}$ decreases with depth, corresponding with decreases in S_p . When S_w is expressed as a percent of S_p , its relative fraction $(S_{w/p})$ increases through the O horizon to the Bw1 horizon and then decreases

down to the 2C horizon. Water desorption of S_p for different horizons ranged from 4% in the 2C horizon to 33% in the BA horizon, and the average for the soil profile as a whole was 22% (Table 3.5). Since one-third of the PO₄³⁻-extractable SO₄²⁻ in the BA horizon is water-soluble, SO₄²⁻ adsorption is more reversible for this soil. The reversibility of SO₄²⁻ retention implies that this soil has a large pool of adsorption sites that do not involve ligand exchange or the formation of insoluble compounds such as precipitates of Fe and Al oxides. The BA horizon also demonstrates a KCI-extractable fraction (S_{k/p}) of 86%. The high fraction of salt-replacable SO₄²⁻ implies that salt attraction reactions largely predominate over ligand exchange processes in the BA horizon. This is also the case in the lower horizons, where the KCI-extractable fraction ranges from 68% to 100%.

The relatively high amount of KCI-extractable $SO_4^{2^-}$ in the lower horizons is noteworthy since S_w is relatively lower in these horizons. A higher KCIextractable fraction implies that $SO_4^{2^-}$ is being retained with less energy than in the surface horizons. One likely cause for this phenomenon may be due to the relative time that $SO_4^{2^-}$ has been present in each section of the profile. The surface horizons, since they are greater sinks for atmospheric input, have historically held $SO_4^{2^-}$ for a longer time period. Hence, $SO_4^{2^-}$ in the lower horizons may not have had time to organize and become specifically adsorbed to the degree that $SO_4^{2^-}$ has had in the surface. Little, if any, of the $SO_4^{2^-}$ in the lower horizons is specifically adsorbed and may therefore be somewhat reversibly adsorbed. However, the lower horizons have a small fraction of $S_{w/p}$,

Horizon	S _p , mmol/Kg	S _k , mmol/Kg	S _w , mmol/Kg	$S_k:S_p$	$S_w:S_p$
0	5.36	2.30	1.13	0.43	0.21
А	9.90	4.36	2.50	0.44	0.25
BA	5.16	4.43	1.69	0.86	0.33
Bw1	4.44	3.02	1.18	0.68	0.27
Bw2	3.66	4.33	0.84	1.18	0.23
BC	3.41	3.02	0.68	0.89	0.20
2C	3.17	3.65	0.14	1.15	0.04

Table 3.5. Sulfate Desorption Values for Profile C

higher DCB-extractable Fe contents, and higher K values from adsorption experiments. These soils are holding $SO_4^{2^-}$ against release to aqueous solutions, but are releasing $SO_4^{2^-}$ at high ionic strengths (1 N KCI). Since forest systems have ionic strengths closer to 0.01 N, the aqueous extraction may be more realistic of natural $SO_4^{2^-}$ release. Hence, there may a relatively small pool of labile $SO_4^{2^-}$ in the lower horizons. This would be especially true in the 2C horizon, where only 4% of the S_p fraction is water-soluble, indicating that $SO_4^{2^-}$ retention involves the formation of insoluble compounds such as precipitates of Fe and Al oxides. However, a mechanism of retention other than specific adsorption is clearly evident in the subsurface horizons.

Moisture Treatments. When the O horizon soil was allowed to air-dry before extraction with KH_2PO_4 , desorption of SO_4^{2-} was almost identical to that of the moist soil during the first day of experimentation (Figure 3.11). During the second day, after total leachate exceeded 125 ml, the air-dry sample began to desorb less SO_4^{2} than the moist sample. At the completion of the experiment, total S_p for the moist soil was 171 mg/L and only 136 mg/L for the air-dry soil. It would seem that in the organic rich O horizon soil, mineralization upon air-drying should result in higher SO_4^{2-} levels in the effluent. However, the data here does not follow this logic and cannot be explained by mineralization alone. Shanley (1992) also observed a decrease in $SO_4^{2^2}$ desorption when forest soils of the Georgia piedmont were air-dried. Even in the O horizon, where Fe and Al oxide levels are relatively low, there may still be formation of new solids upon air-drying which hold SO_4^2 more tightly than for the moist soil. The point at which the desorption curves for the moist and air-dry samples become separated represents the point at which organic retention give way to inorganic retention of $SO_4^{2^-}$. For organic processes, air-drying has little effect on $SO_4^{2^-}$ desorption, but after an initial flush of organically-bound SO₄²⁻, mineral processes become dominant. The air-dry sample then retains more SO_4^{2-} against desorption on solids of Fe and Al oxides.

In the 2C horizon, the air-dry sample actually exceeded the moist soil at all experimental points in desorption of S_p (Figure 3.12). This is completely opposite of desorption observations for the O horizon. However, it has been proposed that $SO_4^{2^-}$ in the subsurface has not had as much time as that in the surface to become organized and specifically adsorbed due to the high deposition environment in which these soils occur. If this is the case, new solids of Fe and and Al oxides may certainly be forming upon air-drying, but some mechanism of retention other than specific adsorbtion must be used to explain the increase in $SO_4^{2^-}$ release that corresponds with air-drying. Although, a slight discoloration of the effluent indicated that dissolved organic carbon (DOC) may have been present in effluent from the air-dry sample, which would indicate that mineralization had taken place even in the 2C horizon soil. In this case, the conversion of organic S to inorganic $SO_4^{2^-}$ would also result in higher values for S_p .



Figure 3.11. Sulfate Desorption O Horizon



Figure 3.12. Sulfate Desorption 2C Horizon

3.5 Summary and Conclusions

 $SO_4^{2^-}$ adsorption isotherm analyses indicate that two soil profiles within the FEF are desorbing $SO_4^{2^-}$ at solution concentrations up to 0.5 mmol/L. Soils at all depths for both profiles may be saturated with respect to natural solution concentrations. Already surface horizons are releasing $SO_4^{2^-}$ to lower horizons and a $SO_4^{2^-}$ front appears to moving down each profile as each horizon progressively reaches equilibrium with input levels and begins to release $SO_4^{2^-}$ to leaching waters. Adsorption was shown to be highly concentration dependent and to increase as input concentrations increase. Therefore, reductions in atmospheric input may result in less $SO_4^{2^-}$ adsorption and more leaching from the surface horizons. Lower horizons may experience a lag time in response as they equilibrate with new input levels but will eventually exhibit less adsorption as well, as the $SO_4^{2^-}$ front moves down the profile.

Under ambient pH conditions and at low ionic strength (0.01N), Fernow soils are divided into two categories: the first category comprises shallow surface horizons which little capacity to adsorb additional $SO_4^{2^2}$, high organic matter, and low Fe-oxide content. The second category comprises deeper subsurface horizons which will adsorb SO_4^2 at higher input levels, have low organic matter, and higher Fe-oxide contents. At all depths, all soils display a weak relationship between additional SO₄² adsorption and Fe-oxide and organic matter content. However, under Langmuir modeling, strong positive relationships develop between these two properties and complete monolayer coverage of SO_4^2 . Since Langmuir modeling accounts for $SO_4^{2^2}$ already on the soil, it may be inferred that present coverage is highly related to Fe-oxide and organic matter content. Additional adsorption, however, seems to be controlled by some other mechanism. Sites related to Fe-oxides or organic matter may be preferential sites for adsorption and be already saturated. Secondary sites such as those associated with mica edges or Al-hydroxy polymers may be taking over as new adsorption sites.

Experimentation with various pH treatments yielded inconsistent results. However, the general trend was that an adsorption maxima was achieved around pH 4.0. Above and below that level, adsorption decreased. Therefore, decisions about anthropogenic liming of these soils should consider ambient pH conditions and the effect that higher pH would have on $SO_4^{2^\circ}$ adsorption. Profile A (ambient pH = 4.6) may be little affected by small increases in soil pH. Profile C (ambient pH = 3.9), however, may display decreased adsorption with only small increases in pH.

The soil with the higher Fe-oxide content did not display an adsorption maximum around pH 4.0. This is attributed to the stability of the Fe-oxides at low pH values and the consequential maintenance of reactive sites for adsorption. Where an adsorption maximum was observed around pH 4.0, it is attributed to dissolution of Al-oxides and the saturation of Fe-oxides.

Organic matter was more weakly correlated with adsorption as pH increased. At the higher pH values, there is less development of positive charge sites associated with organic matter. At low pH values, however, maintenance of natural soil organic matter may be an important mechanism of SO₄²⁻ adsorption and attenuation of leaching. Desorption of SO₄²⁻ by three extractants followed the trend: $KH_2PO_4 > KCI > H_2O$. The low-adsorbing surface horizons with high organic matter and low Fe-oxide contents display the most extractable SO_4^{2-} . These soils have lower capacities to retain $SO_4^{2^2}$ and are more prone to leaching. They have considerable amounts of water-soluble SO_4^{2-} , but also some which is specifically adsorbed, as indicated by the difference between S_k and S_p . The high-adsorbing subsurface soils with low organic matter and high Fe-oxide contents have greater retention of SO_4^{2-} , although there is less of it naturally present in the subsurface. The subsurface soils are also holding SO_4^{2} with less energy than the surface horizons. It is proposed that since these soils are in a high deposition environment, $SO_4^{2^2}$ in the subsurface has not had as much time to organize and become specifically adsorbed as that in the higher soils. The relatively small fraction of S_w in the subsurface implies that it may contain a small pool of labile $SO_4^{2^-}$. Also, the small difference between S_k and S_p in the lower soils implies a mechanism of retention other than specific adsorption. Both innerand outer-sphere complexation models would seem appropriate for these soils.

Air-drying soils was shown to underestimate $SO_4^{2^-}$ adsorption in the O horizon due to masking effects of increased mineralization. Desorption from the air-dry soil showed that mineral processes were also involved, since the air-dry soil eventually retained more $SO_4^{2^-}$ than the moist O horizon sample. Conversely, the 2C horizon adsorbed more $SO_4^{2^-}$ when air-dry, probably due to the formation of new solids of Fe and Al oxides. The 2C horizon also desorbed more $SO_4^{2^-}$ when air-dry.

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Chapter 4 Base Cation Release from Appalachian Forest Soils Under Simulated Acid Rain

4.1 Introduction

Several important impact processes associated with acidic deposition to forest soils are (i) $SO_4^{2^-}$ co-leaching with base cations and the consequential depletion of base cations from soil reserves, (ii) enhanced soil acidity with its associated increase in Al³⁺ mobility, (iii) Al³⁺ saturation of the soil cation exchange complex, and (iv) elevated levels of $SO_4^{2^-}$ and Al³⁺ in receiving waters. The processes of base cation depletion and Al³⁺ saturation can be further impacting after commercial harvesting due to the loss of bases contained in biomass. As a major component of the biochemical cycle, organic matter decomposition acts as a buffering process in which base cations can be recycled between plant tissues and soil reserves.

For soils under acid deposition, base cation replenishment via the biochemical cycle is of optimum importance. This is especially true when geochemical sources of base cations are limiting. Geochemical weathering of soil mineral matter is a second buffering process that replenishes base cations to a soil system. Since harvesting activities are expected to continue throughout much of the northeastern Appalachian forest, the geochemical cycle may become foremost in significance in the buffering of forest soils against the impact processes of acid deposition. The objective of this study was to assess the geochemical capacity of an Appalachian forest soil to replenish base cations under a high acid deposition environment.

4.2 Literature Review

4.2.1 Environmental influences on geochemical weathering

Geochemical weathering is the most important long-term source of base cation replenishment to the soil (Sverdrup and Warfvinge, 1993). It is, therefore, a fundamental process in the neutralization of acid deposition. Because different geologic materials weather differently and vary in their capacity to release base cations, a given landscape will have a characteristic status of bases from the geochemical pool. Factors which can influence the nature of geochemical weathering and the rates at which it occurs include parent mineralogy, climate, vegetation, hydrogeology, landscape position, and time. From the interactions of these factors, a number of chemical processes can occur which result in the alteration of original materials and the release of new materials to the soil complex. According to Dixon and Weed (1989), parent material mineralogy is the most important distinguishing factor in the weathering of soils that are otherwise under similar conditions. For a series of soils developed over different parent materials, it has been generally held that guartz and feldspar materials are the most resistant to weathering and that mafic (Fe- and Mg-bearing) silicates and carbonates are the most susceptible to weathering (Goldich, 1938; White,

1995). The oxides of Fe and AI are perhaps the most resistant to weathering and usually persist in even humid, well leached environments.

Soils may also have similar properties in every manner except precipitation or temperature. Johnson et al. (1993) studied similar soils derived from volcanic ash in Hawaii and observed significant weathering differences under different precipitation environments. Temperature plays a role in geochemical weathering because it controls rates of reactions and the nature of reaction end-products (Steam and Morgan, 1981). Temperature can also influence moisture content and microbial activity, which in turn also effect weathering rates. For a forest ecosystem, higher rates of geochemical weathering may occur after harvesting because of the temperature fluctuations that result in the absence of a vegetative cover (White et al., 1990). While increasing temperature normally increases geochemical weathering rates (Carroll, 1970; Lanyon and Hall, 1979; Kodama and Foscolos, 1981), evidence has been presented that weathering can also be intense under colder environments. According to Reynolds (1971), the leaching that results from winter snowmelt can produce significant alteration of Fe- and Albearing minerals in the surface. This environment is particularly suited for the production of gibbsite, which is usually more common in warmer climates. Under intense leaching, silica is removed from the soil, and gibbsite formation may be favored over other minerals such as kaolinite (Norfleet and Smith, 1989). Furthermore, Robert and Tessier (1992) have stated that weathering can often display seasonal variations.

A series of soils can also vary in terms of landscape position; for example, soils can develop on steep slopes, on bases of hillslopes, or in flood plain areas. The resultant differences in erosion and water dynamics create inherent differences in weathering characteristics (White, 1995). According to Velbel (1992), hydrologic controls are one of the most important factors in determining weathering rates. Depending on the nature and volume of the leaching water, more or less of the reactive surfaces of the soil may actually participate in weathering reactions. Gardner and Walsh (1996) studied weathering rates for a gneiss-derived soil in the Himalayan Mountain region. They observed that a strong hydraulic gradient in that region resulted in intense geochemical weathering throughout the entire soil profile. Water movement was sufficient to produce similar leaching in all horizons, so that weathering was continuous to the base of the parent material. Furthermore, in forest ecosystems, vegetative covers usually prevent significant amounts of runoff, so water infiltration is high and leaching is maximized. Gardner and Jenkins (1995) report less than 5% of rainfall loss due to runoff for a temperate forest system. Slope can also influence weathering rates and the byproducts of weathering reactions. Norfleet and Smith (1989) state that forest soils in the Appalachian regions often contain gibbsite because of the steep slopes that result in decreased silicate accumulation.

In spite of interacting environmental factors, weathering reactions are ultimately controlled at mineral surfaces and are dependent on the concentration and decomposition traits of the soil's activated surface complex (Velbel, 1992). This has important implications for weathering studies, since the total amount of infiltrating water may not be as significant as the amount of exposed surface in contact with the water.

Chemical reactions associated with weathering processes may be quite simple, such as with Fe²⁺ oxidation, or they may be more complex and require intense observation and study to model their pathways (White et al., 1990). Where precipitation is not limiting, hydrolysis reaction may govern overall weathering; where water is more limiting, reactions such as cation exchange, diffusion, and oxidation-reduction can become more important (Robert and Tessier, 1992).

4.2.2 Methods of estimating geochemical weathering

Since weathering occurs over relatively long periods of time, it is usually necessary to study weathering with some sort of laboratory or field model that simulates natural conditions. A number of researchers have used geochemical models to determine weathering rates. These models have been based on experimental and theoretical kinetics studies. Combined with published data on dissolution rates of pure minerals, soil characteristics give rise to kinetic models which can be used to describe dissolution rates of complex soil systems. Velbel (1985) proposed a model constrained by a series of mass balance equations. He accounted for input via atmospheric precipitation and output by biomass uptake, groundwater storage, secondary precipitation, and stream removal. Once he had calculated a mineral's net rate of flux in a system, he applied those rates to a calculated volume of the given mineral per unit volume of rock to determine the time required for the rock to weather by a certain degree.

Van Oene (1992) used a similar model, with biomass uptake integrated with soil nutrient processes as the focus of cation dynamics in the soil. Unlike Velbel's model, he accounted for the nature of the exchange complex but assumed homogeneous and equilibrium conditions. Neither model accounted for water flux, pH, cation interactions, or exposed surface area.

Sverdrup and Warfvinge (1993) argue that exposed surface area is the most important parameter in thermodynamically determining weathering rates. They developed the PROFILE model, which uses soil characteristics of mineralogy, texture, and temperature to relate information on surface area, moisture saturation, and a chemical driving force. This information in turn is used to develop a kinetic expression, and with rate coefficients determined in the laboratory, they were able to theoretically determine base cation input rates from weathering. They compared their results with a mass balance study and observed close agreement between the two.

Aside from kinetic models which are theoretically derived, weathering rates have also been determined from field and laboratory studies. Field studies would be ideal but are limited by time requirements, high variability, and lack of sensitivity (Wolt, 1994). Several workers have used soil and bedrock compositions to estimate weathering since a given geologic event such as the last glaciation for a site. Wright et al. (1993) assumed the element titanium (Ti) to be immobile and thus Ti levels in soil relative to Ti levels in parent bedrock should reflect loss of other elements as well. Using this assumption, with knowledge of the relative amounts of base cations in soil and bedrock, they estimated base cation release in a Norway forest soil to be 12 meq/m²/yr. A common indirect method of determining weathering rates in the field is use of an ecosystem mass balance. Velbel (1992) argues that for forested watersheds, accounting for biomass uptake is crucial in mass balance studies, but few researchers have included this parameter in their work. Taylor and Velbel (1991) demonstrated that failure to account for biomass uptake can introduce errors up to several hundred percent.

Likens and Bormann (1995) have conducted some of the most prominent work in ecosystem mass balances at the Hubbard Brook Experimental Forest in New Hampshire. These researchers do account for biomass uptake, which is so crucial for forest ecosystems. The basic approach is to calculate output by examining streamflow composition or soil solution chemistry, biomass uptake, and changes in the exchange complex. With knowledge of atmospheric inputs of base cations, the weathering rate is then calculated as follows:

Weathering = leaching - atmos. input - biomass uptake - ∆(exchange complex). Laboratory studies have mostly focused on dissolution of pure minerals (Sverdrup, 1986; Knauss and Wolery, 1989; Brantley and Stillings, 1996). However, soils are an assemblage of different mineral components, so weathering in soils is much more complex since the minerals may interact with each other. Furthermore, laboratory studies may sometimes produce overestimates of mineral weathering rates (Frogner, 1990; Sverdrup, 1990). Studies on mixed soil systems are limited, but they are generally divided into studies which use organic acids or water as a leaching substance for soil columns. The use of soil columns may be preferable when it is considered that such experiments allow the observation of wetting and drying cycles that occur naturally in the field (White et al., 1990).

Cronan (1985) used acidified water to simulate rainfall over a series of undisturbed soil columns from forest ecosystems. His eighteen month study compared different acid loading rates with leachate concentrations from the columns. He also accounted for changes in the exchange complex by pre- and post-treatment comparisons of total acidity, CEC, and BS. Furthermore, he used previously obtained data on biomass uptake to supplement his column study. Results showed that weathering rate was inversely related with soil particle size and directly related with total exchangeable bases in the soil profile. Cronan also observed that weathering rates increased as acidic loading rates increased.

To put different means of determining geochemical weathering rates in context with one another, they have been summarized in Table 4.1.

Method	Principal Investigators	Theory or Applications	Major Advantages	Major Disadvanta
Ecosystem Mass Balance	Likens & Bormann (1995); Clayton (1988)	Weathering = output - input for all ecosystem components	Includes estimates for biomass uptake	Sample intensiti time intensive provides only estimate of cu conditions
Laboratory: Column Study	Cronan (1985); Adams & Boyle (1979)	Leachate from columns collected and analyzed for weathering inputs	Potential to closely simulate field conditions; time effective; soil mixtures test for interactions among minerals	Homogenized samples may represent field conditions; do not account fo preferential flo
Laboratory: Pure Mineral Dissolution Study	Brantley & Stillings (1996); Knauss & Wolery (1989)	Treatment of pure minerals with acid or base dissolution or leaching by water	Obtain dissolution rates for various minerals which may comprise a system	Pure minerals only; does no account for mineral interactions in soils
Thermodynamic Modeling	Sverdrup & Warfvinge (1993); Velbel (1985)	Application of soil properties and laboratory dissolution rates to a kinetic model	More practical for long term predictions	Only account boundary conditions ch by the modele

rable the moundable of oldaying onemical freathering rates	Table 4.1.	Methods of	Studying	Chemical	Weathering	Rates
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4.3 Methods and Materials

Experimental soils were collected from two excavated soil pits, Profile A and Profile C, at the Fernow Experimental forest in November 1996. Both pits are within the boundaries of the LTSP research plots and had been previously designated as containing representative soils for the LTSP research area (Section 2.2). Major taxonomic horizons of the two representative profiles were sampled and stored in the laboratory at 0°C until analytical preparation. Each horizon was analyzed for physical, chemical, and mineralogical characterization prior to the initiation of the base release study (Table 4.2).

For the base release study, each horizon sample was allowed to thaw from the frozen state that was maintained during storage. Thawing occurred by allowing the sample to sit in a 4°C refrigerator for 1-2 days. Each sample was then wet-sieved by pressing the thawed moist soil through a 3-mm sieve. Fragments remaining in the sieve were discarded, and the < 3 mm fraction was returned to the 4°C refrigerator for storage. The maximum storage time at 4°C was 2 days. If longer storage time was required, the sample was transferred to the freezer and kept at 0°C.

The sieved soils were packed into clear plastic columns in such a way that they simulated the field soil profile as much as possible (Figure 4.1). For each column, 2 g of glass wool was placed in the bottom and then covered with 50 g of medium laboratory grade sand. Samples of a soil horizon were then placed in the column so that each column represented a small-scale version of the natural



Figure 4.1. Soil Column Schematic

soil profile. A pre-determined mass of soil from each soil horizon was placed in the column and packed to a known depth, so that bulk density was at 1.0 g/cm³ for each horizon. Some horizons were packed more than others because the depth of each horizon varied, while bulk density was set at a constant 1.0 g/cm³ (Tables 4.3a-4.3c). The depth ratios were determined so that they were a scaled down representative of the natural soil profile. Corrections were made for the absence of coarse fragments by subtracting the percentage of coarse fragments from the required depth of each horizon and adjusting the mass of soil in the column accordingly:

$$\begin{split} M_{sc} &= \rho_b V_{sf} \text{ (1.0-Cf)} \\ V_{sc} &= M_c / \rho_b \\ D_h &= V_{sc} / \pi r^2 \end{split}$$

where M_{sc} is the mass of soil placed in the column for a given horizon; ρ_b is the bulk density of the soil, which was assumed to 1.0 g/cm³ in the field and set at 1.0 g/cm³ for each horizon in the columns; V_{sf} is the volume of soil in a given horizon in the field; Cf is the coarse fraction in the horizon; V_{sc} is the volume of soil placed in the column for a given horizon; and D_h is the depth of a given horizon in the column.

Once the profile was placed in the column, the soil was covered with another 50 g of sand. Small plastic beakers were inverted over the tops of the columns to prevent entry of dust particles from the laboratory.

For each of the two profiles, twelve soil columns were packed. Packing was done in the laboratory at room temperature (23⁰C). The columns were placed in a stand and covered with aluminum foil to prevent exposure to light. The beginning of operation, set at the day the columns were packed, was July 15 for Profile A and July 25 for Profile C.

The goal of this study is to expose the profiles to regular additions of water that has been treated with H_2SO_4 . Three treatment levels will be used on 4 replicates of each profile. The treatments will vary only in SO_4 concentrations. SO_4 concentrations in the water will be set at ambient deposition conditions for the Fernow, 2 times ambient conditions, and zero for a control. The volume of acidified water that will be added to each column will be determined from precipitation data and will be constant for all columns.

Prior to the onset of acid additions, an equilibration period is presently being achieved. The columns are being leached with distilled deionized water, and effluent is being monitored weekly. A regimen of regular water additions from the tops of the columns was initiated at day 1 after each column was packed. After the first day, each column received 50 ml of distilled deionized water twice weekly for 4 weeks and then 10 ml twice weekly to date. During the second week of operation, small openings (~ 1 mm diameter) were drilled in the sides of the columns at the BA/Bw1 horizon boundary for both profiles to allow escape of air. Movement of water down through the profiles had caused displacement of

 Table 4.3a.
 Dimensions of Experimental Columns

Column Parameter	Profile A	Profile C
Length, cm	101.6	81.3
Cross-sectional area, cm ²	15.518	15.518
Volume, cm ³	1576.6	1261.3
Operation Day 1	15 July 1997	25 July 1997

Table 4.3b. Packing Parameters of Experimental Column A

Horizon	Field %	Field Depth,	Column Depth,	Mass soil in	Bulk Density,
	Coarse	ст	ст	column, g	g/cm³
	Fragments				
0	20	2.5	2.54	47	1.0
А	20	17.8	14.22	265	1.0
BA	25	12.7	9.53	165	1.0
Bw1	30	27.9	19.56	344	1.0
Bw2	35	30.5	19.81	369	1.0
2C	45	43.2	22.10	406	1.0

	Table 4.3c.	Packing Parameters of Experimental Column C					
Horizon	Field %	Field Depth,	Column Depth,	Mass soil in	Bulk density,		
	Coarse	ст	ст	column, g	g/cm³		
	Fragments						
0	20	1.3	1.27	24	1.0		
А	20	6.4	5.08	95	1.0		
BA	20	10.2	8.13	151	1.0		
Bw1	25	25.4	19.05	375	1.0		
Bw2	30	7.6	19.56	400	1.0		
BC	40	15.2	9.14	190	1.0		
2C	55	27.9	11.43	243	1.0		

	<u></u>				
Horizon	Ca, μmol+/Kg	Na, μmol+/Kg	Mg, μmol+/Kg	K, μmol+/Kg	Total Bases,
					μmol+/Kg
0	14,500	100	2,500	2,500	19,600
А	15,100	200	2,700	2,600	20,600
BA	4,400	200	600	1,200	6,400
Bw1	14,100	200	3,400	1,100	18,800
Bw2	25,700	400	9,000	650	35,750
2C	27,200	300	11,000	950	39,450
Column Total, µmol+/Kg	101,000	1400	29,200	38,200	140,600
Removal to Date, μmol+/Kg (%)	1081 (1)	NA	346 (1)	61 (0.2)	1488 (1)

 Table 4.4a. Exchange Base Cation Levels Per Horizon In Profile A

Table 4.4b. Exchange Base Cation Levels Per Horizon In Profile C

Horizon	Ca, μmol+/Kg	Na, μmol+/Kg	Mg, μmol+/Kg	K, μmol+/Kg	Total Bases,
					μmol+/Kg
0	4,000	100	2,900	2,250	9,250
А	4,200	250	3,100	2,550	10,100
BA	500	200	900	1,250	2,850
Bw1	0	200	400	850	1,450
Bw2	1,600	350	600	700	3,250
BC	4,500	350	1,200	550	6,600
2C	4,100	250	1,900	400	6,650
Column Total, μmol+/Kg	18,900	1,700	11,000	8,550	40,150
Removal to Date, μmol+/Kg (%)	401 (2)	NA	159 (1)	18 (0.2)	578 (1)

air and created void pockets within the profile at the BA/Bw1 horizon boundaries. Once the openings were drilled, the soils settled back to their original position within several days.

Effluent is allowed to drain from the columns by gravity and collected once a week via plastic tubing fitted to the bottom of each column. The effluent volume is recorded at each collection, and it is analyzed for Ca, Mg, K, Fe, Al, and S by ICP. Effluent pH is measured with a pH meter and combined electrode.

4.4 Preliminary Results and Discussion

Effluent analyses for each soil show significant differences between the two profiles (Figures 4.2 to 4.7). Ca is the dominant cation being released by each profile, and on an equivalent basis, cation release follows the trend: Ca>Mg>K>AI. However, Profile A has released approximately 4 times as many total equivalents of base cations (Ca, Mg, K) than Profile C. Profile A also has a much higher effluent pH at around 8.0, whereas the effluent pH for Profile C runs around 4.0 to 4.5. Analyses of Profile A are comparable to those of an illitic glacial till soil by Hartikainen (1996), who observed that leaching with water produced percolates of alkaline material so that effluent leachate was approximately 8.0. Furthermore, water percolation was shown to effectively remove Ca from exchange sites on the soil. As opposed to the base cations, Al release is presently 7 times higher in Profile C than in Profile A. Total SO₄ release is nearly equal for each soil, although Profile A has required a longer



Figure 4.2. Ca Release as a Function of Total Water Percolation



Figure 4.3. Mg Release as a Function of Total Water Percolation



Figure 4.4. K Release as a Function of Total Water Percolation



Figure 4.5. Al Release as a Function of Total Water Percolation



Figure 4.6. SO₄ Release as a Function of Total Water Percolation



Figure 4.7. Soil Column Effluent pH

leaching time and hence more effluent flux to achieve the same SO₄ release as Profile C.

The base cations Ca, Mg, and K comprise a family of similar curves in their release characteristics. The identical shapes of the curves indicate a similar release mechanism for each of the three cations. At this point in the experiment, it is impossible to determine the fraction of cations released from exchangeable versus nonexchangeable pools. The pool of exchangeable bases left in the soil will not be determined until after experimentation with acidity. Although, Hartikainen (1996) observed that simple water elution could remove cations, especially K, from nonexchangeable reserves. A positive difference between total base release and any decreases in the exchange pool would reflect mobility of cations from nonexchangeable pools. This calculation will not be made until the completion of the experiment. To date, total base release is approximately 1.49 mmol⁺/Kg for Profile A and 0.58 mmol⁺/Kg for Profile C (Tables 4.4a-4.4b).

Plotted against cumulative effluent, cumulative base release follows a linear trend. Early in the experiment, base release was similar for the two profiles, but after about 25 cm of effluent had percolated through the columns, Profile A began to surpass Profile C in base release, and the curves separate at that point. At present, the curve slopes of Profile A are now nearly 4 times that of Profile C. Initial chemical analysis of the two soils shows that Profile A has more total bases on the exchange complex and a higher base saturation. The dominant equivalent base cation in the exchange pool is Ca, and it is reasonably the dominant cation in the effluent of both soils. Conventional cation exchange models predict that the concentration of a given cation in soil solution is proportional to its concentration on the exchange complex and total ionic concentration of the bulk soil solution. Profile A obviously has some mechanism of base cation supply, especially for Ca that exceeds that of Profile C.

When effluent concentrations are plotted on a day-by-day basis, trends in ion release with time are more clearly demonstrated (Figures 4.8-4.12). For both soils, ion release increases with time until around the 95th day of operation. Profile A begins at that point to display a steady state, and ion release remains fairly constant to date. However, Profile C began after the 95th day of operation to display a sharp increase in the release of Ca, Mg, and Al. At day 173, release of AI had increased 3 fold since day 95, and that upward trend continues at this point in the experiment. Water additions to Profile C are resulting already in the weathering and subsequent break-down of Ca- and Mg-bearing aluminosilicates. Kaupenjohann et al. (1994) report that once Al concentrations increase in soil solution, there is a greater subsequent release of Ca and Mg due to the fact that they become less efficient at competing for exchange sites and are thus leached out from the soil. Reuss (1983) has demonstrated that as ionic concentrations in soil solution increase, so does the ratio of tri- to di- to monovalent cations. Therefore, increased flux of ions into solution would be expected to result in cation levels: $AI^{3+} > Ca^{2+}$, $Mg^{2+} > K^+$. Data for Profile C follow well this trend,



Figure 4.8. Ca Release as a Function of Time



Figure 4.9. Mg Release as a Function of Time


Figure 4.10. K Release as a Function of Time



Figure 4.11. Al Release as a Function of Time



Figure 4.12. S Release as a Function of Time

and K⁺ levels have remained relatively unaffected by increases in the total cation leaching rate.

According to Hartikainen (1996), a variety of H^+ buffering reactions can take place in the soil that can result in cation release. Solution pH values near 8.0 and above indicate that feldspar hydrolysis is a likely reaction in Profile A soil. The result is a high concentration of effluent Ca. Mineralogical analyses do show that plagioclase feldspar is present in the deepest horizons of Profile A. Hydrolysis reactions may take place with Mg-bearing carbonates so that Ca and Mg will dominate the cation composition of the soil solution, but there are no indications of carbonates in these soils. The Profile A soil displays a much lower degree of AI release than the Profile C soil. The soil pH of Profile A is taken to above that where aluminosilicates react with H⁺ to produce buffering effects. Therefore, there is more release of carbonate materials as opposed to AI, and the resulting solution pH is buffered around 8.0.

Profile C, on the other hand, falls almost entirely within the exchange buffer range (pH 4.2-5.0), where silicate and clay mineral destruction can increase Al concentrations in the soil solution and decrease effective cation exchange as cations are released from the soil. At pH values close to 4.0 to 4.5, a common reaction which may take place would follow the example:

 $-AIO_2M + 4H^+ \leftrightarrow AI^{3+} + M^+ + 2H_2O.$

Kaupenjohann et al. (1994) describe the above reaction as a slow reaction and may explain why release of Al, Ca, and Mg was relatively slow at first in Profile C but then suddenly began to increase. According to Reuss (1983) and Ulrich (1983), once Al release begins to accelerate, however, there can be a rapid shift toward Al dominance of the soil solution. Moreover, Reuss (1983) observed an increase in solution Al concentrations from 10% to 50% accompanying an only 15% decrease in exchange base cations on the soil. The loss of base cations may also be attributable to buffering of H^+ by variable charge organic surfaces:

 $R-(COO)M + H^+ \leftrightarrow RCOOH + M^+.$

Release of K into soil solution has remained steady for both soils. Higher effluent concentrations of K in Profile A are probably most attributable to parent material differences which cause the soil in Profile A to have a larger pool of native K. Wesselink et al. (1994) observed that K release in controlled by interlayer diffusion from minerals such as muscovite or illite and that pH is of minor importance in K release. Wells and Norrish (1968) had earlier observed that K release was relatively unaffected by solution pH, whereas Mg and Ca release could both be affected by treatments at different pH levels. Effluent concentrations of K initially increased with time in both soils, and Fanning and Keramidas (1977) have postulated that rapid initial K release is due to desorption from selective wedge sites. The slower, more steady release of K after about day 80 of the experiment is probably due more to diffusion controlled processes from mineral interlayers.

Effluent Fe concentrations have been below analytical detection limits for both soils to date. Once artificial acidification is initiated, Profile C may release Fe

more rapidly than Profile A since it has a lower pH value and is closer to the range where FeOOH reactions with H⁺ result in the release of Fe to soil solutions. Al release may be accelerated even more in Profile C as acidification begins to enter into the aluminum buffer range where gibbsite (Al(OH)₃) and jurbanite (AlOHSO₄) buffer H⁺ and subsequently release Al³⁺. Profile A may be less susceptible to Al leaching since its pH and BS are higher. Reuss (1983) observed that Al leaching was most strongly controlled by the soil BS such that soils with higher ratios of base cations displayed lower concentrations of labile Al in solution. Others have observed that high levels of effluent Al are only associated with soils having BS values less than 10-15% (Cronan and Schofield, 1990). The effective BS of Profile A is around 30%, while that of Profile C ranges from 3-16%.

The current ratio of Ca:AI remains high (≥ 2) in both soils. However, in Profile C, the Ca:AI ratio is declining with only water additions since AI release is occurring faster than Ca release. Enhanced acidification may result in a more rapid decline in the Ca:AI ratio, especially for Profile C. Several authors have demonstrated that a declining Ca:AI ratio results in nutrient imbalances, plant growth reduction, and root mortality (David and Lawrence, 1996; Cronan and Grigal, 1995). A Ca:AI ratio ≤ 1 is especially detrimental to forest systems (Cronan and Grigal, 1995).

In summary, initial water leaching of the two Fernow soils indicates that there are major differences in the chemical processes which dominate in each soil. Whereas Profile A has a higher amount of exchangeable AI, it also has more base cations on the exchange complex and thus a higher effective BS than Profile C. Consequently, the Profile A soil has released more base cations and less AI so that soil leachate is buffered around pH 8.0. The profile C soil, on the other hand, has a lower BS and displays more release of Al. Also, since the Profile A soil has to date not demonstrated any major increases in cation release. it is likely that leaching in this soil is still being controlled by exchange processes. Release of base cations in Profile C was initially slow but is currently increasing as dissolution of Ca- and Mg-bearing aluminosilicates begins. Thus, cation release from Profile C is beginning to demonstrate control by mineral dissolution processes as well as changes on the exchange complex. The lower BS and lower soil pH for Profile C keep its solution pH values buffered around 4.5 and allow for greater dissolution of Al. Treatments with artificial acidification are expected to enhance cation release from both soils, though Profile A will likely be less susceptible to changes in solution chemistry since it is more buffered. The release of Ca and Mg are more dissolution controlled than that of K, which is more diffusion controlled, and are likely to remain the dominant cations in solution for both soils. The Ca:Al ratios of both soils are still above critical levels, but enhanced acidification may rapidly decrease Ca:AI ratios in soil solution. Current ambient rainfall may already be exerting more of an influence over cation leaching than water, so that Ca:AI ratios observed thus far in the experiment may not be indicative of field conditions. However, observations made thus far during

the equilibration period have provided important insight on the chemical differences between the two soils and will allow for distinction between acid-induced changes and those derived from water leaching alone.

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Chapter 5 Conclusions

A collection of soils from the Fernow Experimental Forest in Tucker County, West Virginia has been characterized and evaluated in terms of nutrient status and inherent susceptibility to enhanced acidification. Research plots within the FEF display differences in their chemical and mineralogical makeup due to parent material differences and the consequential differences in degree of development. For example, soils of one Profile are over sandstone colluviuum mixed with shale residue; these soils are slightly less acidic and have more reserves of base cations. However, soils of Profile C are entirely over sandstone residue and are inherently lower in base reserves. The base saturation ratio for all soils is rarely above 0.10, and even the soil with more base reserves has a high degree of Al saturation on the exchange complex.

Slope is also a major contributing factor in the overall development of different samples within the research area. Steeper slopes, coupled with high precipitation levels, facilitate rapid removal of silica from the soil and result in regions of the research area where weathering is more intense. While steeper soils do have more weathering products such as gibbsite and interlayered vermiculite, they also have higher levels of mica in the surface due to mass wasting of materials to lower areas.

In general, the clay mineralogy of the FEF is dominated by muscovite and vermiculite and weathers in the order:

Muscovite \Rightarrow Vermiculite \Rightarrow HIV \Rightarrow Chlorite.

Sand and silt fractions are dominated by quartz and small levels of Ca-feldspar. Minerals in the clay fraction are in the dioctahedral form and are proposed to have Al³⁺ substituting almost completely for Mg²⁺, since there is no Mg detectable by the total elemental analysis. Hence, Ca and K are the cations in greatest supply from geochemical reserves, although Ca supplies are still relatively low within the geochemical pool.

Chemical analysis shows that these base cations are relatively low on the exchange complex, especially in the subsurface. Geochemical supplies of Mg and K are hence inferred to be low also. The dominant base cation on the exchange complex is Ca, and it is likely supplied from biochemical sources and is not a large product of weathering for Fernow soils. While a preliminary study on base release from two Fernow soils does demonstrate that Ca and Mg release are increasing in response to enhanced water leaching, it is not known at this point the degree of cations simply being removed from the exchange complex in relation to those being supplied by geochemical weathering. It is proposed that much of the Ca release seen thus far in the experiment results from buffering of H⁺ by variable charge organic surfaces, which leads to release of a metal cation.

The preliminary base release study further shows that parent material differences in the two soils give rise to different chemical controls for base release. The soil with more Ca-containing parent material has a higher soil pH and solution pH values buffered around 8.0. Hence, it has displayed rapid release of Ca and lower releases of Al. The other soil, however, is buffered around pH 4.5 and displayed slow initial base release but then a sudden increase as aluminosilicate weathering began. The lower-pH soil is also releasing much more Al. Levels of K release have remained somewhat constant and equal for both soils, demonstrating that K release is less a function of chemical controls and more dependent on time for Fernow soils.

Increased anthropogenic acidification will increase base cation levels in soil leachate, especially in the lower-pH soil because it is less buffered. The $SO_4^{2^-}$ anion will be a major co-ion associated with base cation leaching. Experiments with $SO_4^{2^-}$ dynamics for Fernow soils reveal that surface horizons are already saturated with respect to ambient conditions. Hence $SO_4^{2^-}$ may already be leaching from the surface horizons and creating a $SO_4^{2^-}$ front that moves down the soil profile as each subsequent horizon becomes saturated. Fe-oxides and Al-coated organic matter are the preferential sites for $SO_4^{2^-}$ adsorption, but under ambient solution concentrations, they are unable to adsorb additional $SO_4^{2^-}$ at all depths. Furthermore, many samples display a pH-dependency for adsorption; pH values above and below 4.0 were shown to hinder $SO_4^{2^-}$ adsorption due to the dissolution of Al or the loss of pH-dependent charge.

The following conclusions have been drawn concerning the overall status of Fernow soils:

- I. Fernow soils are inherently low in base cation reserves from the geochemical pool due to dominance by a sandstone parent material. Localized regions which overlie areas of shale residue do have greater base cation supplies.
- II. Organic matter and biochemical cycling should play a large role in the turn-over of base cations. Ca on the exchange complex is especially shown to be dependent on biochemical supplies. Mineralogical characterization reveals no significant geochemical source of Ca.
- III. Soils with more Ca-containing parent material will display a rapid loss of Ca and Mg as they react with H⁺. Conversely, soils dominated by siliceous sandstone parent material have slower release of cations.
- IV. Enhanced acidification is expected to result in greater cation release for all soils of the FEF. Siliceous soils may not necessarily be depleted sooner than siliceous-carbonaceous soils because the latter will be controlled by more rapid reactions that buffer H⁺. However, Al levels will certainly be higher in the effluent of the siliceous soils under enhanced weathering because of less buffering by Ca and Mg.
- V. The surface horizons of Fernow soils are saturated with $SO_4^{2^2}$ with respect to ambient conditions. Subsurface soils will adsorb $SO_4^{2^2}$ only at high input concentrations.

VI. Experiments with $SO_4^{2^-}$ desorption indicate that Fernow soils have little affinity for $SO_4^{2^-}$ retention throughout the profile. Decreases in atmospheric $SO_4^{2^-}$ inputs will accelerate leaching from the surface and result in greater base cation leaching as well. It is important to realize that this will be only the initial response while the surface soils attain a new equilibrium with atmospheric input concentrations. At that point, decreased input will be begin to be paralleled with decreased leaching of base cations. A $SO_4^{2^-}$ front will move down the profile as each subsequent horizon reaches equilibrium and becomes saturated. Hence, if base depletion occurs, it will be experienced first in the surface horizons.

Appendix A. Profile Descriptions for Investigative Soil Pits

Four soil pits were established within the research area of the Fernow Experimental Forest. The pits were described in the field and samples taken from each taxonomic horizon for site characterization purposes. Two of the pits, A and C, were selected for mineralogical analysis. Field descriptions for the four pits are presented here.

	Soil Pit A
Parent Material: Slope: Aspect:	Sandstone colluvium over McCrady shale residue 16% Southeast
	Oi 0-2.5 cm.
	A 2.5-20.3 cm, 20% coarse fragments, 6.4 YR 3/1, loam, very friable, many very fine to coarse roots, clear, wavy boundary.
	BA 20.3-33.0 cm, 25% coarse fragments, 7.5 YR 3/3, loam, friable, many very fine to coarse roots, clear, wavy boundary.
	Bw1 33.0-61.0 cm, 30% coarse fragments, 5 YR 5/4, silt loam, firm consistence, common very fine to medium roots, gradual, wavy boundary.
	Bw2 61.0-91.4 cm, 35% coarse fragments, 5 YR 4/3, silt loam, firm consistence, few very fine and fine roots, clear, wavy boundary.
	2C 91.4-134.6 cm, 45% coarse fragments, 2.5 YR 4/3, silty clay, massive structure, firm consistence, rare very fine to fine roots, clear, wavy boundary.
	2Cr 134.6-139.7 cm, 2.5 YR 5/6, firm consistence.

Soil Pit B

Parent Material:Sandstone ResiduumSlope:8%Aspect:Southeast

Oi 0-1.3 cm.

A1 1.3-6.3 cm, 45% coarse fragments, 7.5 YR 2.5/1, loam, very friable, many very fine to coarse roots, wavy boundary.

A2 6.3-16.5 cm, 35% coarse fragments, 7.5 YR 3/3, loam, very friable, many very fine to coarse roots, clear, wavy boundary.

BA 16.5-22.9 cm, 30% coarse fragments, 10 YR 4/4, silt loam, friable, many very fine to coarse roots, clear wavy boundary.

Bw1 22.9-50.8 cm, 35% coarse fragments, 10 YR 4/6, silt loam, friable, common very fine to coarse roots, gradual, wavy boundary.

Bw2 50.8-76.2 cm, 40% coarse fragments, 10 YR 5/6, silt loam, friable, common very fine to coarse roots, clear, wavy boundary.

Bw3 76.2-99.2 cm, 50% coarse fragments, 10 YR 5/6, loam, friable, few very fine and fine roots, gradual wavy boundary.

 ${\bm C}\,$ 99.2-139.7 cm, 70% coarse fragments, 10 YR 5/8, loam, firm consistence, few fine roots.

Soil Pit C

Parent Material:Sandstone ResiduumSlope:8%Aspect:Southeast

Oi 0-1.3 cm.

A 1.3-7.6 cm, 20% coarse fragments, 2.5Y 3/2, loam, very friable, many very fine to coarse roots, wavy boundary.

BA 7.6-17.8 cm, 20% coarse fragments, 10YR 3/4, loam, very friable, many very fine to coarse roots, clear wavy boundary.

Bw1 17.8-43.2 cm, 25% coarse fragments, 10YR 5/6, silt loam, friable, few very fine to coarse roots, clear wavy boundary.

Bw2 43.2-71.2 cm, 30% coarse fragments, 10YR 6/6, loam, friable, few very fine and medium roots, clear wavy boundary.

BC 71.2-86.4 cm, 40% coarse fragments, 10YR 6/6, loam, firm consistence, very few very fine and fine roots, gradual wavy boundary.

2C 86.4-114.3 cm, 55% coarse fragments, 10YR 6/8 (with inclusions of 10YR 5/3, 10YR 5/2), loam, firm consistence, clear wavy boundary.

Soil Pit D

Parent Material: Weathered Shale Slope: NA									
Aspect:	NA Southeast								
	Oi 0-2.5 cm.								
	A 2.5-12.7 cm, 20% coarse fragments, 10YR 3/1, loam, friable, many very fine to coarse roots, clear wavy boundary.								
	BA 12.7-22.9 cm, 25% coarse fragments, 2.5YR 4/3, loam, friable, many very fine to coarse roots, clear wavy boundary.								
	Bw1 22.9-73.7 cm, 35% coarse fragments, 10YR 5/6, silt loam, friable, common very fine to coarse roots, gradual wavy boundary.								
	Bw2 73.7-111.8 cm, 65% coarse fragments, 10YR 5/4 (with 10YR 7/2 and 6.5 YR 5/6), loam, very firm consistence, few very fine and fine roots, clear wavy boundary.								
	C 111.8-160.0 cm, 65% coarse fragments, 7.5 YR 5/6, loam with silt loam								

pockets, massive structure, firm consistence, no roots, clear wavy boundary.

Appendix B Data Tables

I TSP Plots										
pH										
Plot #										
	Water			KCI			CaCl			
	Depth 1	Depth 2	Depth 3	Depth 1	Depth 2	Depth 3	Depth 1	Depth 2	Depth 3	
1	4.58	4.47	4.37	3.75	3.95	3.98	3.86	4.04	3.93	
1	4.62	4.61	4.46	4.05	4.02	3.79	4.27	4.18	3.98	
1	3.99	4.45	4.4	3.64	4.02	3.99	3.69	4.06	3.98	
2	3.88	4.31	4.37	3.6	3.78	3.76	3.75	3.9	3.91	
2	4.24	4.5	4.45	3.83	4.05	3.95	3.96	4.11	3.91	
2	4.32	4.40	4.47	3.75	3.93	3.91	3.9	3.98	3.97	
3	4.15	4.32	4.03	3.59	3.9	4.03	3.61	3.90	4.09	
3	4.29	4.47	3.03	3.91	3.90	3.03	4.02	4.03	3.95	
3	4.43	4.04	4.09	3.90	4.10	4.09	4.07	4.Z	4.10	
4	4.04	4.09	4.00	4.10	4.21	3.80	4.3	4.57	4.2	
4	4.07	4.75	4.40	4.05 4.00	4.07	3.09	4.14 12	4.14 <u>/</u> 11	4.03	
5	4.07	5 02	4 47	4.09 4.10	1 NF	4 15	-т.2 Д 11	4 1 R	4 16	
5	4 43	4.56	4 73	4 19	4.00	4.10	4 11	4.10	4.10	
5	4 43	4 62	4 46	4 19	4 12	4 01	4 11	4 18	4 67	
6	4.5	4.36	4.28	3.92	4.09	3.94	3.72	3.97	3.87	
6	4.46	4.47	4.32	3.99	4.15	3.98	4	4.07	3.87	
6	4.39	4.48	4.51	4.12	4.1	3.96	4.07	4.04	3.89	
7	4.05	4.42	4.67	3.74	3.87	4.02	3.86	3.83	3.8	
7	4.21	4.51	4.5	4.08	4.08	4	3.96	4.11	3.91	
7	4.2	4.35	4.33	3.86	4	3.81	3.91	3.99	4	
8	4.12	4.24	4.94	3.49	3.87	3.69	3.61	3.8	3.69	
8	3.91	4.23	4.53	3.35	3.95	3.91	3.29	3.83	3.91	
8	4.16	4.46	4.96	3.5	3.99	4.06	3.53	3.95	4.06	
g	4	4.21	4.27	3.7	3.92	3.91	3.77	3.88	3.91	
9	4.41	4.25	4.36	3.75	4.01	4.03	3.89	3.87	4.03	
g	4.11	4.66	4.44	3.69	3.91	3.86	3.75	3.91	3.86	
10	4.39	4.51	4.29	3.82	4.07	3.82	3.69	4.03	3.82	
10	4.2	4.37	4.49	3.98	4.09	4.05	3.94	4.01	4.05	
11	3.01	4.44	4.30	3.52	4.00	4.04	3.00	4.02	2 99	
11	4.30	4.41	4.55	4.12	4.09	3.92	3.95	1 03	3.00	
11	4.22	4.51	4.03	3.84	4 01	3.05	3.0	3 07	3.00	
12	3.92	4 28	4 29	3.59	3.85	3.95	3.58	3.86	3.88	
12	4.47	4.69	4.72	3.85	3.81	5.1	3.92	3.91	3.74	
12	4.42	4.43	4.59	3.81	3.81	3.85	3.85	4.07	3.9	
13	4.24	4.68	4.31	3.65	3.96	3.86	3.69	4.06	3.78	
13	4.3	4.38	4.64	3.73	4.02	3.91	3.67	3.99	3.96	
13	4.3	4.52	4.64	3.73	4.14	3.91	3.67	4.08	3.96	
14	4.3	4.15	4.52	3.69	3.73	3.93	3.81	3.73	3.91	
14	4.48	4.56	4.42	3.89	3.87	3.89	3.84	3.86	3.98	
14	4.13	4.38	4.44	6.54	3.78	3.74	3.76	3.94	3.8	
15	4.01	4.49	4.83	3.65	4.03	3.72	3.62	4.03	4.01	
15	4.47	4.53	4.46	3.97	4	3.9	3.82	4	3.92	
15	3.94	4.47	4.31	3.59	4.13	4.04	3.66	4.09	4.04	
16	4.75	4./1	4.91	5.13	3.68	3.85	3.87	3.77	4.17	
16	4.44	4.42	4.54	3.91	3.83	3.79	3.97	3.82	3.73	
16	4.97	4.80	4.8	4.11	4.07	4.23	4.17	4.12	4.22	

LTSP Plots							
% C							
Plot #	Depth 1	Depth 2	Depth3	Plot #	Depth 1	Depth 2	Depth3
1	7.8	2.41	0.65	9	7.75	2.55	1.25
1	7.21	2.35	0.61	9	7.98	2.61	1.18
1	10.31	3.08	1.25	9	5.35	2.44	1.22
1	10.7	3.31	1.29	9	5.3	2.58	1.32
1	7.39	2.84	1.06	9	4.13	1.36	0.63
1	7.38	2.92	1.08	9	3.99	1.43	0.66
2	5.89	3.5	1.29	10	8.09	2.63	1.09
2	5.27	3.35	1.34	10	7.6	2.73	1.12
2	9.83	4.72	1.31	10	5.31	2.26	0.88
2	9.81	4.75	1.29	10	5.55	2.33	0.81
2	3.83	1.87	1.34	10	7.03	3.24	1.24
2	3.9	2 40	1.33	10	7.12	3.09	1.22
3	6.0	3.40	1.04	11	4.23	1.03	0.03
	0.49	4.04	0.03	11	4.34	3.07	0.70
	3 3 3 2	1.07	0.33	11	6 55	2.86	1.15
3	12 35	5.85	2 18	11	5 45	2.00	0.99
3	12.00	5.74	2.28	11	5.27	2.37	1.04
4	8.45	3.57	1.42	12	5.45	3.15	1.13
4	8.87	3.57	1.41	12	5.36	3.36	1.2
4	6.18	2.65	0.8	12	4.24	1.72	0.71
4	6.15	2.54	0.93	12	4.26	1.71	0.69
4	4.65	1.42	0.71	12	4.83	1.95	0.69
4	4.63	1.38	0.71	12	4.87	1.86	0.69
5	6.18	2.31	1.14	13	4.3	2.32	0.7
5	6.35	2.33	1.11	13	4.29	2.22	0.7
5	6.35	2.69	1.48	13	4.29	1.62	0.5
5	6.35	2.8	1.47	13	4.29	1.45	0.45
5	6.35	3.11	1.38	13	4.63	1.32	0.45
5	6.35	3.14	1.4	13	4.46	1.38	0.45
6	5.81	2.23	0.91	14	4.02	1.31	0.67
6	5.97 8 9.07	2.10	0.9	14	3.91	1.2	0.00
6	8 18	2.43	0.07	14	3 01	2.5	1.52
6	7 65	2.58	1.06	14	3.86	1.58	0.69
6	7.59	2.59	0.95	14	3.73	1.68	0.67
7	5.72	2.47	1.42	15	4.99	2.45	1.54
7	5.82	2.51	1.47	15	4.95	2.4	1.64
7	8.26	2.77	0.77	15	4.2	1.82	0.85
7	9.47	2.85	0.73	15	4.28	1.81	0.82
7	6.23	1.91	0.64	15	9.18	3.43	1.14
7	6.12	1.78	0.64	15	8.97	3.34	1.12
8	10.71	3.36	0.75	16	7.88	4.68	1.78
8	10.03	3.32	0.73	16	7.94	4.64	1.66
8	10.87	3.64	1.06	16	5.25	1.95	0.72
8	9.68	3.44	1.08	16	5	1.97	0.7
8	6.7	1.79	1.77	16	16.32	8.32	3.72
8	6.69	1.95	2	16	16.26	8.47	3.88
	1						

LTSP Plots									
Base Cations, cmol+/	Kg								
		•							
Plot #									
	Ca	Danth 0	Danth 0	Mg Danth 1	Danth O	Danth 0	K Danth 1	Danth O	Danth 0
1		Depth 2		Depth 1			Depth 1	Depth 2	Depth 3
1	0.78	0.21	0.13	0.21	0.04	0.02	0.40	0.20	0.12
1	2 33	0.20	0.14	0.13	0.04	0.04	0.40	0.13	0.13
1	2.56	0.49	0.33	0.49	0.00	0.00	0.58	0.27	0.10
1	0.25	0.13	0.13	0.14	0.04	0.04	0.31	0.14	0.10
1	0.24	0.24	0.30	0.14	0.06	0.06	0.33	0.15	0.12
2	0.70	0.29	0.28	0.16	0.06	0.04	0.31	0.19	0.10
2	0.63	0.31	0.25	0.14	0.06	0.04	0.31	0.17	0.12
2	0.69	0.24	0.19	0.25	0.08	0.04	0.58	0.27	0.17
2	0.68	0.19	0.13	0.25	0.08	0.04	0.54	0.30	0.31
2	0.54	0.19	0.18	0.12	0.06	0.06	0.28	0.19	0.17
2	0.50	0.24	0.16	0.10	0.06	0.04	0.29	0.20	0.18
3	0.73	0.25	0.15	0.16	0.04	0.02	0.30	0.13	0.06
3	0.76	0.23	0.18	0.14	0.06	0.04	0.32	0.13	0.06
3	0.25	0.20	0.13	0.08	0.04	0.02	0.25	0.07	0.13
3	0.28	0.14	0.13	0.06	0.06	0.02	0.25	0.08	0.07
3	0.71	0.26	0.16	0.25	0.10	0.04	0.59	0.24	0.12
3	0.73	0.26	0.19	0.29	0.10	0.06	0.54	0.22	0.11
4	2.90	0.49	0.41	0.45	0.06	0.10	0.53	0.14	0.06
4	2.70	0.51	0.40	0.47	0.12	0.19	0.52	0.10	0.07
4	2.23	0.70	0.01	0.31	0.12	0.19	0.30	0.11	0.08
4	0.83	0.75	0.03	0.31	0.00	0.10	0.31	0.12	0.08
- 4	0.00	0.00	0.40	0.10	0.00	0.10	0.23	0.00	0.00
5	0.34	0.00	0.00	0.00	0.10	0.02	0.19	0.07	0.00
5	0.36	0.11	0.09	0.12	0.04	0.02	0.20	0.06	0.03
5	0.26	0.14	0.14	0.04	0.02	0.14	0.00	0.07	0.06
5	0.28	0.14	0.13	0.04	0.02	0.14	0.00	0.07	0.04
5	0.31	0.15	0.11	0.04	0.04	0.02	0.00	0.08	0.04
5	0.30	0.18	0.13	0.04	0.04	0.14	0.00	0.09	0.05
6	0.35	0.08	0.10	0.14	0.02	0.02	0.29	0.13	0.09
6	0.35	0.09	0.10	0.14	0.04	0.02	0.30	0.13	0.10
6	0.60	0.15	0.19	0.21	0.04	0.04	0.33	0.13	0.09
6	0.64	0.13	0.19	0.21	0.04	0.04	0.34	0.13	0.10
6	0.53	0.13	0.10	0.19	0.04	0.02	0.31	0.14	0.08
6	0.51	0.13	0.10	0.19	0.04	0.04	0.32	0.14	0.10
/	0.40	0.15	0.13	0.12	0.04	0.04	0.29	0.13	0.09
1	0.38	0.14	0.14	0.12	0.02	0.02	0.30	0.13	0.10
7	0.01	0.14	0.10	0.23	0.04	0.02	0.33	0.13	0.09
7	0.00	0.14	0.10	0.23	0.04	0.02	0.34	0.13	0.10
7	0.50	0.14	0.11	0.10	0.04	0.02	0.31	0.14	0.00
8	1.19	0.19	0.04	0.31	0.02	0.02	0.51	0.20	0.10
8	1.16	0.19	0.05	0.29	0.06	0.02	0.51	0.19	0.10
8	0.51	0.09	0.06	0.21	0.04	0.02	0.35	0.13	0.08
8	0.53	0.08	0.05	0.21	0.04	0.02	0.34	0.13	0.08
8	0.65	0.08	0.13	0.23	0.04	0.04	0.36	0.13	0.17
8	0.60	0.08	0.14	0.23	0.04	0.04	0.38	0.13	0.18
9	0.51	0.13	0.11	0.19	0.04	0.02	0.32	0.13	0.11
9	0.53	0.14	0.11	0.19	0.04	0.02	0.31	0.12	0.11
9	0.26	0.10	0.14	0.10	0.02	0.04	0.26	0.09	0.10
9	0.26	0.10	0.14	0.10	0.04	0.04	0.26	0.10	0.10
9	0.38	0.14	0.14	0.12	0.04	0.04	0.26	0.14	0.12
9	0.38	0.14	0.14	0.12	0.04	0.04	0.26	0.14	0.12
10	0.26	0.08	0.04	0.14	0.04	0.02	0.36	0.15	0.10
10	0.26	0.06	0.05	0.14	0.02	0.02	0.36	0.15	0.09

10	0.23	0.05	0.06	0.12	0.04	0.02	0.31	0.15	0.12
10	0.23	0.06	0.06	0.10	0.04	0.02	0.29	0.13	0.12
10	0.26	0.05	0.04	0.14	0.02	0.02	0.30	0.13	0.11
10	0.28	0.05	0.05	0.14	0.02	0.02	0.29	0.10	0.11
11	0.20	0.08	0.05	0.08	0.08	0.02	0.36	0.15	0.10
11	0.18	0.08	0.05	0.08	0.08	0.02	0.36	0.15	0.09
11	0.26	0.06	0.05	0.16	0.08	0.02	0.31	0.15	0.12
11	0.19	0.06	0.05	0.16	0.06	0.02	0.29	0.13	0.12
11	0.23	0.08	0.04	0.14	0.06	0.02	0.30	0.13	0.11
11	0.24	0.06	0.04	0.14	0.08	0.02	0.29	0.10	0.11
12	0.26	0.10	0.05	0.14	0.08	0.06	0.29	0.18	0.12
12	0.26	0.10	0.05	0.14	0.10	0.06	0.28	0.19	0.10
12	0.28	0.11	0.04	0.16	0.12	0.02	0.28	0.15	0.10
12	0.26	0.10	0.05	0.14	0.12	0.02	0.26	0.15	0.10
12	0.24	0.09	0.04	0.16	0.08	0.02	0.33	0.13	0.08
12	0.26	0.09	0.04	0.16	0.08	0.02	0.31	0.13	0.09
13	0.28	0.10	0.05	0.16	0.10	0.02	0.32	0.18	0.10
13	0.26	0.11	0.05	0.19	0.10	0.02	0.32	0.18	0.10
13	0.28	0.10	0.04	0.16	0.08	0.02	0.31	0.18	0.20
13	0.28	0.10	0.05	0.19	0.08	0.02	0.32	0.19	0.20
13	0.24	0.11	0.04	0.19	0.06	0.02	0.29	0.18	0.20
13	0.24	0.10	0.05	0.19	0.08	0.02	0.28	0.18	0.20
14	0.27	0.15	0.08	0.19	0.10	0.02	0.32	0.18	0.10
14	0.24	0.15	0.08	0.19	0.10	0.02	0.32	0.18	0.10
14	0.19	0.19	0.09	0.19	0.12	0.04	0.31	0.18	0.20
14	0.29	0.17	0.08	0.19	0.10	0.02	0.32	0.19	0.20
14	0.25	0.20	0.08	0.16	0.08	0.02	0.29	0.18	0.20
14	0.32	0.15	0.09	0.16	0.10	0.04	0.28	0.18	0.20
15	0.26	0.10	0.08	0.23	0.14	0.06	0.32	0.19	0.11
15	0.26	0.10	0.08	0.23	0.14	0.06	0.32	0.19	0.11
15	0.28	0.11	0.09	0.25	0.14	0.04	0.32	0.18	0.12
15	0.28	0.11	0.08	0.23	0.14	0.04	0.32	0.18	0.12
15	0.26	0.11	0.08	0.23	0.12	0.04	0.32	0.19	0.11
15	0.26	0.11	0.09	0.23	0.14	0.04	0.32	0.18	0.11
16	0.29	0.20	0.10	0.23	0.19	0.08	0.49	0.27	0.20
16	0.29	0.20	0.10	0.25	0.19	0.10	0.47	0.30	0.19
16	0.31	0.15	0.08	0.25	0.16	0.10	0.35	0.13	0.08
16	0.31	0.15	0.10	0.25	0.16	0.10	0.37	0.12	0.12
16	0.30	0.18	0.09	0.27	0.14	0.12	0.69	0.39	0.17
16	0.29	0.19	0.08	0.25	0.19	0.12	0.69	0.40	0.17

LTSP Plots							
TEA Acidity, cmol+/Kg	1						
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Plot #	Depth 1	Depth 2	Depth 3	Plot #	Depth 1	Depth 2	Depth 3
1	22.50	15.67	9.24	9	30.13	16.81	11.48
1	33.34	16.07	6.43	9	28.46	14.76	11.07
1	33.34	19.28	10.85	9	21.12	13.94	8.20
1	36.56	19.68	12.45	9	20.71	14.35	9.02
1	31.33	17.67	9.64	9	26.31	12.30	11.89
1	32.14	18.48	9.64	9	26.54	11.89	11.07
2	28.92	22.50	18.88	10	35.52	19.44	15.46
2	29.73	23.30	17.68	10	36.37	18.57	16.23
2	43.39	26.92	17.68	10	26.78	17.22	10.55
2	42.98	27.32	16.87	10	27.62	16.40	10.96
2	20.89	15.67	15.67	10	33.41	18.22	11.89
2	20.89	15.27	16.07	10	34.67	16.98	11.89
3	37.76	24.50	14.86	11	21.54	12.30	13.12
3	38.16	24.50	13.26	11	30.02	16.57	22.64
3	22.90	16.47	13.26	11	28.75	16.15	11.89
3	22.90	16.47	21.29	11	27.17	16.15	13.25
3	47.40	31.33	19.28	11	23.85	15.74	14.08
3	49.01	32.54	19.50	11	12.71	12.30	14.08
4	38.57	49.01	40.57	12	24.69	6.70	8.52
4	37.36	39.81	40.98	12	25.53	6.28	8.93
4	31.74	44.59	32.54	12	21.34	14.08	11.07
4	31.74	45.39	36.96	12	21.34	13.67	10.66
4	28.52	39.17	25.31	12	22.18	10.25	6.97
4	29.33	39.77	30.93	12	21.34	10.25	7.38
5	29.29	15.48	11.48	13	20.92	14.76	6.10
5	29.71	15.06	10.25	13	20.92	15.17	6.20
5	28.51	16.81	11.89	13	21.58	10.66	6.90
5	27.93	15.58	10.25	13	22.11	6.97	6.09
5	26.34	17.22	11.89	13	22.15	17.04	5.86
5	25.98	17.22	11.07	13	23.08	15.01	5.46
6	34.48	18.67	15.92	14	17.30	18.64	7.79
6	33.20	21.26	19.60	14	18.13	19.05	7.38
6	40.86	22.51	15.92	14	17.99	17.81	12.01
6	39.59	21.26	17.15	14	17.99	16.98	13.25
6	30.65	22.05	15.92	14	20.09	16.90	9.02
6	30.65	16.95	11.02	14	19.68	17.10	10.25
7	22.60	12.84	11.48	15	28.12	16.47	14.46
7	22.60	12.84	11.07	15	28.12	16.47	14.46
7	31.71	15.06	8.20	15	22.50	13.26	11.25
7	31.71	15.06	8.61	15	21.69	12.86	11.25
7	24.72	13.68	8.52	15	33.74	19.68	12.05
7	24.72	12.80	8.52	15	36.96	19.28	12.45
י א	24.19	16.89	7.38	16	19.68	18.88	11.65
с я	24.62	17.30	6 15	16	25.31	10.00	10.04
R R	27.91	15 74	8 46	16	20.89	10.44	10.04
с я	27.91	16.57	7 19	16	20.00	30.93	16.87
R R	20.20	9 11	8 20	16	33 34	29.73	17 27
8	21.95	9,11	8.61	16	36.15	12.45	17.27

Vita Mary Gilchrist Lusk

Mary Gilchrist Lusk was born in Charlotte, North Carolina on August 24, 1972 and developed an early appreciation for agriculture on her uncle's dairy farm, where she often spent her summer vacations. She entered the University of North Carolina in 1990 as a student in broadcast communications but soon realized a stronger desire to pursue agricultural research. After only one year at UNC, she transferred to Brigham Young University in January 1992 and received a Bachelor of Science Degree in Agronomy from there in August 1994. While at BYU, Mary focused on the environmental aspects of agricultural production and was involved in specific research on the environmental fate and transport of the pesticide atrizine.

Upon graduation from BYU, she immediately began work at the Ciba-Giegy Corporation's Environmental Technology Center in Greensboro, North Carolina. While at Ciba, she studied the chemical degradation potential in soils of toxic hydrocarbons from polluted sites. The research was the basis for later development by Ciba of innovative technologies for the remediation of hazardous wastes in soil and groundwater.

Mary entered Virginia Tech in August 1995 as a graduate teaching assistant in the Department of Crop and Soil Environmental Science. Her work at Virginia Tech has focused on nutrient dynamics of an Appalachian forest soil under high levels of atmospheric acidic input. She completed her Master of Science in Soil Science in January 1998 and continues as a teaching assistant in the department's soil science program.