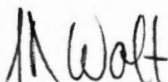


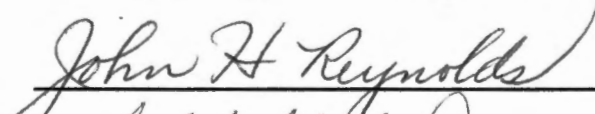
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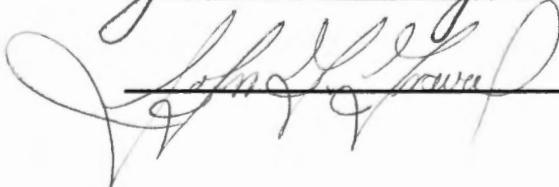
I am submitting herewith a thesis written by Guy Wesley Haun entitled "Soil Solution Composition and Orchardgrass Germination as Influenced by Simulated Acid Rain in a Field Environment." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Science.



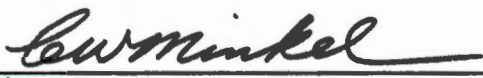
J. D. Wolt, Major Professor

We have read this thesis
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Vice Provost
and Dean of The Graduate School

SOIL SOLUTION COMPOSITION AND ORCHARDGRASS GERMINATION
AS INFLUENCED BY SIMULATED ACID RAIN IN A
FIELD ENVIRONMENT

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Guy Wesley Haun

March 1987

AG-VET-MED.

Thesis

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ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to those individuals providing various contributions to the completion of this thesis.

The Plant and Soil Science Department (Dr. John Foss, Head) for providing financial support and field and laboratory facilities for this research project.

The contributions of my major professor, Dr. Jeffrey D. Wolt served to improve this manuscript. His patience, assistance, and advice has been greatly appreciated. His knowledge of the subject matter and willingness to help has earned my respect as a professional and as a friend.

Dr. John Reynolds and Dr. John Graveel provided assistance, advice, and constructive criticisms which added significantly to this investigation while serving as members of my graduate committee.

Several other individuals were involved throughout the course of this study:

Mr. David Walker for his technical advice and assistance in maintenance of experimental plots and in collection, preparation, and analysis.

Mrs. Cynthia Campbell, Mrs. Zoellen Smith, Dr. Kien Luu, and Mr. Tony Jenkins for their assistance during various aspects of this research project.

Dr. David Hammer for his technical advice and encouragement throughout my graduate program.

Dr. David Coffey and Mr. Brian Pennell for assistance with computer graphics. Dr. Robert D. von Bernuth and Mr. Earl Vories with the Agricultural Engineering Department for assistance in the physical characterization of simulated rainfall.

Fellow graduate students for their friendship and encouragement during my graduate studies. I thank Mrs. Teresa Herring for typing this manuscript.

I must thank my parents Mr. and Mrs. Glen T. Haun and sister Rosa, for their continued interest and encouragement. I am grateful to my wife, Earlene, for her love, patience, and support throughout this educational venture.

Finally, it was through the love and grace provided by my Lord and Savior Jesus Christ which permitted this research endeavor to be successful.

ABSTRACT

Alteration of surface soil chemistry by acid rain may influence establishment of small seeded forage grasses. Orchardgrass (Dactylis glomerata L.) germination was monitored concurrently with application of simulated acid rainfall applied at 0.46 cm per event on Etowah silt loam (Typic Paleudults) and Statler variant sandy loam (Humic Hapludults) surface soils. Ambient rainfall was not excluded from the experiment which received five rainfall events totaling 6.4 cm (avg. pH 4.28) throughout the 29-day duration of the study. The range of simulated rainfall selected (pH 4.3 to 2.5) had been identified as the region of maximum biological response in previous controlled environment studies.

Orchardgrass germination was differentially influenced by rainfall pH over time after initiation of simulated rainfall treatments. Germination was significantly affected by rainfall pH on six of sixteen counting dates. Increasing rainfall acidity stimulated more rapid onset of germination and resulted in higher total percent germination on both soils throughout the

ment. Responses were indicative of an interactive effect of rainfall composition on biological response of seeds and seedlings.

Surface soil samples were collected from all test plots to a 1.5 cm depth and soil solutions obtained by vacuum displacement. Soil solutions were analyzed for pH, EC, Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al^{3+} , NH_4^+ , Cl^- , NO_3^- and SO_4^{2-} . Soil solution pH decreased and EC increased with increasing acidity of simulated rainfall. Generally, increasingly acid rainfall resulted in linear (sometimes quadratic) increases in cation and anion components of soil solution with the exception of Al^{3+} , Na^+ , and NH_4^+ . Effects of soil series (Etowah vs. Statler) were significant except for Al^{3+} , Ca^{2+} , and Cl^- , but the rainfall pH by soil interaction was seldom significant with Al^{3+} and Na^+ being exceptions. Calcium activity increased slightly while Al^{3+} activity increased markedly with decreased rainfall pH, resulting in decreased Ca^{2+} : Al^{3+} mol ratios with decreasing pH of simulated rainfall. Several subtle changes occurred within the soil solution following additions of acid rain, but no association between orchardgrass germination responses and soil solution changes was apparent.

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CHAPTER 1

INTRODUCTION

Acid deposition is generally considered a serious environmental problem of anthropogenic origin (Krug and Frink, 1983). Beginning in the mid 1950's, published data indicated lower than expected levels of precipitation acidity in western Europe and the eastern United States (Fisher et al., 1968; Likens et al., 1972). From 1955 to 1984, increasingly acidic deposition was observed for the northeastern United States, with the occurrence of acid deposition moving progressively southward with time (Gorham, et al., 1984; Haines, 1979).

Acidic deposition has been postulated to damage terrestrial and aquatic life as an indirect result of acid-induced soil chemical changes (Bloom and Grigal, 1985; Cosby et al., 1985; Environ. Res. Ltd., 1983; McFee et al., 1983; Norton, 1977; Reuss, 1980; Reuss and Johnson, 1985). Various investigators have reported that forest and aquatic ecosystems are more sensitive to acidic deposition than is the agricultural ecosystem.

This has been attributed to low supply of weatherable minerals, reduced nutrient supply, and aluminum (Al) buffering present in watersheds of most susceptible reservoirs and in most forest soil systems (McFee et al., 1983; Voigt, 1980). Most research concerning adverse terrestrial affects of acidic deposition has, therefore, centered on the forest ecosystem.

Research to date concerning acid deposition effects on agricultural soils has been limited, and for the most part only gross measures of soil chemical composition (i.e., cation exchange capacity (CEC), base saturation, pH, and extractable nutrients) have been evaluated. In contrast, current investigation of acid deposition impacts on forest soils centers on subtle changes in soil solution composition such as: the soil calcium (Ca) and (Al) exchange complex (Reuss, 1983), organic matter mineralization (Foy, 1984; Voigt, 1980), and nutrient (N and S) cycling within the forest soil system (Hern et al., 1985; Olson, 1983). It appears reasonable that consideration of soil solution composition in agricultural soils may give information on more subtle changes in soil properties as influenced by acid rainfall. This could be particularly true with regard to evaluation of

the impact of acidic deposition on soils supporting low management hay and pasture crops.

This research project was conducted with orchardgrass (Dactylis glomerata L.) cultivar 'Potomac' and evaluated whether short-term changes in soil solution composition resulting from simulated acid rain influenced germination. The null hypotheses (H_0) proposed for this investigation were:

- (1) There are no changes in soil solution composition following application of simulated acid rainfall of varied pH in a field environment.
- (2) Simulated acid rainfall has no effect on orchardgrass germination.

The objectives established for this project were:

- (1) Determination of changes occurring in soil solution with short-term (less than 30-days) application of ambient and simulated acid rain.
- (2) Determination of the effect of simulated acid rain on orchardgrass germination.

CHAPTER II

LITERATURE REVIEW

1. OVERVIEW OF THE ACID DEPOSITION PHENOMENON

Acid deposition can be defined as all acidifying atmospheric components, both wetfall and dryfall, having a $\text{pH} < 5.6$. In more generalized terms, "acid rain" or "acid precipitation" are often used in place of acid deposition, but these terms can be misleading. Precipitation (wetfall) includes any state of water which condenses and falls to the earth's surface, while atmospheric deposition refers to both dry deposition (particulate matter and gases) and precipitation that falls to the earth's surface (Fowler, 1980; Cowling and Linthrust, 1981; Record et al., 1982).

The most common chemical measurement utilized in evaluating precipitation acidity is pH. The pH value is equal to the negative logarithm of hydrogen ion (H^+) activity. Since pH is based on a logarithmic scale, a one unit change in pH represents a ten-fold change in the H^+ activity. Most researchers are in agreement that natural rainwater in equilibrium with atmospheric carbon dioxide at ambient pressure and temperature forms a

dilute solution of carbonic acid (H_2CO_3) with an average pH 5.6. Therefore, acid deposition is considered to be deposition with pH < 5.6 (Cowling and Linthurst, 1981).

Acid deposition occurs at varying degrees in most areas of the world. Eastern North America and western Europe seem to be the most affected areas. These regions are located downwind of highly industrialized regions and tend to have soils with lower geochemical ability to buffer external acidic additions (Calvert, 1983). The lower geochemical activity has been attributed to very low amount of soil formation situated over predominately granite bedrock which has limited buffering capacity, very low organic matter content, and low clay content (Pratt, 1983; Cowling and Linthurst, 1981; McFee et al., 1977).

Atmospheric deposition with pH < 4.9 has been reported throughout much of the eastern United States (Cogbill and Likens, 1974; Evans, 1982; Frohlinger and Kane, 1975). Atmospheric deposition in eastern North America and western Europe is acidified by two major contributors: (1) strong mineral acids, predominantly sulfuric acid (H_2SO_4) and nitric acid (HNO_3) of anthropogenic origin (Charlson and Rodhe, 1982; van Breeman et al., 1984; Galloway et al., 1976) and (2) weak organic

acids from natural environmental processes (Frohlinger and Kane, 1975; Galloway et al., 1976),

Various anthropogenic sources may alter the acidity of atmospheric deposition. The major sources have been utility and industrial companies which burn coal, oil, and gas. Combustion of these products releases nitrogen oxides (NO_x), sulfur oxides (SO_x), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl).

It has been estimated that approximately 90% of the SO_x in the atmosphere results from emissions from industrial and electrical utilities (Homolya, 1983). Sulfate (SO_4) emissions are primarily from combustion of coal and oil. Coal combustion contributes the greatest amount of HCl . Nitrogen oxides are emitted into the atmosphere primarily from electric utilities and the transportation industry, which contribute 35% and 43% of the total, respectively (Record et al., 1982).

Charlson and Rodhe (1982) and Olson (1983) concluded that an in-depth evaluation of man-made acidification would require consideration of the nitrogen (N) and sulfur (S) cycles which naturally influence atmospheric acidity. Geophysical sources (volcanos, sea spray) release SO_4^{2-} salts, sea salts, organic chlorides, and gaseous compounds (SO_2 , H_2S , CO_2 , SO_4^{2-} ,

H_2SO_4 , NaCl , and CH_3Cl) which can contribute to the natural acidity of atmospheric deposition (Robinson, 1983). Nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), and ammonia (NH_3) are the major forms of nitrogen in the atmosphere. Geochemical reactions (natural soil reactions) and fertilizer nitrate amendments contribute significant levels of NO_2 to the atmosphere (Nelson and Bremner, 1970; Thomas and Hargrove, 1984). All of the nitrogen forms except NH_3 can lower the pH of atmospheric deposition, whereas NH_3 reacts as a base.

Hydrogen ion (H^+) concentration in precipitation from remote areas of North America was found to be controlled by different combinations of acids and bases than that in eastern North America. In remote areas precipitation was found to contain mainly weak acids most of which are thought to be organic acids (Galloway et al., 1984; Frohlinger and Kane, 1975). Significant percentages (10-35%) of organic acids have been reported in atmospheric deposition in the northeastern United States (Cronan and Schofield, 1979; Galloway et al., 1976; Galloway et al., 1984). Measurements by Frohlinger and Kane (1975) indicated that weak organic acids were sometimes present and accounted for > 50% of

the total acidity in rainwater sampled in suburban Pennsylvania. Galloway et al. (1976) identified several weak organic acids (acetic, butyric, formic, succinic, glycolic, propionic, and isocitric) in precipitation collected in New York and New Hampshire. The principal source of atmospheric organic acids is considered to be decomposition of organic matter.

Ecologically, the strong mineral acids probably have a more consequential effect upon precipitation acidity than the weak organic acids (Likens and Bormann, 1974).

2. GENERAL EFFECTS ON NATURAL ECOSYSTEMS

A. Aquatic Ecosystem

Freshwater aquatic ecosystems are potentially the environmental component most susceptible to acid deposition perturbation (Burton, et al., 1982). The susceptibility of an aquatic ecosystem to acidic deposition is a function of climate, geologic, topographic, morphologic, biotic, and anthropogenic factors (Gorham and McFee, 1980). The above factors determine the volume and content of drainage water from soil systems which enters aquatic systems through their control of temperature, humidity, ratio of precipitation to evapo-

ration, activity of living organisms, and the soils ability to buffer acidic additions (Gorham and McFee, 1980).

Fresh water lakes and streams in some areas are very sensitive to acidic inputs (Hagen and Langeland, 1973). The extent of the effects from direct and indirect inputs on water chemistry depends on the buffering capacity of the watershed, reservoir, and its tributaries (Cowling and Linthurst, 1981). The buffering capacity of a body of water is controlled by bedrock and soil within the watershed (Hagen and Langeland, 1973). The ionic forms of metals present in lakes and streams are transformed by changes in pH levels (Cowling and Linthurst, 1981). Acid deposition in conjunction with natural processes of mineral weathering and water movement through a soil with $\text{pH} < 5.0$ may result in increased mobility of Al, mercury (Hg) and manganese (Mn). Elevated concentrations of these elements are very toxic to fish and other aquatic life (Cowling and Linthurst, 1981; Burton et al., 1982; Cronan and Schofield, 1979).

Fish, especially eggs and fry, are very sensitive to pH changes. Biotic effects on fish populations have been given major priority in evaluating the negative

impacts of acidic deposition on aquatic ecosystems (Hagen and Langeland, 1973). The reader is encouraged to refer to the following publications for more in-depth information concerning acidic deposition and aquatic ecosystems: Baker et al., 1985; Goldstein et al., 1985; Kwain and Rose, 1985; Sharpe et al., 1984; Van Der Putte and Brinkhorst, 1985.

B. Terrestrial Ecosystem

Aquatic and terrestrial ecosystems interact and support each other such that any affects of acid deposition on the aquatic ecosystem should be evaluated within the context of affects on vegetation, soils and geology of the terrestrial ecosystem (Cowling and Linthurst, 1981). The vegetation canopy acts as an interceptor and sink for atmospheric deposition (Lindberg et al., 1982; Miller, 1984). Vegetation response to acid rainfall depends on factors such as exposure time, acid content, size of rain drops, rainfall intensity, and environmental conditions prior to and following exposure to acidic rainfall (Irving, 1983a).

Previous investigators have reported various conclusions concerning vegetation interaction with acid deposition, predominately wetfall. MacDonald et al.,

(1986) conducted an investigation to evaluate simulated acid rain (pH 2.0-4.7) effects on jack pine (Pinus banksiana Lamb.) seedling development in a greenhouse environment. Germination was greatly reduced and the mortality of those which germinated was > 95% at pH 2.0. Root weight decreased and vegetative weight increased at pH 2.5. There were no adverse effects on germination and seedling establishment at pH > 3.0.

Visible injury to soybean (Glycine max L.) and pin oak (Quercus palustris L.) foliage was observed as chlorosis and necrotic lesions (Evans and Curry, 1979). Damage to the leaf surface cells resulted in increased nutrient loss, although some nutrient leaching is normal and serves an important role in the nutrient cycle (Jacobson, 1980; Miller, 1984). There have been varied responses reported in growth and yield of plants subjected to simulated acidic precipitation (Evans and Lewin, 1981; Jacobson, 1980). Evans et al., (1977) found that leaf morphology and surface characteristics were important features which influence acid deposition effects on plants. Some of the direct effects of acidic deposition were a function of soil nutrient supply, plant nutrient requirements, plant growth stage

(Lindberg et al., 1982) and concentration of H^+ , SO_4^{2-} , and NO_3^- ions in deposition (Irving, 1983b).

More specific information concerning interactions between the terrestrial ecosystem and acidic deposition may be obtained from: Amthor, 1984; Chen et al., 1985; Craker and Bernstein, 1984; Evans et al., 1985; Reich et al., 1986.

3. AGRICULTURAL ECOSYSTEMS

Concern has increased steadily over the last ten years regarding the potential negative impact of acid deposition on agricultural crop production. Most research to date with agricultural crops has been with simulated acidic rainfall under greenhouse conditions, with limited field work. Crop damage has been reported as a direct and indirect result of simulated acid precipitation, although, very little if any economic loss has been sustained from acidic deposition (Cowling and Linthurst, 1981).

Lee et al. (1981) conducted an investigation utilizing greenhouse and field growth chamber facilities with twenty eight crops. Simulated acid rainfall (pH 5.6 to 3.0) inhibited growth of five crops and stimulated growth of six crops. No consistent effects were observed for the seventeen other crops. It was found that

foliar injury was not always directly related to crop yields (Banwart, 1985; Irving and Miller, 1981; Lee et al., 1981). Visible injury (necrotic lesions) was detected on the youngest leaves of soybean subjected to simulated acidic rain at pH 3.0 in a growth chamber environment. Only small areas of the leaves (< 1%) were affected with no adverse effect on growth or yield (Irving and Miller, 1981).

Several researchers have reported varied yield response of soybean to simulated acidic rainfall. Banwart (1985) revealed yield increases and yield decreases in various soybean cultivars. 'Essex' and 'Forrest' had the greatest increase in yield with increased rainfall acidity. 'Crawford' and 'Pixie' had the highest yield reduction with increased rainfall acidity. Evans et al., (1981) observed yield decreases and Jacobson (1980) reported a yield increase, all under field conditions. Banwart and Evans et al. utilized ambient rain exclusion shelters in their investigations. Irving and Miller (1981) discovered an increase in photosynthesis in initial stages of the growing season, but observed no differences in yield of soybean subjected to acidified rain in a field rainfall exclusion facility. Based on preliminary results, it has been proposed that

soybean response to simulated acidic precipitation may be predictable utilizing their genetic relationships and specific location of production (Allen and Bhardwaj, 1986).

In a field study, corn (Zea mays L.) exhibited a 9% yield reduction to simulated acid rain at pH 4.0 (Lee, 1982). There were, however, no significant effects on yield of field grown corn for varieties tested when subjected to simulated acidic precipitation with ambient rain exclusion (Banwart, 1985). Preliminary results indicated that in one variety of corn, 'Pioneer 3747', the reproductive process was reduced as result of simulated acidic precipitation at pH 3.6 (Craker et al. 1985).

4. ACID DEPOSITION AND FORAGE ECOSYSTEMS

Several investigators in the past decade have attempted to determine if atmospheric deposition containing increased levels of H^+ , NO_3^- , SO_4^{2-} ions (and other components) can have a positive or negative impact on yield and quality of agricultural crops, but research regarding forage crops has been somewhat limited.

Some of the major forage crops which have been evaluated to determine their response to simulated acid deposition are: alfalfa (Medicago sativa L.), red clover (Trifolium pratense L.), orchardgrass, tall fescue (Festuca arundinacea Schreb.), bluegrass (Poa pratensis L.), perennial ryegrass (Lolium perenne L.), and timothy (Phleum pratense L.) grown in field, greenhouse and growth chamber environments (Cohen et al., 1981; 1982; Lee et al., 1981; K. T. Luu, personal communication, 1986). The results have been inconsistent among years and locations. Monocotyledons and dicotyledons exhibit some growth stimulation from simulated acid rainfall. As a group, monocotyledons are less susceptible to foliar injury by H_2SO_4 deposition than are dicotyledons (Lee et al., 1981). Lee et al. (1981) and Lee (1982) reported all legumes and grasses tested, except bluegrass, sustained some foliar damage resulting from simulated acid rain pH < 3.5. Only bluegrass developed some foliar damage at pH 4.0. Alfalfa, tall fescue, orchardgrass, and timothy yields increased at pH 3.5 to 3.0. Other crop yields were unaffected by increasing acidity of simulated acid rainfall, although, ryegrass and tall fescue root growth was suppressed at pH 3.0 to 4.0. Wolt et al. (1986) reported increased foliar injury with

decreasing pH on orchardgrass and tall fescue in greenhouse environments. No effects on tall fescue yields were observed while orchardgrass yields increased with decreasing pH of simulated acid precipitation in a greenhouse environment. Lee et al. (1981) found no significant yield increase among any of the previously discussed crops in a field environment when exposed to simulated sulfuric-nitric acid (2:1) deposition.

In their greenhouse experiments, Wolt et al. (1986) found N and S contents of tall fescue and orchardgrass tissue were erratic among treatments of varied rainfall pH. Overall, orchardgrass and tall fescue had an increase in concentration of N as simulated precipitation pH decreased. Sulfur concentration was unchanged in either grass cultivar. However, in a field environment Reynolds et al. (1986) found linear (sometimes quadratic) increases in S concentration of orchardgrass forage as rainfall pH decreased, while N concentration was unaffected. Consequently, decreased rainfall pH frequently decreased the N:S ratio of forage.

Acid deposition is just one of several factors which may influence establishment and management of forage crops. Establishment problems associated with small seeded forages are somewhat different than for most

other agricultural crops. Generally, high seeding rates are commonplace in managing forage crops as result of the risks involved in establishment. Oftentimes, the success of establishment will be low, where approximately 30-35% of seeds sown will produce seedlings (Decker and Taylor, 1985).

Most researchers who have evaluated seed germination are in agreement that the major cause of reduced germination rates can be attributed to low water potential, especially under field conditions (Laford and Baker, 1986; McWilliam et al., 1970; Collis-George and Sands, 1962). Moore (1943) stressed the importance of a firm seedbed with sufficient loose soil for shallow seed coverage. Proper seedbed preparation serves two purposes by preventing placing of seeds too deep (optimum, 1.25 cm) and improves seed to soil contact. Murphy and Arny (1939) also emphasized the critical importance for shallow placement (0.5-1.5 cm deep) of forage seeds and noted a firm seedbed was more important in coarse textured soil.

Considering the requirements necessary for sufficient forage seed germination, acid deposition can have positive or negative influence on seed germination.

Simulated acid rain applied in short term applications resulted in the upper 3 cm of the soil exhibiting decreased pH, increased exchangeable Al^{3+} , and greater exchangeable and total acidity (Strayer and Alexander, 1981) which could adversely affect germination. The acidity and dissolved salts present in acid deposition may decrease the osmotic potential of soil water in the zone of seed germination (Roseberg et al., 1986), this could delay seed germination as the seeds would not imbibe water normally. Strong mineral acid content of acidic deposition could possibly disrupt the seed coat cells and alter their permeability. This would permit some of the imbibed water with its dissolved constituents within the seed to leach into the soil environment. This effect could be interactive with soil temperature, as increased temperature results in increased leaching of seed solutes (McLaughlin et al., 1983). Acid present in acid deposition could possibly alter seed covering permeability. An investigation by Walker (1982) revealed a decrease in grass seed germination with increasing acidity of H_2SO_4 - water solution on filter paper. Seed germination was 71% and 100% greater at pH 5.7 than at pH 2.6 for red fescue (Festuca rubra L.) and Kentucky bluegrass, respectively. Wolt et al.,

(1986) reported delayed grass seed germination on filter paper with decreasing acidity of simulated rain solution and reduction of root growth and coleptile growth. Germination in soil media treated with acidified rain solution had no adverse effects on germination and coleptile growth. Root elongation was reduced with increasing acidity of simulated rain solution. They concluded that the tolerance to increasingly acidic rain solution was fescue > orchardgrass > timothy > bluegrass. Their experiment was conducted in a controlled environment germination chamber with seeds and growth media placed in petri dishes.

In normal agricultural practices the germinating seed is surrounded and covered by mineral soil, organic matter and plant residue. These factors offer some buffering protection to acidic precipitation (McLaughlin et al., 1983). Management practices for establishment of small-seeded forages, however, would lead to a large portion of seeds on the surface or within the upper 0.5 cm of the seedbed. Under such conditions the buffering effect of acidic deposition by soil may be lessened.

5. EVALUATION OF ACIDIC DEPOSITION IMPACT ON SOILS

Once sufficient number of seeds have germinated and produced a good stand of seedlings, they are subject to failure by various soil interactions. Undesirable pH, low fertility, inadequate moisture, and poor drainage are some of the soil conditions that must be monitored in successful forage cropping systems (Decker and Taylor, 1985). These factors may be interactive with acidic deposition since soil acidification from acid deposition can result in reduction and loss of basic cations, reduction in CEC, and increased Al availability (McFee, 1980). Therefore, nutrient availability to plants is a function of soil pH (Arthur and Wagner, 1982; Tisdale et al., 1985). Nitrogen and S cycling may be suppressed by acidic deposition (Hern et al., 1985; Cowling and Linthurst, 1981).

A. Acid Deposition and its Influence on Soil Processes

Aside from potential direct foliar effects of acidic deposition, the effect of acidic deposition on soil processes appears to be the pivotal concern in assessment of acidic deposition impacts on aquatic,

natural, terrestrial, and agricultural ecosystems. Soil is a dynamic system in which a complex series of continuous biological and chemical reactions is occurring. It serves as an efficient storage and filtering system while serving as a growth medium for plants. Most soils have the ability to neutralize varying degrees of acidic additions including acid deposition. Acid deposition entering the soil has three possible fates: (1) it may be neutralized by free bases such as calcium carbonate (CaCO_3) or sodium carbonate (NaCO_3), (2) it may move through the soil into ground water or drainage water, or (3) it may react with cations filling the exchange sites on soil particles (McFee et al., 1977).

The addition of acid deposition to the soil system will hypothetically increase the rate of acidification (Cowling and Linthurst, 1981; McFee et al. 1977; Krug and Frink, 1983). As soil acidity increases, organic matter decomposition decreases due to fluctuations in soil microbial populations. Biological decomposition is controlled by fungi at $\text{pH} < 5.5$, whereas, bacteria dominate at $\text{pH} > 5.5$ (Foy, 1984; Voigt, 1980). Since microbial activity is a function of pH, microorganisms

are considered to be partially responsible for the solubility of several micronutrients and Al^{3+} (Foy, 1984).

Nitrogen fixation by leguminous plants is the result of bacteria residing on the plant roots. Rhizobium nodulation of kidney beans (Phaseolus vulgaris) grown in the greenhouse and field environments and soybean grown in greenhouse were inhibited by simulated H_2SO_4 acidified rain (pH 3.2). It was concluded that acidic deposition could be a stress factor on leguminous plants as they depend on bacterial symbiosis (Shriner and Johnston, 1981).

Plant toxicity problems exist at soil pH < 5.5. Soil acidity determines elemental solubilities, deficiencies, and toxicities (Foy, 1984). When base saturation and lime potential decrease, acid deposition facilitates leaching of H^+ and Al^{3+} ions instead of basic cations (Krug and Frink, 1983; Reuss, 1980; Rutherford et al., 1985). When soil acidity increases, the solubility of cationic components increases resulting in greater potential loss by leaching (CAST, 1984; Wiklander, 1980). Cation leaching is greatly influenced by the presence and mobility of the anions (Wiklander, 1980; Hern et al., 1985; Reuss, 1980).

Care must be exercised when evaluating cation leaching. Sulfate adsorbing soils do not leach cations as rapidly as non-sulfate adsorbing soils. Loss of nutrient cations, on sulfate adsorbing soils from acidic deposition ($\text{pH} < 4.0$), probably would only be detectable over a period of many years (Reuss, 1980). Cation concentration, CO_2 partial pressure, degree of Al^{3+} solubility, and their interactions with several soil processes influence the degree of leaching and later ground water and stream water chemistry (Cosby et al., 1985; Reuss and Johnson, 1985). Phosphorus (P) and Al^{3+} interact at low pH to reduce P available for plant uptake (Cowling and Linthurst, 1981; Cronan and Schofield, 1979; Foy, 1984).

Acid weathering of soil influenced by acidic deposition contributes to CEC reduction due to increased Al^{3+} availability and deterioration of clay minerals (Norton, 1977). Most soils exhibit decreasing CEC with increasing acidity (Foy, 1984). The CEC controls soil buffering capacity which is influenced by various soil properties (McFee, 1980). Various systems have been proposed to group soils as to their sensitivity to acid deposition based on their CEC, pH values, buffering capacity, base saturation, type of soil management

utilized and soil carbonate content. These systems differ, but offer a systematic approach to determine those soils that should be given priority in evaluating acidic deposition effects (Arthur and Wagner, 1982; McFee, 1983).

Agricultural soils under intensive management have not shown any major adverse effects from acidic deposition since they have sufficient buffering capacity to neutralize acid inputs (CAST, 1984; McFee, 1983; 1980; Wiklander, 1973). Less intensively managed agricultural soils supporting hay and pasture crops may, however, demonstrate sensitivity to acidic deposition somewhat analogous to that of forest soils.

B. Acid Deposition and its Interaction with Soil Acidification

Soil acidification is a dynamic natural process and is defined as a reduction in acid neutralizing capacity (van Breeman et al., 1984). The humid climate of the eastern United States supplies sufficient rainfall to exceed water loss in evaporation, transpiration, and runoff. Excess water flows through the soil displacing cations and anions. The soil becomes acid when cation removal by leaching and plant uptake exceeds the rate that they are replaced via mineral weathering and

recycling due to decomposition of plant residues. This process is controlled by soil pH and content of weatherable minerals (McFee et al., 1983; van Breeman et al., 1984). Bloom and Grigal (1985) and Ulrich (1983) indicated that cation exchange buffering may have a greater influence than mineral weathering in alleviating the effects of acid deposition, especially in the pH range 5.0 to 4.0. The acidification of the most sensitive soil by acid deposition would be a slow process requiring, possibly, several decades to obtain measurable changes due to soil buffering capacity (Bloom and Grigal, 1985; McFee et al., 1977; Wilkander, 1973). Wiklander (1973) stated that acidification of a soil sensitive to acid precipitation was determined by the concentration of acidic cations in relation to the sum of the basic cations present. Neutral salts present in atmospheric deposition will increase total salts entering the soil solution; therefore, reducing soil solution pH as result of the "salt effect". Evaluation of soil acidification by H_2SO_4 and HNO_3 deposition without consideration of the "salt effect" will tend to magnify any adverse effects observed (Reuss 1980; Wiklander, 1975; Wolt, 1987).

Organic acids (humic and fulvic) and cationic acids (soluble oxides of Mn, Al, Fe) are natural sources of soil acidity. Nitrification results in acidification when it produces more nitrate than can be utilized by plants (Huttermann and Ulrich, 1984). Hydrogen ion inputs by atmospheric deposition are probably minimal in relation to H^+ ions supplied by organic acids from natural soil processes (McFee et al., 1977; Petersen, 1980).

Soil pH influences nutrient absorption and plant growth through direct response of the acidic cations or by affecting nutrient availability (Brady, 1974). When soil acidity increases, the solubilities of basic cations increase resulting in greater losses by leaching (CAST, 1984; Wiklander, 1980). Plant roots and root hairs are directly affected by acid soils ($pH < 5.5$). Cation absorption is reduced and ion transport and permeability of cell membranes are altered, and consequently, root development is reduced. Influence of pH on plant roots is varied and often confounded by other soil system interactions (Moore, 1974).

C. Elemental Cycling as Influenced by Acidic Deposition

Nutrients of major concern in relation to agriculture and acid deposition are N and S. In present day

acidic deposition, SO_4^{2-} and NO_3^- are the dominant anions (CAST, 1984; Charlson and Rodhe, 1982; Cogbill and Likens, 1974; Cowling and Linthurst, 1981; Galloway et al., 1984; Haines, 1979; Vermeulen, 1980).

Atmospheric SO_4^{2-} and NO_3^- deposition may have positive economic effects on agricultural crop production.

Sulfate is not added in most commercial fertilizers whereas, NO_3^- is one of the major nutrients formulated in fertilizers. Nitrogen additions from acidic rainfall probably would have very small if any benefit to forage crops, while acidic rainfall could be a critical source of SO_4^{2-} (Arthur and Wagner, 1982; CAST, 1984; Troiano et al., 1983). Nitrate and especially SO_4^{2-} present in acid deposition may serve as foliar nutrients (Toriano et al., 1983).

Hern et al. (1985) conducted an experiment with two Canadian forest soils under laboratory conditions and applied simulated acid rain at varied pH levels over a two-year period. They determined that simulated acid rain had very little if any effect on total soil N. Ammonification was unaffected, but soil nitrification was reduced at the lowest pH treatment level (pH 2.0) which was attributed to the high input of NO_3^- in the simulated rain. Britton et al. (1985), Strayer and

Alexander (1981), and Hern et al. (1985) concluded that simulated acid precipitation decreased N mineralization with increased soil acidity.

Total soil S increased in the A horizon with increasing acidity of simulated acidic rain applied to two forest soils (Hern et al., 1985). Sulfur decreased sharply immediately below the A horizon and increased somewhat in the B horizon where the greatest concentrations of Al^{3+} and Fe^{3+} oxides were located. Reynolds and Wolt (1987) found similar results in soil supporting fescue, where total S was approximately the same in the Ap and Bt3 horizons. The accumulation of SO_4^{2-} in the B horizon may influence the movement of basic cations through the soil profile (Hern et al. 1985).

Acidic deposition has some potential adverse ecological effects, predominately from Al^{3+} solubility which is pH dependent. An increase in soil Al^{3+} content would result in alterations in clay mineralogy, weathering rates, and base saturation (McFee and Cronan, 1982; McFee, 1980). Aluminum ion exchange at pH 5.0 - 4.0 in soils with low levels of permanent charge is influenced by the organic matter content (Voigt, 1980; Bloom et al., 1979). There was much greater concentration of available Al^{3+} in upper regions of profile at pH

< 5.0 in two Canadian forest soils subjected to simulated acid precipitation. Calcium and Al^{3+} leaching was intensified at the pH 2.0 treatment level (Rutherford et al., 1985). Soil acidification by Al^{3+} mobilization was most active in top 2 cm of the soil (Mayer and Ulrich, 1977). The Al^{3+} concentration in the surface soil was a function of the base saturation and organic matter content (Voigt, 1980; Bloom et al., 1979). Soil and crop management are important factors in establishing and maintaining forage crops. Soil acidification by acid deposition and most other natural soil acidifying properties can be controlled by maintaining soil pH 6.0-6.5 with appropriate amendments. At these pH levels many of the previously described soil acidity problems are alleviated (Wiklander, 1973).

CHAPTER III

MATERIALS AND METHODS

1. ORCHARDGRASS GERMINATION

A field experiment was conducted in fall 1985 at the Plant and Soil Science Field Laboratory, Knoxville, to investigate orchardgrass response to simulated acid rain when germinated on two surface soils. The experimental configuration was a randomized complete block design with a split plot arrangement of treatments. Main plot treatments had four simulated acid rain pH values (4.3, 3.7, 3.1, and 2.5) in four replications. Split plot treatments were surface soils of two series, Etowah silt loam (Typic Paleudults) and Statler variant sandy loam (Humic Hapludults). Some physical and chemical properties of both soils are presented in Appendix A-1.

Simulated acid rain solution was prepared using a stock rain solution which approximated the ambient precipitation composition for East Tennessee. The base rain solution ($20 \text{ } \mu\text{mol L}^{-1} \text{ SO}_4^{2-}$, $20 \text{ } \mu\text{mol L}^{-1} \text{ NO}_3^{-}$, $19 \text{ } \mu\text{mol L}^{-1} \text{ Cl}^{-}$, $19.5 \text{ } \mu\text{mol L}^{-1} \text{ Ca}^{2+}$, and $5 \text{ } \mu\text{mol L}^{-1} \text{ K}^{+}$) was added to deionized water with pH treatment levels obtained through addition of a stock acid solution consisting of a 1:1 mol ratio of H_2SO_4 and HNO_3 .

Test plots received 19 short duration (2 min.) applications of simulated acid rainfall (.46 cm per event) from stainless steel fulljet HH50WSQ nozzles (Spraying Systems, Inc., Wheaton, IL) suspended 2.5 m above the soil surface. Simulated rainfall composition was monitored by sampling above the plant canopy for each rainfall event. Ambient rainfall was monitored with an on-site TVA wet/dry deposition collector and ambient rainfall amounts were obtained from a nearby climatological station.

Chemical composition of ambient and simulated rainfall was monitored by analyzing for pH, electrical conductivity (EC), Ca^{2+} , Mg^{2+} , K^+ , Cl^- , NO_3^- , and SO_4^{2-} on an eventwise basis. The pH measurement was obtained by utilizing a hydrogen ion electrode and EC was obtained by a conductance meter. Calcium and Mg^{2+} were determined by atomic absorption spectroscopy of La-buffered solutions. Potassium was determined by flame emission spectroscopy. Chlorine, NO_3^- and SO_4^{2-} were determined via ion chromatography (Tabatabai and Dick, 1983).

Enough soil was removed from each main plot treatment for the placement of two adjacent plexiglass frames (30.5 cm x 30.5 cm x 10.2 cm) into the soil. Field moist batch

samples of Etowah and Statler surface soils (0-15 cm) were sieved to pass a 0.64 cm screen. Soils were packed to a depth of 8.2 cm at an approximate bulk density of 1.35 Mg m^{-3} into the adjacent plexiglass frames on each main plot.

Orchardgrass (cv. 'Potomac') was seeded on September 10, 1985 in all test plots at 24 kg ha^{-1} ($200 \text{ seeds plot}^{-1}$) after which simulated rainfall applications were initiated. Total number of seeds germinated was determined by counting throughout the term of the experiment. The terminal event of germination was determined by the emergence of either the radicle or the coleptile from the seed covering or soil surface, whichever was observed first. Germination was first observed on the sixth day following seeding and daily counts were made through day 16 after which counts were conducted every other day for the remainder of the 29-day term of the experiment. At conclusion of the germination evaluation, seedlings were collected from each plot. They were rinsed with 0.01M HCl solution and deionized water. Dry matter content of seedlings was determined after drying 24 hours at 60°C in a fan-forced oven.

2. SOIL SOLUTION COMPOSITION AND EXTRACTABLE ELEMENTS

At the termination of the germination experiment, subplots were soil-sampled to a 1.5 cm depth with a stainless steel spatula. Soils were stored in polyvinyl plastic bags at 6°C until prepared for soil solution determinations.

Soil solutions were obtained in triplicate by vacuum displacement (Wolt and Gravel, 1986) and analyzed for pH, EC, Al^{3+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , NO_3^- , Cl^- , and SO_4^{2-} . A combination microprobe (Microelectronics, Inc. Londonderry, NH) was used to measure pH, and EC was measured with a conductance meter utilizing a 3 mL sample cell with a 1.0 cm^{-1} cell constant. Total Al^{3+} was determined by the 8-hydroxyquinoline complexation and butyl acetate partitioning method (James et al., 1983). Calcium and Mg^{2+} were determined by atomic absorption spectroscopy of La-buffered solutions. Potassium and Na^+ were determined by flame emission spectroscopy. Ammonia was determined with a gas-sensing microprobe (Microelectronics, Inc. Londonderry, NH). Nitrate, Cl^- , and SO_4^{2-} were determined by ion chromatography using a Dionex 2120 ion chromatograph (Tabatabai and Dick, 1983).

An ion speciation computer model, GEOCHEM (Sposito and Mattigod, 1979) was used to convert the mean concentrations of soil solution ions to free ionic concentrations. Ion activities were then calculated from the free ionic concentrations determined by GEOCHEM using the extended Debye-Huckel equation. The ionic activities and concentrations were then compared to similar calculations from ALCAP (Adams and Patterson, 1975), (Appendix B-1; B-2).

Each soil sample was analyzed for extractable nutrients (Ca, Mg, K, and P) via the Mehlich I procedure (0.05M HCl and 0.025M H₂SO₄), (Johnson, 1984). Soil pH was measured for each batch soil sample and for each treatment with a combination hydrogen electrode in 1:1 soil to water and 1:1 soil to 1M KCl mixtures.

Exchangeable bases were determined for pH 7 NH₄OAc extracts and extractable Al by extraction with 1M KCl. The CEC was calculated as the sum of exchangeable bases plus extractable Al (Soil Conservation Service Staff, USDA, 1982).

3. RAINFALL CHARACTERIZATION

Simulated rainfall was physically characterized utilizing a ground based precipitation probe GBPP-100 (Particle Measuring Systems, Inc. Boulder, CO.). The precipitation probe employed a laser beam which measured and counted rain droplets electronically. Several parameters were obtained including: droplet sizes, volume per droplet, mean droplet size, kinetic energy of rain droplets, and mean bucket intensity. Previous investigators have concluded that these parameters are basic characteristics for rainfall simulation (Bubenzer, 1979).

4. STATISTICAL ANALYSIS

An analysis of variance (ANOVA) utilizing the GLM procedure of statistical analysis system (SAS) was used to determine significance of rainfall pH and soil on germination (SAS, 1984). If differences were significant at 0.05 level, treatment responses were evaluated by polynomial regression analysis (Snedecor and Cochran, 1967).

Simulated acid rain influence upon soil solution composition was evaluated by subjecting the data to an ANOVA, utilizing the GLM procedures of SAS, (SAS, 1984). When significant differences were located at the 0.05 level treatment effects were analyzed by polynomial regression.

CHAPTER IV

RESULTS AND DISCUSSION

1. CHARACTERIZATION OF SIMULATED AND AMBIENT RAINFALL

Simulated rain was applied for 19 days of the 29-day term of the experiment. There were five ambient rainfall events which occurred on five days during the last two weeks of the experiment. Due to the ambient rainfall events, there were lesser amounts of simulated rain applied to the experimental plots during the latter two weeks. The distribution of ambient and simulated rainfall is shown in Figure IV-1.

Physical characteristics of simulated rainfall, as measured by a ground based precipitation probe, were as follows: mean rain drop size, 1.4 mm; kinetic energy, 52 J m⁻² hr⁻¹; total kinetic energy, 916 J m⁻² hr⁻¹; mean bucket intensity, 8.41 cm hr⁻¹. The rain drop sizes ranged from 0.4 mm to 3.4 mm and 62% of total rain volume occurred within the 1.0 - 2.2 mm range. Rainfall droplet sizes and volume distribution are shown in Figure IV-2.

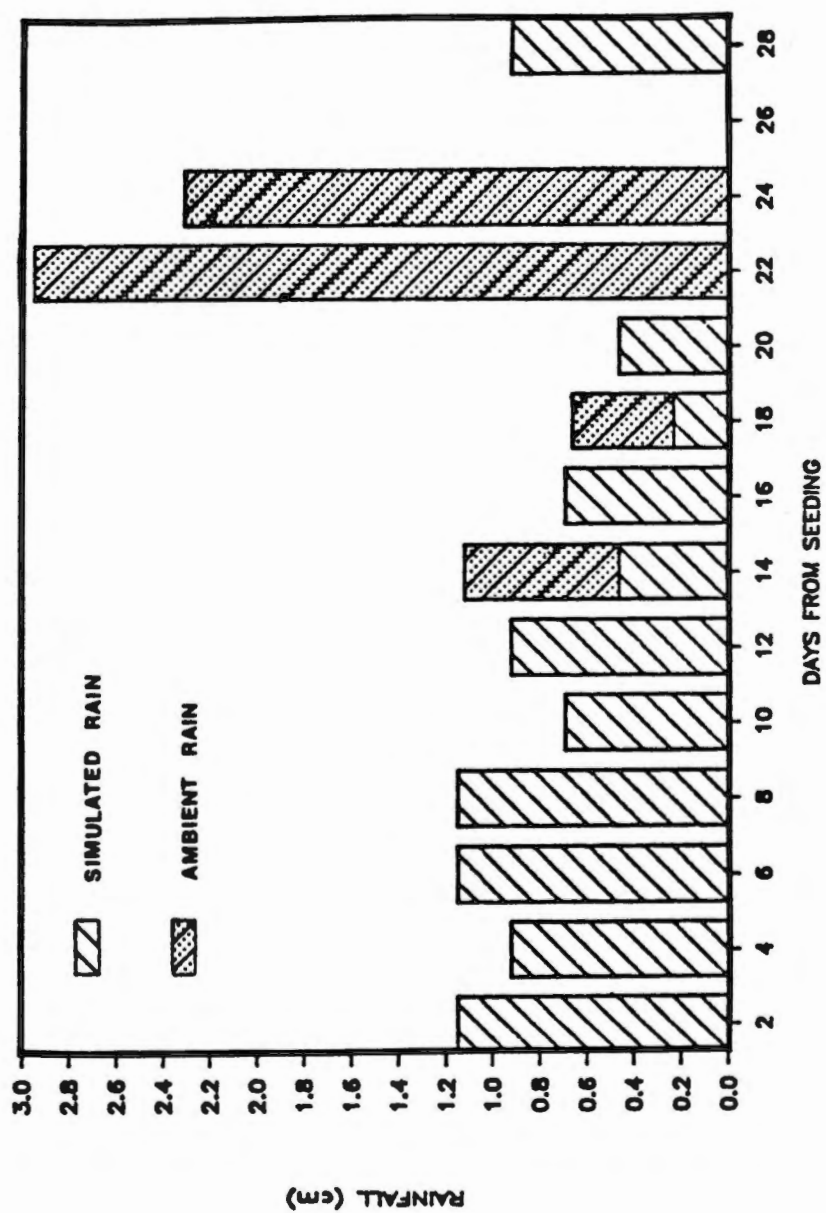


Figure IV-1. Distribution of ambient and simulated rainfall.

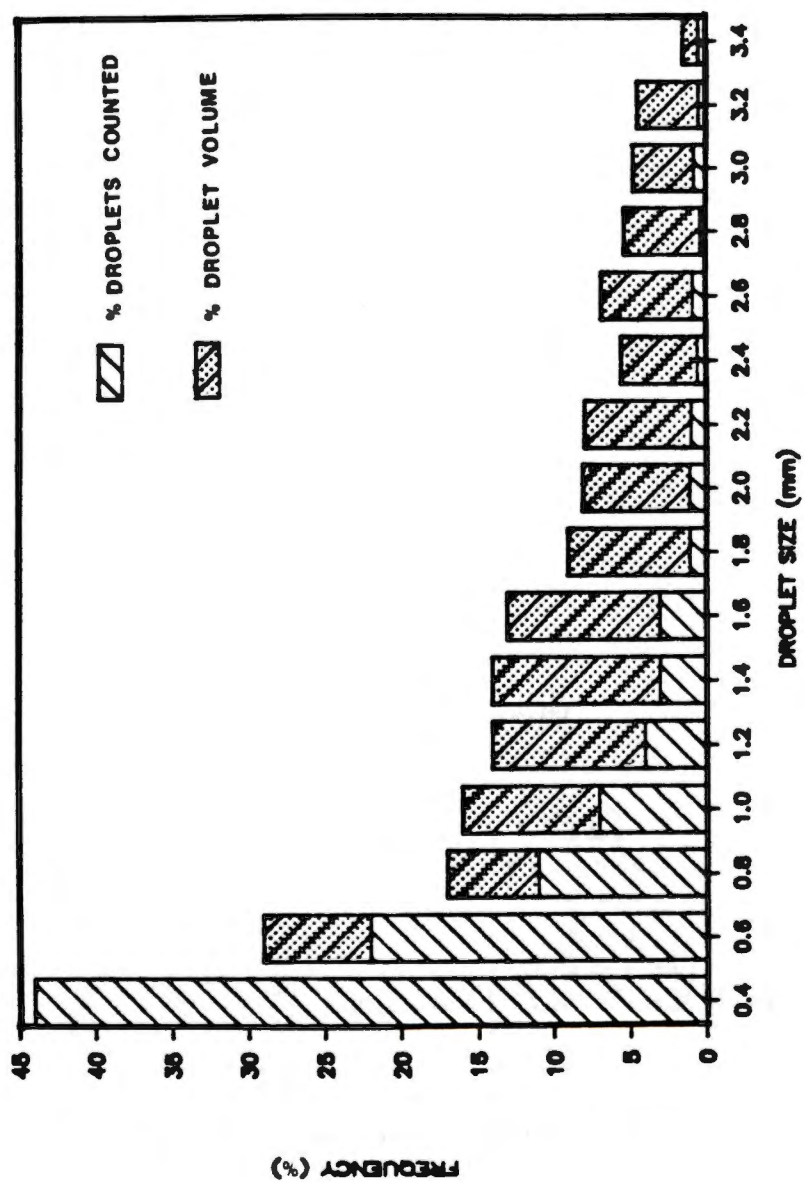


Figure IV-2. Droplet size and volume distribution of simulated rainfall.

Simulated and ambient rainfall chemical composition was monitored throughout the duration of the experiment. The weighted mean of the simulated rainfall composition is presented in table IV-1. Ambient rainfall composition and its weighted mean is given in table IV-2. Ambient rainfall events resulted in a dilution of simulated rainfall treatments which were reflected in the weighted mean values for ambient and simulated rainfall combined (Table IV-3).

Rainfall acidity is most often reported as a pH measurement. The pH and dose of acid rain must be compared to the concentration and duration of exposure to accurately express plant responses to acid rain (Irving, 1983a). The H^+ , NO_3^- and SO_4^{2-} ions deposited by simulated and ambient rainfall during the experiment were expressed as a dosage (Table IV-4). These ions dominate the rainfall composition and they increased most drastically at rainfall pH 3.1 and 2.5. The dosage of the remaining cations and anions were not calculated as their concentrations tended to remain relatively constant across all treatment levels (Table IV-3). As the pH of treatments decreased, the increase in H^+ , NO_3^- , and SO_4^{2-} ions, as well as increase in EC, were attributed to the rain solutions. Any effect of acid rain-

Table IV-1. Weighted mean of simulated and ambient rainfall composition.[†]

Treatment	pH	EC	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	K ⁺	NO ₃ :SO ₄	Ion Diff.	Volume
			----- μmol L ⁻¹ -----				-----			%	cm
4.3	4.48	.025	22	25	21	13	3	5	.88	14	8.7
3.7	3.71	.075	66	74	19	12	3	4	.89	6	8.7
3.1	3.12	.295	265	300	16	10	3	4	.88	6	8.7
2.5	2.60	1.116	920	1026	24	9	3	4	.90	8	8.7
Ambient	4.28	.023	15	18	5	3	1	1	.83	-	6.4

[†]Weighted mean = $\sum_i [(concentration)_i (volume)_i] / \sum_i (volume)_i$, where i represents a rainfall event.

Table IV-2. Ambient rainfall composition and weighted mean for duration of the experiment.

Date	Volume	pH	EC	Ca ²⁺	Mg ²⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	NO ₃ :SO ₄
Days from Seeding	cm		dS m ⁻¹	-----	-----	-----	-----	-----	-----	mol ratio
13	0.66	4.21	.022	4.4	1.5	0.0	3.7	17.0	19.4	0.88
17	0.43	3.99	.033	2.0	0.6	--	2.9	17.8	32.2	0.55
22-24 [†]	5.26	4.28	.022	3.1	0.9	1.1	5.8	9.7	16.5	0.59
Total	6.35									
Weighted Mean [‡]		4.28	23	3	1	1	5	15	18	0.83

[†] Composite of rainfall collected.

[‡] Weighted mean = $\sum_i [(concentration)_i (volume)_i] / \sum_i (volume)_i$, where i represents a rainfall event.

Table IV-3. Weighted mean of combined ambient and simulated rainfall composition.[†]

Treatment	pH	EC	NO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	K ⁺	NO ₃ :SO ₄	Volume
		ds m ⁻¹	-----	-----	μmol L ⁻¹	-----	-----	-----	mol ratio	cm
4.3	4.38	.024	19	22	14	8	2	3	.86	15.1
3.7	3.88	.053	44	50	13	8	2	3	.88	15.1
3.1	3.34	.180	159	180	11	7	2	3	.88	15.1
2.5	2.83	.653	536	599	16	6	2	3	.89	15.1

[†] Weighted mean = $\sum_i [(\text{concentration})_i (\text{volume})_i] / \sum_i (\text{volume})_i$, where i represents a rainfall event.

Table IV-4. Dose of H^+ , NO_3^- , and SO_4^{2-} supplied by simulated and ambient rainfall.

Treatment pH	Weighted mean rainfall pH	H^+		NO_3^-		SO_4^{2-}	
		mol m^{-2}	mol ha^{-1}	mol m^{-2}	mol ha^{-1}	mol m^{-2}	mol ha^{-1}
4.3	4.38	0.006	6.30	2,900	2.9×10^7	3,322	3.3×10^7
3.7	3.88	0.021	21.4	6,600	6.6×10^7	7,550	7.6×10^7
3.1	3.34	0.069	69.0	24,000	2.4×10^8	27,180	2.7×10^8
2.5	2.60	0.379	379.3	80,900	8.1×10^8	90,449	9.0×10^8

fall on soil solution composition and orchardgrass germination may clearly be a consequence of these interactive factors rather than the direct effect of rainfall pH per se. In the following discussion rainfall effects are discussed in terms of treatment levels of simulated rainfall (pH 4.3, 3.7, 3.1 and 2.5), recognizing that responses are in fact a function of the interaction of ambient plus simulated rainfall as well as H^+ , NO_3^- and SO_4^{2-} dose.

2. ORCHARDGRASS GERMINATION

Analysis of variance indicated significant effects of date (days from seeding), simulated rainfall pH, soil, and rainfall pH by soil interaction on percent germination of orchardgrass (Table IV-5). When plotted against time, germination reached its peak between days 17 to 24 from seeding for all treatments on the Etowah soil (Figure IV-3). Experimental plots subjected to simulated acid rainfall at pH 3.1 and 2.5 exhibited very similar trends in percent germination until day 17. The rainfall pH 2.5 resulted in peak orchardgrass germination (50%) on day 17, while rainfall pH 3.1 resulted in peak orchardgrass germination (56%) on day 24. Simulated rainfall of pH 4.3 and 3.7 resulted in slight

Table IV-5. Analysis of variance for germination experiment.

Source of Variation	df	Mean Square	F Value
Date (D)	16	13181	111.73*** [†]
Rainfall pH (R)	3	8038	68.14***
D * R (error term a)	48	118	1.07
Soil (S)	1	471	6.39*
R * S	3	417	5.66 **
D * R * S (error term b)	64	74	0.67

[†] Effects were significant at 0.1% (***), 1.0% (**), or 5.0% (*) level.

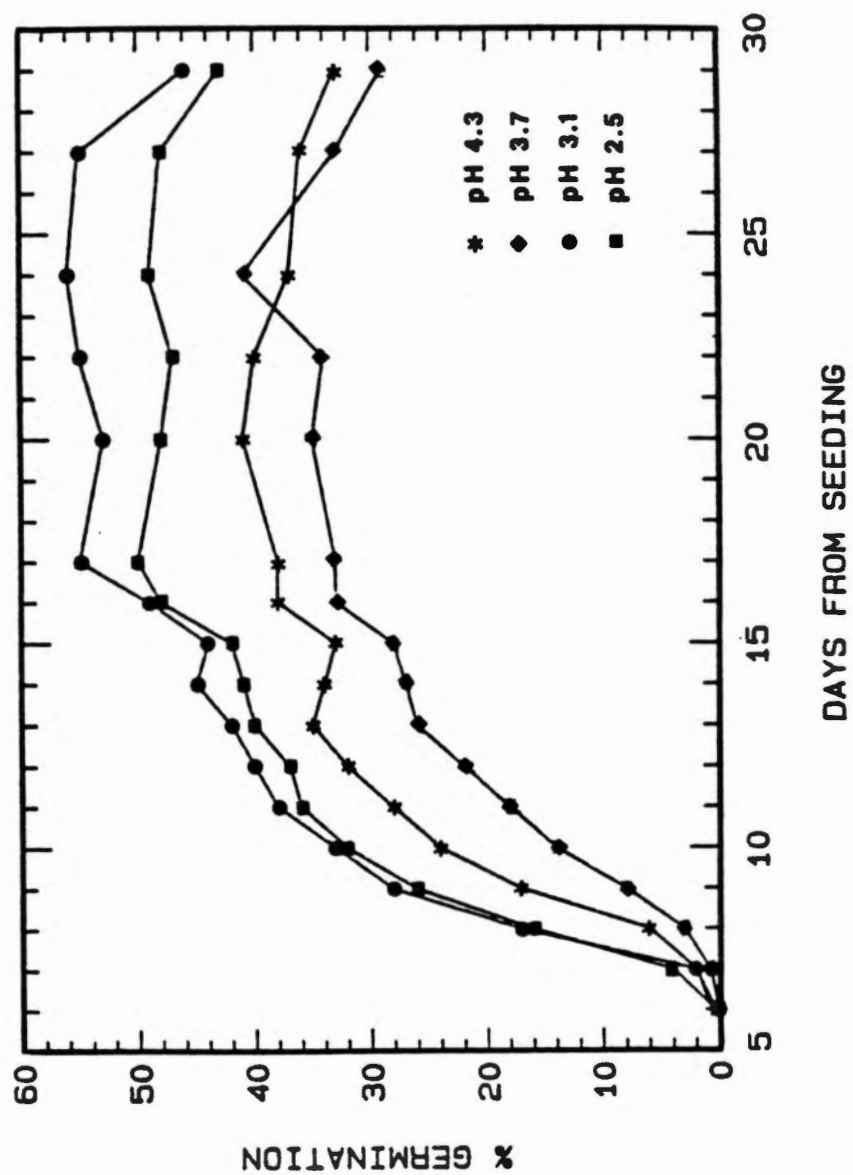


Figure IV-3. Orchardgrass germination on Etowah soil as influenced by ambient and simulated rain at varied pH levels.

delays in the onset of germination and in lower total percent germination as compared to rainfall of pH 2.5 and 3.1. This effect was most pronounced for pH 3.7. After day 24 all pH treatment levels experienced rapid declines in germination, perhaps as an adverse consequence of heavy ambient rainfall (5.26 cm) occurring on days 22 through 24.

Germination responses on the Statler soil at rainfall pH 2.5 and 3.1 were similar up to day 10, after which germination percent tended to level off with pH 2.5 rainfall while with pH 3.1 rainfall, germination continued to increase (Figure IV-4). As for the Etowah soil, simulated rainfall pH 4.3 and 3.7 exhibited a slight delay in the onset of germination as compared to rainfall pH 2.5 and 3.1. At pH 4.3, peak germination (44%) occurred much earlier (day 17) than for the other treatments. Peak germination (56%) was exhibited at rainfall pH 3.1 on day 24 and rainfall pH 3.7 and 2.5 on day 22 (42% and 48%, respectively). The order of maximum germination was consistent between soils with pH 3.1 > 2.5 > 4.3 $\approx$ 3.7.

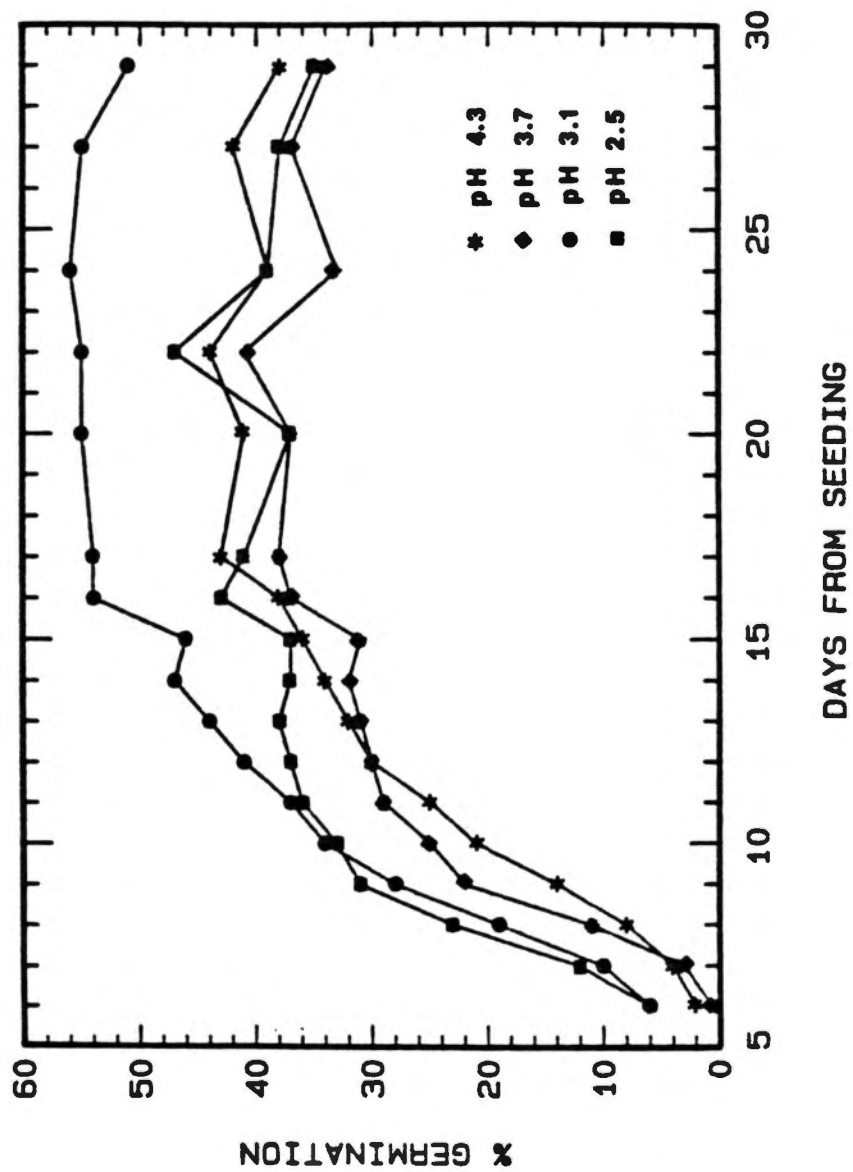


Figure IV-4. Orchardgrass germination on Statler soil as influenced by ambient and simulated rain at varied pH levels.

Orchardgrass germination was differentially influenced by rainfall pH over time after initiation of simulated rainfall treatments. Germination was influenced significantly by rainfall pH on six of sixteen counting dates. There were no significant effects until day 9, after which there were significant differences on days 9, 10, 11, 13, 14, and 17 following seeding (Table IV-6). Effects of pH were generally described by linear and/or cubic polynomial responses. On day nine, there was a tendency for decreased germination with decreasing rainfall pH. For the other dates, germination tended to decline from pH 4.3 to pH 3.7 after which germination tended to reach a maximum near pH 3.1 and decline somewhat at pH 2.5. Only days 6 and 7 demonstrated a significant difference between soils, which indicated Statler surface soil favored a somewhat more rapid onset of germination as compared to the Etowah soil.

Germination on both soils tended to follow similar trends in response to simulated acid rainfall and ambient rainfall. Ambient rainfall occurred on days 13, 17, and 22 through 24 following seeding (Table IV-2 p. 42). Following each ambient rainfall event, most treatments on both soils demonstrated declines in

Table IV-6. The effect of acidic rainfall and soils on orchardgrass germination for dates (days from seeding) which exhibited significant differences.

Effect	Days From Seeding							
	6	7	9	10	11	13	14	17
Rainfall pH	----- Mean % Germination -----							
4.3	1	3	29	22	27	34	34	41
3.7	0	2	28	19	24	28	30	35
3.1	3	6	15	33	37	43	46	54
2.5	3	8	16	32	36	39	39	46
F-Test	NS [†]	NS	LC	LC	L	LC	LC	C
Soil								
Etowah	0	2	20	26	30	36	36	44
Statler	4	7	24	28	32	36	38	44
F-Test	* [†]	*	NS	NS	NS	NS	NS	NS

[†]Polynomial regression is significant at the 5% level and is linear (L), cubic (C) or is not significant (NS).

[†]Effects significant at 5.0% level or not significant (NS).

percent germination (Figures IV-3 and IV-4). The microplot frames extended above the soil surface to prevent erosion of soil and seeds from the test plots. When the rainfall rate exceeded the soil infiltration rate, the microplots became flooded. Therefore, the ambient rainfall seemed to have a deleterious effect on germination which may have limited the observed biological response of orchardgrass germination to rainfall of varied pH levels. Simulated and ambient rainfall resulted in greater fluctuations between treatments on the Statler soil than on the Etowah soil, although the peak germination was consistent between both soils (Table IV-7). The more consistent response on the Etowah soil may have been the result of higher base saturation in the surface soil. These responses seem to indicate an interactive effect among the rainfall composition, the soils, and seedling biological response.

The initial stages of water imbibition by seed result in greater solute loss from the germinating seeds until the concentration gradient between the seed and the soil is reduced by osmosis (McDonough and Chadwick, 1979; Berrie, 1984). Seed cell membranes are composed of protein and phospholipid bilayers. During germination

Table IV-7. Mean peak percent orchardgrass germination on Etowah and Statler soils.

Rainfall pH	Soil	
	Etowah	Statler
	----- Germination, % -----	
4.3	42	44
3.7	42	42
3.1	58	58
2.5	50	48

these membrane components become misaligned and/or displaced due to rapid influx of water; therefore, solute leakage occurs until reformation of the proteins and phospholipids (Bewley and Black, 1985). Solute loss is thought to be a function of seed size, hydration rate of seed constituents, and temperature (McDonough and Chadwick, 1970; Berrie, 1984). In this study, these factors were possibly influenced by the reduction of water surface tension resulting from H_2SO_4 and HNO_3 additions to the simulated rain. The reduced surface tension of the rain solution may have contributed to increased wetting of the seeds, and therefore a more rapid onset of germination.

Dilute solutions of potassium nitrate (KNO_3) are often used to promote seed germination during testing of several species (Copeland and McDonald, 1985). The simulated rain solution contained constant amounts of K^+ at all pH treatment levels and NO_3^- increased with increasing acidity of the pH treatments; therefore, increased germination at rainfall pH 2.5 and 3.1 on both soils may be attributed to possible alteration of the seed covering, decreased osmotic potential in soil solution, possible stimulation from NO_3^- in the simulated rain, and reduced surface tension of simulated

rain. These factors may have been interactive in their effects on orchardgrass germination and resulted in more rapid seed imbibition of water and accelerated germination at the lower pH treatments.

Upon completion of the germination evaluation, seedlings were collected from each plot and dry weights were determined (Table IV-8). The pH 4.3 and 3.7 treatments were lower in mean seedling dry weight than pH 3.1 and 2.5 treatments. The effect of soil or the rainfall pH by soil interaction on seedling dry weight was not significant.

3. SOIL SOLUTION COMPOSITION

Short term application of simulated acid rainfall resulted in significant effects of rainfall pH upon soil solution composition (Table IV-9). Those components significantly affected were pH, SO_4^{2-} , and N:S ratio. Differences were most prominent between soils (Etowah and Statler) for pH, K^+ , Mg^{2+} , Na^+ , NH_4^+ , SO_4^{2-} , NO_3^- , and N:S ratio, while the rainfall pH by soil interaction was not significant, except for Na^+ . The effect of displacement was significant only for Cl^- and interactive effects of displacement with rainfall pH and soil were seldom significant; therefore, the data were composited by rain-

Table IV-8. Mean seedling dry weight.

Effect	Seedling Dry Wt.
Rainfall	
pH	mg
4.3	0.17 b
3.7	0.20 b
3.1	0.81 a
2.5	0.71 a
Sig. of F-test	* [†]
<u>Soil</u>	
Etowah	0.51
Statler	0.44
Sig. of F-test	NS

[†] Effects significant at the 5.0% (*) level or not significant (NS).

Table IV-9. Analysis of variance summary of soil solution composition following exposure to ambient and simulated acid rain.

Source	d.f	pH	E.C.	K ⁺	Ca ²⁺	Mg ²⁺	Mean Square							N:S
							Na ⁺	NH ₄ ⁺	Al ³⁺ †	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻		
Blocks (B)	3	0.073	105318.6	0.014*†	0.614	0.080	0.002	0.014	0.022	0.469	0.073	12.44	576.5	
Rain pH (R)	3	3.30***	111269.8	0.006	1.333	0.076	0.003	0.066	0.086	0.166	1.21***	10.67	176.1**	
M.P. Error (a)	9	0.230	47642.5	0.003	0.529	0.198	0.007	0.022	0.084	0.381	0.052	4.10	334.1	
Soil (S)	1	10.1***	162914.8	0.970**	0.795	2.19**	0.009*	0.079*	0.011	0.051	0.256**	9.18*	2816.9**	
R*S	3	0.102	152430.9	0.004	0.546	0.125	0.012**	0.049	0.091	0.231	0.064	0.920	244.0	
S.P. Error (b)	12	0.089	28731.7 [¶]	0.005	0.287	0.096	0.216	0.015		0.259	0.019	1.218	156.3	
Displacement (D)	2	0.011	1248.7	0.0002	0.005	0.0037	0.0006	0.030		0.004**	0.002	0.077	15.58	
S * D	2	0.034	903.3	0.0002	0.016	0.0007	0.0004	0.706		0.0001	0.002	0.094	5.05	
R * D	6	0.052*	252.2	0.0002	0.014	0.003	0.0007	0.402		0.0008	0.004	0.013	2.56	
R*S*D	6	0.055*	1301.6	0.0004	0.016	0.004	0.0008	0.499		0.0009	0.002*	0.116	13.69	
S-S Plot Error (c)	48	0.017	904.4 [§]	0.0002 [†]	0.017 [§]	0.004 ^{††}	0.0004 [†]	0.025 ^{¶¶}		0.0006 ^{††}	0.0008 ^{††}	0.106 ^{§§}	8.19 ^{§§}	

† Effects significant at the 0.1 (***), 1.0 (**), or 5.0 (*) % level.

‡ Al³⁺ displacement was not analyzed.

§ d.f. = 11

§ d.f. = 40

†† d.f. = 44

††† d.f. = 43

¶¶ d.f. = 28

§§ d.f. = 39

fall pH and soil combinations and reanalyzed. Where effects were significant polynomial regression analysis was utilized with subsamples composited (Table IV-10).

There were linear increases in EC, K^+ , Ca^{2+} , and Mg^{2+} with decreasing rainfall pH. The EC increased due to increased soluble salt concentrations with lower rainfall pH resulting from additions of H_2SO_4 and HNO_3 to achieve the desired rainfall treatment levels. Potassium, Ca^{2+} , and Mg^{2+} are the major basic cations existing on the cation exchange complex and they shifted as expected in response to the rainfall pH effect upon the soil solution pH. Their increased concentrations in solution as rainfall pH decreased were attributed to cation exchange reactions.

The pH and Cl^- of soil solution demonstrated quadratic decreases, while SO_4^{2-} exhibited a quadratic increase with increasing acidity of simulated rainfall. The decreased pH and increased SO_4^{2-} also derived from the elevated concentrations of HNO_3 and H_2SO_4 in simulated rain (Table IV-1 p.41). The soil solution pH was between 6.0 - 5.0 for all treatments; therefore, cation exchange buffering was the operative mechanism controlling the pH changes. Response of Cl^- in soil solution was probably the result of slight fluctuations in Cl^- content of

Table IV-10 Treatment means of soil solution composition following exposure to ambient and simulated acid rainfall.

Effect	pH	E.C.	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	NH ₄ ⁺	Al ³⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	N:S Ratio	Ion Diff.
		ds m ⁻¹					mmol L ⁻¹						%
Rain pH:													
	4.3	329	0.129	0.90	0.520	0.132	0.06	0.04	0.498	0.106	1.36	20.7	23.0
	3.7	354	0.117	0.95	0.565	0.104	0.04	0.05	0.281	0.100	3.05	34.5	0.0
	3.1	432	0.140	1.23	0.657	0.120	0.07	0.05	0.300	0.203	2.80	15.7	9.0
	2.5	496	0.156	1.49	0.697	0.105	0.14	0.07	0.362	0.634	2.52	4.46	9.0
Significance	L Q †	L	L	L	L	NS	NS	NS	Q	L Q	L Q C	L Q C	Q
Soil:													
Etowah	5.87	448	0.101	1.23	0.768	0.127	0.05	.05	0.389	0.204	2.78	24.7	13.0
Statler	5.22	352	0.168	1.05	0.453	0.104	0.09	.05	0.326	0.299	2.12	12.6	10.4
Significance	* ‡	*	*	NS	*	*	*	NS	NS	*	*	*	*

[†] % Ion Diff. = $[\Sigma(\text{cations}-\text{anions}) \div \Sigma(\text{cations} + \text{anions})] \times 100$, calculated for mean values.

Polynomial regression is significant at the 5.0 % level, or is not significant (NS) and is linear (L), quadratic (Q) or cubic (C).

† Effects significant (*) at 5.0% level or not significant (NS).

simulated and ambient rainfall. The NO_3^- and N:S ratio exhibited a cubic response with increasing rainfall acidity. Fluctuations in NO_3^- may be indicative of a nitrogen mineralization response to pH changes. Roseberg et al. (1986) found a significant interaction among soil pH, Cl^- , and SO_4^{2-} salts which influenced the nitrification rate on two western Oregon soils. There were specific ion ($\text{Cl}^- > \text{SO}_4^{2-}$) and soil solution osmotic potential effects which decreased nitrogen mineralization. The sharp increase in SO_4^{2-} at pH 2.5 would decrease the osmotic potential of the soil solution resulting in the observed NO_3^- response. The N:S ratio decreased due to the quadratic increase in SO_4^{2-} and increase in NO_3^- concentrations with declining rainfall pH. Sodium, NH_4^+ , and Al^{3+} responses were not significant at the 5% level; although, Al^{3+} did exhibit a trend in increasing concentration with decreasing rainfall pH. The two soils differed in their solution composition for all components except Ca^{2+} , Al^{3+} , and Cl^- . The effect of rainfall pH by soil was not significant for any solution component.

The presence of excess SO_4^{2-} anions supplied from the simulated rainfall would serve as cation carriers and potentially facilitate cation leaching. Previous re-

searchers have agreed that basic cation concentrations, (predominantly Ca^{2+} and Mg^{2+}), in the B horizon are governed by the presence of the SO_4^{2-} anion (Reuss, 1977; Wiklander, 1973; 1975).

The Etowah and Statler soils contained low levels of SO_4^{2-} , especially in the Ap horizon which contained relatively high amounts of organic matter (Appendix A-1). In these surface soils, organic matter would tend to control SO_4^{2-} retention and cycling (Reynolds and Wolt, 1987) compared to sesquioxides which control SO_4^{2-} retention in the lower horizons (Hern et al., 1983). Consequently, the SO_4^{2-} ions probably did not directly influence the observed increase in cation concentrations with decreased rainfall pH. The increased cation concentrations were attributed to temporal changes occurring on the soil cation exchange complex. There were increased levels of H^+ ions entering the soil system as the simulated rainfall pH decreased. As a result, the H^+ ions displaced K^+ , Ca^{2+} , and Mg^{2+} cations from the cation exchange complex and released them into the soil solution. These free basic cations in solution were evident as soil solution pH decreased (Table IV-10). Free cations in soil solution are susceptible to leaching and result in increasingly acidic soil conditions

(Lee and Weber, 1982; McFee, 1980; Wiklander, 1980). Cation retention and solubility in a given soil is determined by bonding strength and associated anions (Wiklander, 1980). Leaching however, was not a factor in this short term experiment with only moderate amounts of total rainfall inputs (15.1 cm), (Table IV-3, p.43).

Phosphorus in solution was below the detection limits for the analytical procedures utilized ($< 6 \text{ umol L}^{-1}$). The ion difference was $< 10\%$ for all treatments, except for pH 4.3 which had an ion difference of 23% (Table IV-10). Soil solution baseline data was determined on batch soil samples collected prior to establishing the experimental plots for both soil series (Appendix C-1), and indicated some shifts in overall soil solution composition from the time rainfall treatments were initiated to the termination of the experiment.

In general, Ca^{+2} and Mg^{2+} are the predominant cations in the soil cation exchange system at $\text{pH} > 5.0$ and Al^{3+} is mobilized and replaces Ca^{2+} as the dominant cation at $\text{pH} < 5.0$ (Bohn et al., 1979; Reuss, 1983). Therefore, the Ca^{2+} to Al^{3+} ratio in the soil provides some insight into the changes which occur in the soil system resulting from acid rain inputs. Soils containing a base saturation of $> 15\%$ are controlled by Ca^{2+} and other

basic cations. Below the 15% value Al^{3+} becomes mobile and dominates the exchange complex (Reuss, 1983; Ulrich, 1983). The shift in Ca^{2+} to Al^{3+} activities with decreasing rainfall pH is illustrated in (Table IV-11), where free ionic activities were determined from mean soil solution concentrations. There was a slight increase in Ca^{2+} activity with increasing rainfall acidity, whereas a much greater increase in Al^{3+} activity occurred with increasing rainfall acidity. The Ca:Al activity ratio reflected the shift rather dramatically as there was a 115 fold change in the Ca:Al activity from rainfall pH 4.3 to pH 2.5.

The ionic activities of K^+ and Cl^- reflected decreases with increasing rainfall acidity, whereas, Mg^{2+} , Na^+ , NH_4^+ , SO_4^{2-} , and NO_3^- demonstrated increased ionic activity with increasing rainfall acidity. The H^+ and ionic strength decreased and increased proportionally to decreased rainfall pH levels.

Free ionic concentrations were determined for the cations and anions from the mean soil solution concentrations. This data reflected the similar trends demonstrated by the ionic activities (Appendix D-1). Soil solution results from this study are consistent with the conclusions of other researchers as total Al^{3+}

Table IV-11. Effect of simulated acid rain on ionic activities in soil solution using GEOCHEM. [†]

Rain pH	I [†]	H ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	NH ₄ ⁺	Al ³⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Ca:Al
	mmol L ⁻¹ ----- -log activity ----- Activity ratio -----											
4.3	4.03	5.89	3.91	3.19	3.41	3.92	4.25	7.25	3.33	4.16	2.90	11500
3.7	4.92	5.69	4.01	3.17	3.39	3.96	4.43	6.58	3.59	4.20	2.55	2570
3.1	5.73	5.58	3.95	3.07	3.34	3.89	4.19	6.29	3.56	3.91	2.59	1660
2.5	6.84	5.02	4.02	3.03	3.35	3.85	3.89	5.02	3.48	3.45	2.64	100

[†] Computed for mean concentrations reported in Table IV-10 using GEOCHEM (Sposito and Mattigod, 1979).

[†] I = ionic strength = $1/2 \sum c_i z_i^2$, where c_i and z_i are the concentration (mol L⁻¹) and valence, respectively, of the i th species.

concentrations increased with soil acidity, especially in surface soils (Foy, 1984; Mayer and Ulrich, 1977; Strayer and Alexander, 1981).

4. EXCHANGEABLE CATIONS AND EXTRACTABLE NUTRIENTS

Exchangeable cations and CEC were determined for each treatment and soil (Table IV-12). In most cases, the rain pH by soil interaction was significant and data were summarized by individual soils. A rainfall pH by soil interaction may be attributed to a combined effect of chemical differences between soils and rainfall pH. All exchangeable bases demonstrated decreases with decreased rainfall pH on both soils, except K^+ on Etowah soil and Na^+ on Statler soil which were not significant. Calcium and Mg^{2+} revealed a quadratic decline with decreasing rainfall pH on both soils. Potassium showed a quadratic decrease with increasing rainfall acidity only on the Statler soil, whereas, Na^+ had a cubic decrease with decreasing rainfall pH on the Etowah soil. The Al^{3+} reflected a quadratic decrease on Etowah soil and a cubic decrease on Statler soil with increasing rainfall acidity. The CEC demonstrated a quadratic decrease with decreased rainfall pH on both soils.

Table IV-12. Exchangeable bases and CEC of Etowah and Statler soils after exposure to ambient and simulated acid rainfall.

Cations														
	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺				Al ³⁺				Exch. Bases	CEC	
SOILS														
	E	S	E	S	E	S	E	S	E	S	E	S	E	S
Rainfall	pH	----- cmol(+) kg ⁻¹ -----												
4.3	5.3	3.8	1.8	.85	.37	.21	.05	.03	.02	.08	7.5	4.9	7.5	5.0
3.7	5.1	4.3	1.8	.94	.33	.23	.04	.04	.02	.12	7.2	5.5	7.3	5.6
3.1	4.9	4.1	1.6	.78	.33	.22	.04	.03	.02	.19	6.9	5.0	6.9	5.3
2.5	4.1	3.2	1.3	.56	.26	.19	.04	.03	.19	.94	5.7	4.0	5.9	4.9
Significance	LQ [†]	LQ	LQ	LQ	NS	Q	C	NS	LQ	LQC	LQ	LQ	LQ	Q

[†]Polynomial regression is significant at the 5.0% level and is linear (L), quadratic (Q), cubic (C) or not significant (NS).

Acid rain has been hypothesized to contribute to base cation leaching as a consequence of H^+ input and subsequent release of bases from the exchange complex to soil solution (McFee, 1983; Norton, 1977; Wiklander, 1980). This process is illustrated in this study, where simulated rainfall contributed increased H^+ with decreasing rainfall pH levels. As the H^+ inputs increased, basic cations were displaced from the cation exchange complex. This is typical of CEC buffering in soils with cation exchange complexes dominated by exchangeable bases (Bloom and Grigal, 1985; McFee, 1980; Ulrich, 1983). Both the Statler and Etowah soils had percent base saturations of $\geq 90\%$. As rainfall pH decreased, exchangeable bases demonstrated slight decreases as well. The reduction in basic cations was more evident for the weakly buffered Statler soil than for the Etowah soil. Exchangeable Al^{3+} increased with increasing rainfall acidity, again this was most evident in the Statler soil. The magnitudes of these shifts in any instance were not great due to the short duration of the experiment and relatively low doses of H^+ added. Soil pH changes were slight decreasing from pH 5.3 to 4.7 (Table IV-13), and remained within the region where cation exchange buffering would control shifts in soil pH

Table IV-13. Mean Mehlich I extractable nutrients and pH.

Effect	pH [†]		Extractable Nutrients				
	H ₂ O	KCl	K	Ca	Mg	P	
Rainfall pH							
			----- mg kg ⁻¹ -----				
4.3	5.30	4.40	83	802	146	4	
3.7	5.25	4.35	78	801	144	4	
3.1	5.12	4.25	77	739	134	4	
2.5	4.68	3.87	71	618	106	4	
F-Test	L [‡]	L	NS	L	L	NS	
Soil							
Etowah	5.50	4.55	88	842	164	6	
Statler	4.68	3.89	66	638	101	2	
F-Test	*** [¶]	***	***	***	***	*	

[†] Soil pH was measured in 1:1 mixture with H₂O and with 1M KCl.

[‡] Polynomial regression is significant at the 5.0% level and is linear (L) or is not significant (NS).

[¶] Effects significant at 5% level (*), 1% level (**) or 0.1% level (***).

(Ulrich, 1983). Hydrogen ion exchange with Ca^{2+} on exchange sites is the major contributor to pH buffering in this study. The exchangeable bases will continue to buffer soil acidity as long as the exchangeable Ca^{2+} is greater than 15% of CEC (Reuss, 1983; Ulrich, 1983).

Despite the relatively small shifts in the exchangeable cations on the cation exchange complex, there were dramatic changes in soil solution composition. Since the cations in soil solution account for a relatively small proportion of the cations present in the soil a relatively small dose of external H^+ input and a resultant small shift in exchangeable cations contributed to significant increases of cations in soil solution. Changes of cation concentrations in soil solutions were evident across all levels of rainfall pH (i.e., all doses of H^+), (Tables IV-4, p. 44 and IV-10, p. 59). In contrast, there were seldom consequential changes in exchangeable cations for rainfall pH 4.3 to 3.1. A much greater shift in exchangeable cations occurred at rainfall pH 2.5 (Table IV-12).

Mehlich I extractable soil Ca^{2+} and Mg^{2+} demonstrated linear decreases as rainfall pH decreased (Table IV-13). These declines occurred as expected due to the increased removal of Ca^{2+} and Mg^{2+} by H^+ from the exchange sites

with decreasing pH. Potassium and P were not significantly affected by rainfall pH levels. There were significant differences between soils for Mehlich I extractable K, Ca, Mg, and P, although there were no significant rainfall pH by soil interactions. The Etowah soil consistently provided a higher level of extractable nutrients than the Statler soil. The greater amount of nutrients extracted from the Etowah soil may be attributed to greater base saturation than the Statler soil.

Mean values for both H₂O and KCl pH exhibited a linear decline with decreasing rainfall pH and both measurements differed between Etowah and Statler soils (Table IV-13). The soil to water pH values were approximately 0.50 pH units lower than the pH values obtained in soil solutions. This difference in soil solution pH and 1:1 soil to water pH may be attributed to a possible dilution effect from the 1:1 soil to water mixture. Another possibility may be the time in which 1:1 soil to water mixture was allowed to reach equilibrium with atmospheric CO₂. Soil solution pH was measured immediately following displacement and exposure to the atmosphere was minimized while obtaining the pH measurement.

These research results are in agreement with hypotheses proposed by previous researchers concerning acid rain influence upon soils. There were reductions in soil pH, CEC and percent base saturation due to increased rainfall acidity (McFee, 1983; 1980; Norton, 1977; Strayer and Alexander, 1981; Wiklander 1973; 1980).

CHAPTER V

SUMMARY AND CONCLUSIONS

A field environment study was conducted to evaluate the potential impact acidic rainfall may have upon soil solution composition and orchardgrass establishment. Simulated rain was applied at varying acidity levels (pH 4.3, 3.7, 3.1, and 2.5) with an average rate of 0.46 cm per event over a 29-day period without ambient rainfall exclusion. The simulated rain was formulated to best represent background composition of ambient rain. Orchardgrass germination was evaluated concurrently with rainfall application on two different soils. Following the conclusion of the germination evaluation, each test plot was soil sampled to a 1.5 cm depth and analyzed to determine the changes in solution composition, exchangeable cations, CEC, and extractable nutrients. Lower rainfall pH levels (3.1 and 2.5) tended to accelerate the initiation of germination and resulted in a higher total percent germination on both soils evaluated. Germination was consistent between soils with rainfall pH $3.1 > \text{pH } 2.5 > \text{pH } 4.3 \approx \text{pH } 3.7$. The mean seedling dry weights also reflected results that corresponded with the germination data. Rainfall pH 3.1

and 2.5 treatments yielded significantly higher seedling dry weights than pH 4.3 and 3.7 treatments.

In the soil solution analysis, it was determined that simulated acid rain did alter soil solution composition of the surface soil. Significant differences occurred for all cations and anions evaluated, except Na^+ , NH_4^+ , and Al^{3+} . All ions exhibited increased concentrations with increasing rainfall acidity, except Cl^- and Na^+ . Decreasing rainfall pH resulted in increased soil solution acidity and the Ca^{2+} : Al^{3+} activity ratio shifted accordingly. The cation exchange process was responsible for increased concentrations of the basic cations as the H^+ ions displaced Ca^{2+} , Mg^{2+} and K^+ into soil solution. There was an 83% increase in SO_4^{2-} which was attributed to H_2SO_4 added to the simulated rain solution.

Calcium and Al^{3+} are the predominant cations on the cation exchange complex. Their participation in the cation exchange process was illustrated by the ionic activities determined via an ion speciation model utilizing the mean total concentration values. The ionic activities reflected Ca^{2+} dominance at all pH treatment levels which was influenced by CEC buffering.

Generally, there were decreased exchangeable bases with increased rainfall acidity and increased soil acidity. Subsequently, CEC demonstrated a decreasing trend as rainfall pH declined.

While the cations in soil solution increased with decreased rainfall pH, the exchangeable Ca^{2+} , Mg^{2+} , and K^{+} decreased with increasing rainfall acidity. The soil solution represents only a small percentage of the cations active on the exchange complex. A small addition of acid to the soil resulted in a relative slight shift in exchangeable cations, subsequently, resulting in rather large increases in cations in soil solution. There were significant changes in cation concentration of soil solution at all rainfall pH treatment levels, whereas, infrequent changes occurred in exchangeable cations at all rainfall pH levels, except pH 2.5. These cation exchange reactions occurred in the pH range dominated by cation exchange buffering. Exchangeable bases and CEC manifested greater decreases in the weakly buffered Statler soil than the Etowah soil.

Extractable soil Ca^{2+} and Mg^{2+} decreased as rainfall pH decreased. Although these more gross measures of soil chemical composition indicated acid rain effects

on soils, they were not as clearly evident and as broadly generalized across soils as was soil solution composition.

Some potential benefits seem evident in the early stages of orchardgrass establishment from acidic rainfall. The most prominent advantage was inducing more rapid onset and higher percent germination. The observed germination response at lower pH treatment levels (3.1 and 2.5) may be indicative of a biological interaction of rainfall pH upon the seeds and seedlings. Acid rainfall entering forage ecosystems may increase acidification of the soil, especially in the root zone. The soil acidification process is slow, but could adversely affect production over a period of several years under low management situations.

Some prominent and subtle changes occurred within the soil system following acidic rainfall additions which may have influenced the soil-plant system as to influence germination of orchardgrass. Because of the interactive influence of acid rain on plant-soil systems, no association between orchardgrass germination responses and soil solution changes was apparent. This investigation revealed:

- (1) Several changes occurred in soil composition. As rainfall pH declined, soil solution pH and Cl^- decreased, while EC, cations, NO_3^- and SO_4^{2-} increased following short-term application of simulated rainfall. Soil pH, CEC, and extractable nutrients decreased with increasing soil acidity attributable to acid rainfall.
- (2) Orchardgrass germination was differentially influenced by simulated acid rain. The lower pH treatments demonstrated more rapid onset of germination and maintained higher total percent germination.

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APPENDICES

APPENDIX A

A-1. Physical and Chemical Properties of Etowah Silt Loam
(Typic Paleudults) and Statler Variant Sandy Loam
(Humic Hapludults) Surface Soil (1-15 cm).

PHYSICAL	SOIL	
	ETOWAH	STATLER
Easily Oxidizable Organic Matter, $\text{g kg}^{-1}\dagger$	22	36
Mechanical Analysis, $\text{g kg}^{-1}\ddagger$		
Sand	235	676
Silt	326	116
Coarse Silt	174	97
Clay	245	111
Clay-Sized Minerals: [¶]	HKMQG	KHQG
Moisture Equivalent g kg^{-1}		
0.03 MPa (1/3 bar) [§]	21.4	20.4
1.50 MPa (15 bars) ^{††}	14.8	10.1
Bulk Density, Mg m^{-3}	1.36	1.42
<u>CHEMICAL</u>		
pH (1:1 soil/water)	5.9	5.1
Exchangeable Cations, $\text{cmol}(+) \text{kg}^{-1}\dagger\dagger$		
Ca	4.15	3.30
Mg	1.80	0.89
Na	0.05	0.06
K	0.29	0.23
Acidity	0.20	0.58
CEC	6.49	5.06
Extractable Nutrients, $\text{mg kg}^{-1}\dagger\dagger$		
Ca	862	656
Mg	294	186
K	92	63
P	8	23
Total, g kg^{-1}		
C	12.1	14.0
N	2.3	2.3
S	1.4	1.5
Soil Solution Composition, mmol L^{-1}		
Ca	1.82	2.94
Mg	1.24	1.58
K	0.097	0.280
Na	0.229	0.262
NH_4	0.139	0.015
Cl	0.368	0.540
SO_4	0.087	0.097
NO_3	5.72	9.52

[†] Walkley-Black Method (Nelson and Sommers, 1982; Richards, 1954).

[‡] Pipette Method (Day, 1965; Kilmer and Alexander, 1949; Soil Conservation Service Staff, 1982)

[¶] K=Kaolinite, H=Hydroxy Interlayer Vermiculite, Q=Quartz, G=Gibbsite, M= Mica.

[§] Porous Plate Method (Richards, 1948; Richards, 1954).

^{††} Pressure Membrane Method (Richards, 1954).

^{‡‡} Bases Exchanged with pH 7.0 1M NH_4OAC , Acidity extracted with 1M KCl, CEC by summation of exchangeable bases and KCl extractable acidity (Soil Conservation Service Staff, 1982).

^{¶¶} Mehlich I (Johnson, 1984).

APPENDIX B

B-1. Effect of simulated acid rain on ionic activities in soil solution using ALCAP.[†]

Rain pH	I [†]	H ⁺	(K ⁺ + Na ⁺)	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Al ³⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
	mmol L ⁻¹									
4.3	4.2	5.89	3.82	3.17	3.40	4.25	7.60	3.33	4.16	2.90
3.7	5.2	5.69	3.69	3.15	3.37	4.43	7.08	3.59	4.20	2.55
3.1	6.0	5.58	3.62	3.05	3.32	4.19	6.85	3.56	3.91	2.59
2.5	7.2	5.02	3.62	3.00	3.32	3.90	5.61	3.48	3.43	2.64

[†] Computed for mean concentrations reported in Table IV-10 using ALCAP (Adams and Patterson, 1975).

^{††} I = ionic strength = $1/2 \sum c_i z_i^2$, where c_i and z_i are the concentration (mol L⁻¹) and valence, respectively, of the i th species.

B-2. Effect of simulated acid rain on free ionic concentrations in soil solution using ALCAP.[†]

Rain pH	I [†]	H ⁺	(K ⁺ + Na ⁺)	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Al ³⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
	mmol L ⁻¹									
4.3	4.2	5.89	3.79	3.05	3.29	4.22	7.35	3.30	4.03	2.89
3.7	5.2	5.69	3.65	3.03	3.25	4.40	6.80	3.55	4.06	2.51
3.1	6.0	5.58	3.58	2.92	3.19	4.15	6.56	3.52	3.76	2.55
2.5	7.2	5.02	3.58	2.85	3.18	3.86	5.30	3.44	3.27	2.60

[†] Computed for mean concentrations reported in Table IV-10 using ALCAP (Adams and Patterson, 1975).

^{††} I = ionic strength = $1/2 \sum c_i z_i^2$, where c_i and z_i are the concentration (mol L⁻¹) and valence, respectively, of the i th species.

APPENDIX C

APPENDIX D

D-1. Effect of simulated acid rain on free ionic concentrations in soil solution using GEOCHEM.[†]

Rain pH	I [‡]	H ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	NH ₄ ⁺	Al ³⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	Ca:A1
		mmol L ⁻¹ ----- -log [mol L ⁻¹] ----- mol ratio										
4.3	4.03	5.89	3.88	3.06	3.28	3.89	4.22	6.96	3.30	4.03	2.87	7950
3.7	4.92	5.69	3.98	3.02	3.25	3.93	4.40	6.26	3.55	4.06	2.52	1740
3.1	5.73	5.58	3.92	2.92	3.19	3.85	4.15	5.95	3.52	3.76	2.55	1050
2.5	6.84	5.02	3.98	2.86	3.18	3.81	3.85	4.64	3.44	3.27	2.60	60

[†] Computed for mean concentrations reported in Table IV-10 using GEOCHEM (Sposito and Mattigod, 1979).

[‡] I = ionic strength = $1/2 \sum c_i z_i^2$, where c_i and z_i are the concentration (mol L⁻¹) and valence, respectively, of the i th species.

VITA

Guy Wesly Haun was born in Morristown, Tennessee on August 16, 1956. He is the son of Mr. and Mrs. Glen T. Haun of Whitesburg, Tennessee. In May 1974, he graduated from Morristown-Hamblen High School East in Morristown.

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