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Effects of Acidic Precipitation on the Soil Chemistry and Bioavailability of Aluminum, Manganese, and Copper

A. C. Stam
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Environmental Sciences Division
Publication No. 3507

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ENVIRONMENTAL SCIENCES DIVISION

EFFECTS OF ACIDIC PRECIPITATION ON THE SOIL CHEMISTRY AND BIOAVAILABILITY OF ALUMINUM, MANGANESE, AND COPPER[1]

A. C. Stam[2], S. B. McLaughlin, and J. F. McCormick[3]

Environmental Sciences Division
Publication No. 3507

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Date of Issue -- December 1990

Prepared for the
Ecological Research Division
Office of Health and Environmental Research
(Activity No. 42 01 59 40 3)

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
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UNDER CONTRACT DE-AC05-84OR21400

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ACKNOWLEDGEMENTS

The authors gratefully acknowledge the following for their valuable advice and assistance related to this work: John Foss, Ed Clebsch, and Jeff Wolt provided constructive comments on early manuscripts. Dale Johnson, Robert Luxmoore, Roger Minear, Rob Turner, and John Reuss provided valuable comments regarding research design. Bill Selvidge and Arnold Hunley assisted in the greenhouse study and Joy Roddy assisted in the field study.

Research was jointly supported by funds provided by the National Park Service and the Northeastern Forest Experiment Station's Spruce–Fir Research Cooperative. This cooperative is a part of the joint U.S. Environmental Protection Agency-USDA Forest Service Forest Response Program and National Acid Precipitation Assessment Program. This report has not been subject to EPA or Forest Service peer review and should not be construed to represent the policies of either agency.

ABSTRACT

A. C. STAM, S. B. MCLAUGHLIN, and J. F. MCCORMICK. 1990. Effects of acidic precipitation on the soil chemistry and bioavailability of aluminum, manganese, and copper. ORNL/TM-11569. Oak Ridge National Laboratory, Oak Ridge, Tennessee. 287 pp.

The effects of acidic precipitation on the soil solution chemistry and bioavailability of Al, Mn, and Cu in soils from spruce-fir and oak-hickory forests were examined in laboratory, greenhouse, and field studies.

Simulated acidic precipitation increased LMAl concentrations in the laboratory equilibration and greenhouse studies, but not in the field plot studies in oak-hickory and spruce-fir forests. In all studies, acidic treatments decreased NLMAl concentrations following treatment. These results confirm the hypothesis that acidic precipitation can alter the speciation of soil solution Al. There is also evidence that the acidic treatments mobilized soil Al; although this evidence comes from the laboratory equilibration and greenhouse studies and was not present in all examined soils. This latter evidence, in turn, supports the proposition that acidic precipitation can increase the soil solution concentration of Al that is in a potentially bioavailable form.

The plant actively influenced soil Al chemistry through rhizosphere acidification and effects on soil organic matter. Loblolly pine and red spruce increased rhizosphere concentrations of total monomeric Al (TMAl) and NLMAl. The pine also increased LMAl concentrations. The plant influenced acidic treatment effects on rhizosphere Al although the effect varied with tree species and soil type. Such effects of acidic treatment ranged from decreased (loblolly pine potted in mineral soil with comparatively high exchangeable Ca/Al), to similar (red spruce potted in organic soil), to increased (loblolly pine potted in mineral soil with comparatively low exchangeable Ca/Al) solubilization of LMAl relative to that in the nonrhizosphere soil. While acidic treatment decreased NLMAl concentration in non rhizosphere soils, the effect was not present in the rhizosphere. The results confirm the hypothesis that the plant can moderate the effects of acidic precipitation on soil Al chemistry.

Acidic treatment only increased Al bioavailability (as indicated by elevated foliar Al concentration or content) in the greenhouse study of loblolly pine potted in mineral soil with comparatively low exchangeable Ca/Al). There was no evidence of enhanced Al

bioavailability under acidic treatment in any of five plant species (red spruce, loblolly pine, bracken fern, Carolina buckthorn, and hog peanut) treated in the field studies or in loblolly pine (potted in mineral soil with comparatively low exchangeable Ca/Al) and red spruce in the greenhouse studies. Mobilization of soil Al versus Ca by acidic treatment appears to be related to the Ca/Al exchange status of a soil. Acidic treatment increased foliar Ca/Al values in loblolly pine potted in mineral soil with comparatively high exchangeable Ca/Al and may have decreased Ca/Al values in loblolly pine potted in mineral soil with comparatively low exchangeable Ca/Al. Together, the results do not strongly support the hypothesis that acidic precipitation increases the bioavailability of soil Al under all soil conditions; rather a spectrum of effects can occur dependent upon soil base saturation (indicated by exchangeable Ca/Al values).

Acidic treatment increased foliar concentrations of Cu in red spruce and fern at the spruce-fir forest site. Conversely, acidic treatment decreased foliar Mn in red spruce and fern at the spruce-fir forest site and in loblolly pine at the oak-hickory field sites.

I. INTRODUCTION

A wide variety of tree species are experiencing a loss of vigor and, sometimes, increased mortality in a number of forests in eastern North America, Europe, and Scandanavia (McLaughlin, 1985). Several hypotheses that emphasize various air pollutants as the primary cause have been proposed to explain this forest decline. Acid precipitation (Rehfuess, 1981), heavy metals (Klein, 1984), aluminum (Ulrich *et al.*, 1980), ozone, sulfur dioxide (Krause *et al.*, 1983), nitrogen oxides (McLaughlin, 1985; Nilgard, 1985), and organic chemicals (Hinrichsen, 1987) have been implicated as significant contributing stresses in different hypotheses.

This investigation focuses on specific aspects of one of these hypotheses--that of the enhancement of metal toxicity by acidic precipitation. Under this hypothesis of forest decline, acid precipitation directly solublizes soil metals (Cronan and Schofield, 1979) or alters ecosystem processes of H^+ generation and consumption causing solublization of metals (Ulrich *et al.*, 1980). Consequently, concentrations of metals in forms available for plant uptake (i.e., bioavailable forms) are increased at the plant root-soil interface. Uptake of the metals increase and result in toxic effects on, and physiological impairment and/or dieback of, fine roots of trees. Water and nutrient uptake by the trees becomes impaired and the trees experience a decrease in vigor and, possibly, death. This hypothesis was initially proposed for aluminum by Cronan and Schofield (1979) and Ulrich *et al.* (1980) and has subsequently been expanded to include heavy metals (Klein, 1984).

Cronan and Schofield (1979) found that soil solution concentrations of Al in fir forests of the White Mountains in New Hampshire, and Adirondack Mountains in New York, were elevated compared to Al concentrations found in mountains in Washington (Ugolini *et al.*, 1977) and in New Mexico (Graustein, 1976). They hypothesized that

acid precipitation was mobilizing soil Al and suggested that this was responsible for fish kills in area lakes and had implications in the health of plant communities. Ulrich *et al.* (1980) found that concentrations of Al and Fe in the equilibrium soil solution in soils from a beech forest in West Germany had increased from 1966 to 1979. Loss of manganese from soil exchange sites also occurred over the same period. Additionally, a summer dieback of fine roots (noted by Gottsche, 1972) coincided with high concentrations of equilibrium soil solution Al, suggesting a toxicity relationship. They hypothesized that acid precipitation, in combination with altered natural pulses of soil acidity, was solublizing soil Al and other metals and endangering forests of central Europe. Klein (1984) has also hypothesized that the present dieback of red spruce in eastern North America is related to metal mobilization by acid precipitation.

The studies of Cronan and Schofield (1979) and Ulrich *et al.* (1980) are not without their deficiencies and it should be stressed that these works present hypotheses of metal mobilization by acid precipitation, not the verification of such an occurrence. Richter (1983) noted that because of differences in chemistry and parent material of soils, the Washington and New Mexico sites should not be compared to the Adirondack and White Mountains sites studied by Cronan and Schofield (1979). He also pointed out the very limited sampling and questionable statistical procedures that were used by Ulrich *et al.* (1980) as a basis for their hypothesis. In addition, Rehfuess (1981) has suggested that the root dieback noted in the Ulrich *et al.* (1980) study could result from natural processes, particularly drought, and may not be an effect of acid precipitation.

An increase in the bioavailability of soil metals by acid precipitation is, however, supported by work on the concentrations of metals in xylem tissues of trees by Baes and McLaughlin (1984 and 1986) and Scherbatskoy (1984). Baes and McLaughlin (1984) found elevated concentrations of Zn, Al, Cu, Fe, Cr, and Ti in tree rings produced during the last thirty years (1950 to 1980) in short leaf pine (*Pinus echinata* Mill.)

in eastern Tennessee. A similar pattern of concentrations of Al, Cd, Cu, Fe, and Ni was also found in pitch pine (*Pinus rigida* Mill.), eastern hemlock (*Tsuga canadensis* (L.) Carr), Fraser fir (*Abies fraseri* (Pursh) Poir.), and red spruce (*Picea rubens* Sarg.) in the Great Smoky Mountains National Park, Tennessee (Baes and McLaughlin, 1986). Scherbatskoy (1984) reported similar results for Al, As, Ge, and Vd in red spruce and sugar maple (*Acer saccharum* Marsh) from the Green Mountains in Vermont. The results of these three studies support the hypothesis that acid precipitation is mobilizing soil metals and that the metals are in a bioavailable form.

Certain criteria which are necessary for the metal toxicity hypothesis of forest decline to be valid have received little consideration. Four specific criteria are (1) the mobilization of soil metals must affect the portion of the soil which contains the fine roots of trees; (2) this mobilization must increase concentrations of potentially bioavailable species (or forms, e.g., inorganically complexed metal) of the metals; (3) the bioavailable species must exist in the soil solution for a period of time that is sufficiently long to detrimentally affect plants; and (4) the influence of the plant on the bioavailability and, therefore, the toxicity of soil solution metals, must be impaired in some manner.

An examination of the published data of Cronan and Schofield (1979) that supports the mobilization of soil Al by acid precipitation shows that increased concentrations of Al in soil water occur below the A_2 horizon, not in the O horizon where the majority of the fine roots would presumably occur. This indicates that at that site, the major change(s) in the chemistry of soil Al is (are) occurring in a soil horizon which is (are) presumably below the soil zone of fine roots and, thus, does (do) not support the metal toxicity hypothesis of forest decline.

An important point that has been neglected in considerations of the metal toxicity hypothesis is that the mobilization must result in an increase in the bioavailable species

of the metals. Bioavailability and toxicity of a metal are dependent upon speciation of the metal (e.g., Thornton, 1981). In the case of Al, ionic activity of Al^{+3} has been correlated with Al toxicity (e.g., Adams and Lund, 1966) and organic-Al complexes are less toxic to plants than inorganic Al (Marschner, 1986). In the metal toxicity hypothesis, it is therefore necessary to consider the speciation of the dissolved metals of interest. If soil metals are solublized by acid precipitation, concentrations of bioavailable species of the metals must increase if there is to be an increase in toxic effects on forest plants (all other factors being equal). It is possible that, if metal mobilization actually does occur, the solublized metals may be in nonbioavailable forms. Alternatively, soil metals may not be solublized to a significant degree by acid precipitation, but the speciation of the dissolved metals may be altered, increasing the concentrations of species of the metals which are toxic to forest plants.

The importance of metal speciation has not previously been stressed in the evaluation of the metal mobilization hypothesis, although the need for this has been expressed by Ulrich and Pankrath (1983) and Johnson and Siccama (1983). Since the work of Cronan and Schofield (1979) does not support increased solublization of Al in the soil zone of fine roots by acid precipitation, the alteration of Al speciation (with an increase in bioavailable species) in that soil zone is necessary for the metal (Al) toxicity hypothesis of forest decline to be valid.

An additional important consideration is the duration of the hypothesized effects of acid precipitation on the soil solution chemistry of the metals following a precipitation event. It is possible that the ability of the soil to buffer the soil solution chemistry of the solublized metals through adsorption and complexation reactions would limit the duration of any changes in metal chemistry; thereby limiting the presence of bioavailable forms of the metals in the soil solution. Alternatively, any changes in the chemistry of soil metals that would be permanent (or of relatively long duration) would

have much more serious consequences in forest ecosystems.

The plant also has a significant influence on soil solution chemistry of soil metals. Changes in soil pH (Barber, 1971), and Eh (Godo and Reisenauer, 1980), and production of organic chelates (Lindsay, 1971) are all means by which plants can alter the soil solution chemistry of metals and effect changes in their bioavailability. Soils of many of the forests that are experiencing decline are naturally acidic (commonly < pH 4) (e.g., Tomlinson, 1983; Richter, 1983). Since solubility of soil metals generally increases with decreasing pH (e.g., Hutchinson and Collins, 1978), these soils should have naturally high concentrations of metals in the soil solution. Indigenous plant species that grow on these soils would be expected to be adapted to this metal chemistry and have means of reducing the bioavailability and toxicity of the metals through chemical changes within the rhizosphere and/or the plant. Therefore, these plants may have the ability to alter the soil solution chemistry of any soil metals that are solublized by, or have altered speciation due to, acid precipitation. Thus, a reduction in bioavailability of metals within the rhizosphere may occur, countering any alteration in the soil solution chemistry of metals by acid precipitation.

The objectives of the following study were to examine the effects of acid precipitation on selected aspects of the soil solution chemistry of Al in forest soils. The following hypotheses were proposed relative to the mobilization and enhanced bioavailability of soil metals by acid precipitation:

(1.) Acidic precipitation will not significantly mobilize Al in the soil zone that contains the fine roots, but will significantly alter the speciation of dissolved Al in this soil zone. This alteration will occur as an increase in free ionic Al plus inorganic Al complexes relative to organic Al complexes.

(2.) The chemistry of Al in the rhizosphere will differ from that in the nonrhizosphere soil, with the rhizosphere having relatively greater concentrations of

organically-complexed Al. Acid precipitation will affect the Al chemistry of the rhizosphere soil less than that in the nonrhizosphere soil.

(3.) Acidic precipitation will increase the bioavailability of soil Al through increases in inorganic forms of dissolved Al.

Field, laboratory, and greenhouse studies were used in a combined approach to test these hypotheses. The soil zone of fine roots in spruce-fir and oak-hickory forests were treated with acidified and nonacidified artificial precipitation. The effects of treatment pH on the soil solution chemistry of Al were monitored over time following application using a metal speciation scheme that determined operationally-defined organic and inorganic species of Al. Seedlings of two tree species were also treated with acidified and nonacidified artificial precipitation. Concentrations of Al in needles of these plants were measured to infer the effect of treatment pH on metal bioavailability. Aluminum chemistry of the rhizosphere soil of these seedlings was compared to that of the bulk soil to determine the effects of treatment pH on the influence of the plant upon the soil solution chemistry of Al.

This study also provided the opportunity to examine effects of acid precipitation on selected parameters of several other elements pertinent to the metal toxicity hypothesis of forest decline. Copper and manganese represent two metals which may also be affected by acid precipitation. Elevated concentrations of Cu have been found in tree xylem produced since 1950 in locations within Tennesse (Baes and McLaughlin, 1986) which were near the sites of this present study. Ulrich *et al.* (1979) related Mn depletion in study soils of the Black Forest in Germany to acidic deposition.

Calcium was also chosen for study. Calcium interactions with Al are important in Al uptake by plants. Increased solution Ca has been found to have an important moderating effect on Al toxicity by Rost-Siebert (1984). This may be due to the fact that the increasing of concentrations of solution Ca will decrease the activity of solution

Al. Indeed, this effect has been reported by Bingham (1984). It has also been suggested that Al toxicity increases when the molar ratio of Ca/Al in the soil solution is less than one (Rost-Siebert, 1984). Magnesium-Al interactions also appear to be important in Mg uptake by plants. Increased solution Al has been found to cause Mg deficiency and result in "golden tip chlorosis" of needles in Norway spruce (*Picea abies* (L.) Karst.) (Hecht-Buchholz, *et al.*, 1987).

Since Ca and Mg were both affected similarly by either acidic treatment or the plant in this present study, and because Ca-Al interactions appear to be better characterized than Mg-Al interactions with regard to Al toxicity to tree species, only Ca was selected for examination in conjunction with Al in this study. Total dissolved concentrations of Cu, Mn, and Ca in a portion of the soil solutions, and exchangeable concentrations of these elements in the soils, as well as plant tissue concentrations were examined for effects of acidic precipitation.

II. METHODS

A. Treatment Effects on Soil Solution Aluminum

1. Field Study.

Artificial precipitation treatments were used to test for effects of precipitation pH on soil solution Al in soils from two types of forests. Paired field plots were established at each of two field sites in an oak-hickory forest and at one field site in a spruce-fir forest in east Tennessee. The use of the two sites in the deciduous forest allowed for the comparison of the response of two soils of different parent materials. Soil solution chemistry of Al in the soil zone of fine roots was monitored over time following selected precipitation events in the early and late growing season.

a. Descriptions of field sites. The spruce-fir forest site was located in the Mt. Collins area of the Great Smoky Mountains National Park (GSMNP), Tennessee (35°38' N, 83°26' W, 1800 m elevation). The soil was a Typic Haplumbrept (R. B. Harrison, Oak Ridge National Laboratory, 1986, pers. comm.) and was underlain by the Precambrian Thunderhead Sandstone (King *et al.*, 1968).

The oak-hickory forest sites were located at the Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee (35°58' N, 84°17' W). One site was in the Melton Branch watershed (MBW) (265 m elevation). The soil at this site is an Aquic Hapludult (Shelocta series, Apison silt loam, D. A. Lietzke, Univ. of Tennessee, 1985, pers. comm.) and is underlain by Middle Cambrian Maryville Limestone (Rothschild *et al.*, 1984). At the site, the bedrock is predominantly siliceous shale with some limestone members (R. J. Luxmoore, Oak Ridge National Laboratory, 1985, pers. comm.).

The second site was in the Walker Branch watershed (WBW) (330 m elevation). The soil at the site is a Typic Paleudult (Fullerton Series, Peters *et al.*, 1970, Minvale silt loam, R. J. Luxmoore, Oak Ridge National Laboratory, 1985, pers. comm.) and is

underlain by Lower Ordovician Chepultepec Dolomite of the Knox Group (R. J. Luxmoore, Oak Ridge National Laboratory, 1985, pers. comm.). The soils of this study are described in Appendix A. 1.

The climate of east Tennessee is damp temperate (Caf) following Köppen (Trewartha, 1957). The mean annual temperature at the GSMNP site falls between 7.2 to 9.4°C (Shanks, 1954). July is the hottest month (average temperature between 15 to 17.2°C), and January is the coldest (between -0.5 to 1.7°C). At the ORNL sites, the mean median temperature is 14.5°C. July is the hottest month (average temperature 25.1°C), and January is the coldest (4.4°C) (Johnson and Van Hook, 1988). The mean annual precipitation exceeds 192 cm at the GSMNP (Shanks, 1954) and is 151 cm (Henderson *et al.*, 1978) at the ORNL sites. Mean precipitation in east Tennessee during the growing season is approximately 9.6 cm per month (U.S. Dept. Commerce, 1968) with June (8 cm) and July (15 cm) representing the extremes in the ORNL area (Johnson and Van Hook, 1988). The GSMNP site also receives an unknown amount of precipitation through cloud water inputs.

b. Description of field plots. Paired plots were established at each of the three field sites. The locations of the plots were based upon accessibility--for the transportation of the artificial precipitation to the plots; the absense of tree trunks--to facilitate the isolation of the individual plots from the ambient precipitation; and minimal slope--to minimize the lateral flow of soil water into the plots. In addition, the plots were located a minimum of 30 m from the nearest road to minimize their contamination by roadside dust and automobile emissions. The circular plots (3-m-diameter) were positioned adjacent to each other normal to the general slope at the site. The plots were isolated from the ambient precipitation by a clear polyethylene sheet that was attached to a wooden frame (3.5 m x 3.5 m) which was supported by wooden legs one meter above the soil. The soil upslope of the plots was trenched to divert the flow of

shallow soil water around the plots. The paired plots were enclosed by chicken wire fencing to keep out herbivorous mammals. The WBW and GSMNP field plots are shown in Appendix A. 2, Figures 1 and 2. Vegetation of each field site is described in Appendix A. 3

c. Chemistry of artificial precipitation. At each site, the plots were treated with artificial precipitation of either pH 3.5 (treatment) or pH 5.0 (control). These pH values represent the extremes in the precipitation pH values that were recorded at the Walker Branch Watershed, ORNL, during 1983 (G. M. Lovett, Oak Ridge National Laboratory, 1984, pers. comm.). Acidity in the artificial precipitation was established using HNO_3 and H_2SO_4 at a NO_3^- : SO_4^{-2} ratio of 1: 3.2 (molar basis). The artificial precipitation solutions also contained neutral salts at the mean concentrations that were recorded at the WBW during 1983. Stock solutions of the artificial precipitation were made at 50 x and were diluted with distilled water for use. See Appendix A. 4 for the detailed chemistry of the artificial precipitation solutions.

d. Plot treatment. Plots were treated weekly with 2.5cm of artificial precipitation applied over one hour. The ORNL plots were treated from mid-April to late-October, 1985. The GSMNP plots were treated from May to October, 1985. The artificial precipitation was supplied to each plot using a portable rain system (see Appendix A-5 for its representation). With this system, the artificial rain was emitted from an over-head spray nozzle (Full Jet, Thomas Engineers, Birmingham, AL) that was attached to and positioned three meters above the plot by a portable PVC frame. The artificial precipitation was transported to the sites in 24.6 L carboys and pumped to the nozzle using a 2.5 amp gear pump (Micropump, Cole Parmer, Chicago, Il) that was powered by a 4.5 HP portable generator. The generator was positioned 25 m from the plots to minimize the impact of its emissions on the plots.

e. Collection of soil samples. Soil samples, from which the soil water was to be extracted, were collected at 1h, 1d, 3d, and 6d following single artificial precipitation

treatments. Four replicate samples per plot were collected at each sampling period. Collection was made from the ORNL sites in early May and late October, 1985, and from the GSMNP site in late May and mid-October, 1985. The initial sequence of sampling followed the third treatment of the field plots with the artificial precipitation.

Soil samples were collected using a 4 cm-diameter polypropylene tube. After the litter layer was brushed away, the tube was pushed into the soil to a depth of approximately 4 cm, and then withdrawn. The soil samples were 4 cm in diameter and approximately 4 cm in depth. This depth was sufficient to sample the soil zone which contained the majority of the fine roots at all three sites. This represented the Oe(F) and the A_1 horizons at the GSMNP and ORNL sites, respectively. The hole made by the collection of sample was refilled with a similar soil core taken from the peripheral portion of the plot. This replacement was done to minimize any alteration in the pattern of water infiltration into the soil during subsequent treatments. The replaced soil was marked with a plastic marker to prevent its subsequent sampling. The sample collection was restricted to the area which was bounded by two circles of 1- and 2.5-m diameter. This restriction of the area of soil collection was necessary because the intensity of treatment solutions over this area was even, but decreased in both directions outside of it. All samples were collected at a minimum of 8 cm apart.

The soil samples were kept in the collection tubes and were placed in polyethylene bags to prevent evaporation of the soil water. They were stored in a portable cooler to minimize any change in temperature during the period of transportation from the field sites to the laboratory. Once in the laboratory, the soil solution was extracted from the samples using centrifugation and then treated with the procedure for the speciation of Al. Solution pH and dissolved organic matter of these samples were also measured. In some cases, total dissolved concentrations of Al, Ca, Mn, and Cu were also determined. The specific methods of analysis for these chemical

parameters will follow in parts E and F of this portion of the Methods chapter.

2. Laboratory Equilibration Study.

Due to the high variability in the soil solution chemistry of Al that was found in the field study at the spruce-fir site and the presence of the dieback of red spruce that is occurring in northeastern North America, the effects of treatment pH on the chemistry of soils from spruce-fir forests was further examined in the laboratory. This permitted the treatment of a greater number of spruce-fir soils (four) and the monitoring of the soil solution chemistry of Al over a longer period following individual artificial precipitation treatments than were included in the spruce-fir field study. Two of these soils were from the GSMNP and allowed for the comparison of the effects of treatment pH on the soil solution chemistry of Al in the Oe(F) horizon of soils that were developed from different parent materials. The other two spruce-fir forest soils were from Whiteface Mountain in the Adirondack Mountains of New York, and permitted the comparison of the effects of treatment pH on the soil solution chemistry of Al in the Oe(F) horizon of soils from forest stands in different stages of forest decline.

a. Sample collection. The GSMNP soils were developed on sandstone (Precambrian Thunderhead sandstone) (Collins Gap site) and shale (Precambrian Anakeesta shale, King *et al.*, 1968) (Indian Gap site). The Collins Gap soil was collected adjacent to the GSMNP plots that were used in the field study. The Indian Gap soil was collected near Indian Gap which is located approximately 6 km northeast of the Collins Gap site (35°36' N, 83°26' W, 1530 m elevation). Both Adirondack Mountains soils were developed on anorthosite (A. J. Friedland, Univ. of Pennsylvania, 1986, pers. comm.). One sample (Adirondack Mountains-healthy forest site) was collected from a healthy spruce-fir stand (elevation 875 m), and the second (Adirondack Mountains-unhealthy forest site) was collected from a spruce-fir stand in which the spruce were

experiencing dieback (elevation 963 m). The Adirondack Mountains soils were provided to the author by Dr. A. J. Freidland, University of Pennsylvania.

The Oe(F) soil horizon was collected at all four sites. The litter layer was brushed aside and the Oe(F) was collected as a grab sample, with a portion of the living roots removed at that time. The samples were collected in early August and mid-August, 1986, from the Great Smoky Mountains and Adirondack Mountains sites, respectively.

b. Sample preparation. In the laboratory, the soils were seived through 1/2 cm nylon mesh and then mixed by hand. Subsamples of each soil type were placed in 3 cm x 5.5 cm-diameter polypropylene cylinders. A polyethylene tray (25 cm x 50 cm x 6 cm) held these subsamples and facilitated the drainage of the treatment solutions from them during the treatments. The tray contained a 1-cm layer of the seived soil which was covered with a fiberglass mesh (7 mesh/cm). Forty tubes were placed on the mesh and then filled with subsamples of the appropriate soil. The subsamples of the Great Smoky Mountains and Adirondack Mountains soils were approximately 17 g and 8 g, respectively. Additional soil was placed on the mesh in the spaces between the sample holders to form an even layer of soil. This was done to minimize differences in evaporation across the surface of the tray. This layered arrangement prevented the waterlogging of the samples by facilitating the drainage of the treatment solutions from the samples during and following treatment. The mesh prevented the sampling of the lower layer of soil and also prevented the migration of soil from the sample holders during the study. The sample tray is presented in Appendix A. 6. Between treatments, the samples remained in the sample tray and were stored in an upright incubator which was set at 15° C.

c. Sample treatment. Samples were treated with artificial precipitation of pH 3.5 (treatment) or 5.0 (control) on a rainfall simulator (Shriner, 1979). The detailed chemistry of the two treatment solutions is presented in Appendix A. 4. The

treatments were weekly and consisted of 2.4 cm of solution applied over a one hour period. The soil solution was collected from the Great Smoky Mountains samples using centrifugation at 1h, 1 d, 3 d, 7 d, and 14 d following the initial treatment and the treatments at weeks 10 and 15. The Great Smoky Mountains soil samples were very dry when collected and required an initial wetting with the treatment solutions. This wetting was followed three days later by the first full treatment. Because of a limited amount of soil, the soil solution from the Adirondack Mountains samples was collected only at 1h, 3 d, and 7 d after the initial watering and at week 10, and at 1h, 1 d, 3d, and 7 d following the final treatment at week 15. When the subsamples were removed from the sample tray, they were replaced with Oe soil to maintain even evaporation from the tray. These replaced samples were marked to prevent their subsequent sampling.

The methods for the speciation of Al in the soil water samples were the same as those that were used in the field study, except that the initial filtration through a 0.4 μm filter was eliminated. This was done out of a concern for the scavenging of dissolved metals and organic matter by the filters. Solution pH, dissolved organic matter, and concentrations of 1N KCl-exchangeable and total dissolved Al, Ca, Mn, and Cu were also determined on selected samples. The specific methods of analysis for these chemical parameters are given in parts E and F of this portion of the Methods chapter.

3. Method of Collection of Soil Solution.

Soil solution was collected from the soil samples using the drainage during centrifugation method of Davies and Davies (1963). The description and representation of the constructed centrifugation tube is presented in Appendix A. 7. For collection of the soil solution, soil samples were placed in centrifuge tubes and centrifuged at 2500 times gravity for one-half hour, in a Beckman Model J-21 Centrifuge using swingout buckets. Centrifuge tubes were then disassembled, and the soil water that had collected in the

water collection cup of each tube was transferred to a 6-mL polyethylene vial using a micropipette. The solutions were then treated with the aluminum speciation procedure.

4. Method of Speciation of Soil Solution Aluminum.

At the beginning of this study, several procedures for the fractionation of dissolved Al into the organically-complexed and the ionic plus inorganically-complexed fractions of monomeric Al were available (Driscoll, 1984, Campbell *et al.*, 1983, and LaZerte, 1984). Two additional procedures were subsequently developed by Campbell *et al.* (1986) and Lalande and Hendershot (1986). These procedures differ primarily in the method used to fractionate the monomeric Al into the organic and inorganic fractions. The different methods used are exchange reactions with either a cation exhange (Driscoll, 1984) or a chelating exchange resin (Campbell *et al.*, 1983, and 1986), dialysis (LaZerte, 1984), or complexation with an organic extractant at varied extraction pH and duration of reaction (Lalande and Hendershot, 1986). With the exception of that of Campbell *et al.* (1983), these procedures extract monomeric Al from the water samples using complexation with 8-hydroxyquinoline. The concentration of total monomeric Al (TMAl) is determined in one unfractionated subsample. The concentration of nonlabile monomeric Al (NLMAl) is determined in a second subsample in which the monomeric Al has been fractionated through the removal of labile monomeric Al (LMAl) from solution. The concentration of LMAl is determined by the difference between the concentrations of TMAl and NLMAl. The initial Campbell *et al.* (1983) procedure included a photooxidation step to decompose organic-Al complexes. This has been subsequently eliminated and replaced with an extraction using 8-hydroxyquinoline (Campbell *et al.*, 1986), resulting in a speciation procedure that is almost identical to the one developed independently in this study.

It was necessary that the speciation procedure, which was to be used in this

study, be able to speciate Al into treatment labile and nonlabile fractions; work with small volumes of sample; and process a large number of samples relatively rapidly. At the time of the development of the speciation procedure that was used in this study, the second procedure of Campbell *et al.* (1986) and that of Lalande and Hendershot (1986) had not been published. This author thus had the choice of the other three procedures, all of which had characteristics that made their use inappropriate in this study. The Driscoll (1984) procedure required too large a subsample volume in the cation exchange procedure. The photooxidation procedure of Campbell *et al.* (1983) has problems with the precipitation of soluble iron (which could scavenge dissolved Al) and would be difficult, and expensive, to adapt for use with the number of samples required in the study. The dialysis procedure of LaZerte (1984) required a treatment period that would be too long for use, considering the time constraints of the chosen sampling schedule. Due to the limitations of each of the above-mentioned procedures, it was thus necessary to develop a different speciation procedure for use in this study.

The speciation procedure for Al that was developed for use in this study fractionates dissolved monomeric Al into operationally-defined nonlabile and labile fractions. With this procedure, TMAl and NLMAl are directly measured and LMAl is determined by the difference between the concentrations of TMAl and NLMAl. This speciation procedure is a hybrid of those of Driscoll (1984) and Campbell *et al.* (1983). A chelating resin is used to fractionate the LMAl and NLMAl species (Campbell *et al.*, 1983) and the 8-hydroxyquinoline extraction is used to complex and extract the monomeric Al (Driscoll, 1984). This procedure is appropriate for small volumes of sample, with a minimum of 2 mL necessary. This compares with > 50 mL of sample required in the procedure of Driscoll (1984). The speciation of Al with this procedure is relatively rapid, and when the procedure is coupled with the centrifugation method of soil solution collection, up to 20 samples a day can be processed. The validity of this

speciation procedure is supported by the development of a like procedure by Campbell *et al.* (1986).

The speciation procedure is represented in Fig. 1. All labware used in these speciation procedures were cleaned by soaking in 10% HNO_3 for 24 hours, followed by 6 rinses in distilled water and 3 rinses in deionized water. Following collection, the water samples were filtered under suction through 0.4 μm Nuclepore polycarbonate filters, using a mini-suction filtration apparatus that was developed to minimize any loss of the sample during the filtration. This apparatus is described in Appendix A 8. After filtration, a 0.5 to 1.0 mL subsample (subsample A) and a 1.3 mL subsample (subsample B) were transferred to separate 6 mL polyethylene vials by micropipette. Any additional sample was saved for subsequent determinations of pH, dissolved organic matter, and, in some cases, concentrations of total dissolved Al. These subsamples were stored at 4° C until the desired analyses were performed.

The TMAL in subsample A was complexed with 8-hydroxyquinoline buffered at pH 5.1 and extracted into methylisobutylketone (4-methyl pentanone-2) (MIBK) following the procedure of James *et al.* (1983). The MIBK, as used by Barnes (1975), was substitued for n-butyl acetate in the procedure. The subsample volume in this study was less than that used by James *et al.* (1983), but the same proportions of the reagents and sample were used. Distilled water and 1M sodium acetate were premixed to minimize manipulations during the extraction procedure and 1.5 mL of this solution was added by micropipette to 1 mL of sample. This was followed immediately by the addition of 0.4 mL of 1% 8-hydroxyquinoline by micropipette to the sample. The sample was capped and shaken vigorously for 15 seconds. During this time, the 8-hydroxyquinoline complexes the monomeric Al to form Al-quinolinate. This step was followed immediately by the addition of 0.5 mL of MIBK which stopped the complexation reaction. The sample was then recapped and shaken vigorously for thirty seconds to extract the Al-quinolinate

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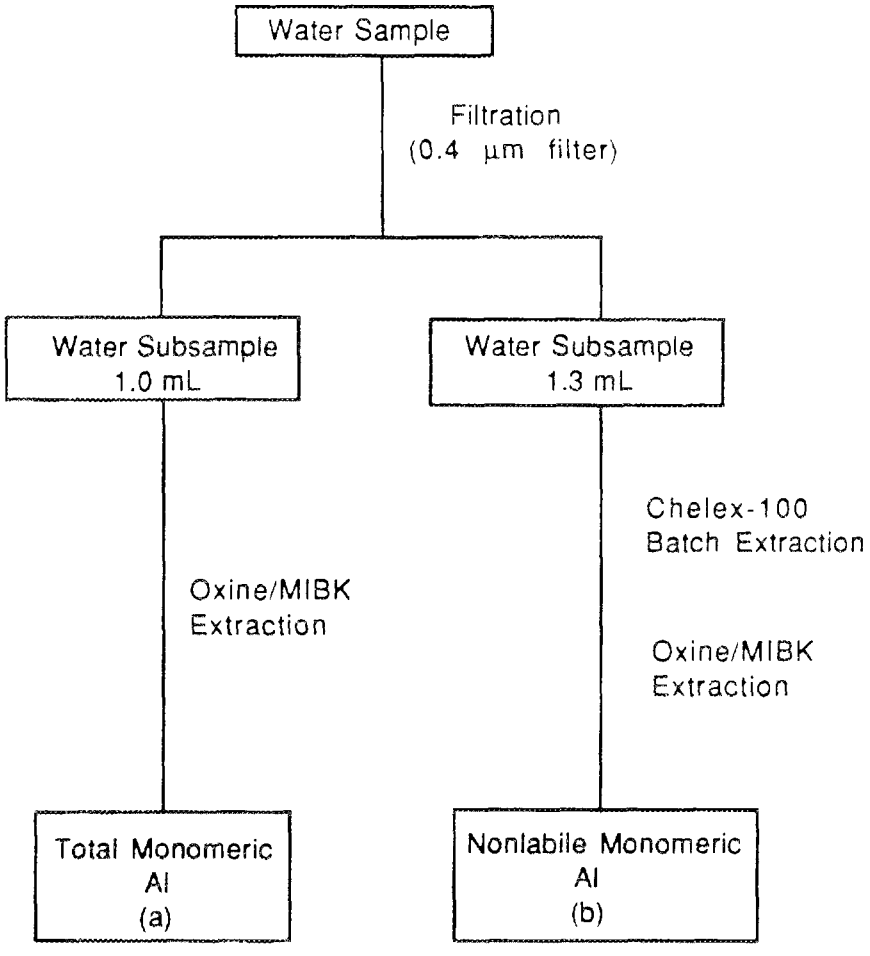

DISSOLVED ALUMINUM PARAMETERS

(1) Total Monomeric Al (a)
(2) Nonlabile Monomeric Al (b)
(3) Labile Monomeric Al (a - b)

Fig. 1. Scheme for the fractionation of parameters of dissolved monomeric aluminum examined in this study.

into the MIBK. The layer of MIBK, containing the Al-quinolinate, was then removed by micropipette, transferred to a 0.5 mL polypropylene centrifuge tube, and stored at -5° C until the samples were analyzed. When less than 1.0 mL of sample was used in this extraction procedure, the volumes of the reagents were proportionately reduced.

In subsample B, NLMAl was separated from LMAl using the Chelex-100 chelating resin following the procedure of Campbell *et al.* (1983). The sample was treated with a resin batch extraction during which LMAl is chelated by the resin and removed from solution, leaving the NLMAl as the only form of monomeric Al in solution. The NLMAl was then extracted using the 8-hydroxyquinoline complexation procedure that was described above.

The chelating resin was prepared with minor modifications of the procedure of Campbell *et al.* (1983). The Chelex-100 resin (Bio-Rad Laboratories, 100-200 mesh) was obtained in the sodium form and converted to the hydrogen form following the supplier's instructions. The resin was then equilibrated in a synthetic solution containing concentrations of H^+ and Ca^{+2} similar to those found in soil water of the study areas. The pH and the Ca^{+2} concentration of the equilibration solution were established with 0.01M HNO_3 and 0.0125 M $Ca(NO_3)_2$, respectively. The pH of the resin was equilibrated at pH 4.0, 5.0, and 6.0 for soil solution samples from the spruce-fir forests, the oak-hickory forest (WBW), and the oak-hickory forest (MBW), respectively. These pH values were based upon pH measurements of soil solution from the specific field sites by this author. The resin was equilibrated at Ca^{+2} concentrations of 1 and 2 mg/L for the samples from the spruce-fir and the oak-hickory forests, respectively. These concentrations were chosen based upon field data from similar forest types (spruce-fir forest, Jones *et al.*, 1983; oak-hickory forest, D. E. Todd, Oak Ridge National Laboratory, 1984, pers. comm.). Initial $Ca(NO_3)_2$ additions of 5.5 mL and 11 mL per 250 mL of equilibration solution equilibrate the resin at 1 and 2

mg/L, respectively (M. Bisson, University of Quebec, 1984, pers. comm.). During equilibration, the solution was stirred continuously and neutralized to the desired pH using 0.1 N NaOH. Once the desired pH of the solution was reached and remained stable for 30 minutes, the resin was recovered by filtration and stored damp at 4° C until needed.

For the resin extraction of subsample B, 3 mg of the prepared resin was volumetrically measured using a Pasteur pipette that had been calibrated gravimetrically. The resin was transferred to subsample B and these subsamples were placed on a shaker table for 30 minutes. The subsamples were then filtered through 0.4 µm Nuclepore filters to remove the resin. A measured volume of each subsample was then transferred to a 6 mL polyethylene vial and the NLMAl was extracted with 8-hydroxyquinoline into MIBK as described above.

Concentrations of Al in the MIBK extracts were determined using graphite furnace, atomic absorption spectrometry (GFAAS). Aqueous solutions having known concentrations of Al were prepared from 1000 mg/L Atomic Spectral Standards (J. T. Baker Chemical Co., Phillipsburg, N.J.). Analytical standards were made from these known solutions using the 8-hydroxyquinoline/MIBK extraction as described above. Those samples having greater than 0.75 mg/L Al were diluted with MIBK (1 : 10) for the accurate determination of Al concentrations. A minimum of two GFAAS analyses per sample were made. Additional analyses were made in cases where the GFAAS absorbance values varied by greater than 5%. The mean absorbance value of all of the analyses of a sample was used to determine the concentration of the metal in that sample. Blanks were carried through the treatment procedures to determine metal contamination. Aluminum contamination was less than 0.01 mg/L.

5. Determination of Other Soil and Soil Solution Parameters.

Several soil and soil solution parameters were monitored to help characterize the chemical nature of the solid and liquid soil phases. It was also desireable to investigate factors that should influence the metal chemistry of the soil solution and the effects of treatment pH on that chemistry. Soluble organic matter, pH, and total dissolved Al are solution parameters that were of particular interest to this investigator. Solution concentrations of Ca, Mn, and Cu were analyzed in selected samples. The concentrations of exchangeable Al, Ca, Mn, and Cu, and soil pH are soil characteristics that were examined.

The pH of the soil solution was determined using a Cole-Parmer pH meter with a pH combination electrode with Ag/AgCl reference electrode. Dissolved organic matter (DOM) was estimated using absorbance at 250 nm (Stewart and Wetzel, 1981) using a Bausch and Lomb Spectronic 21 spectrophotometer. A 0.2 mL of sample was added to 2.0 mL 0.1 N NaOH (pH 13), shaken, and the absorbance was measured. This pH was chosen because it causes high dispersion of the organic matter and provides for high absorbance readings (Kumada, 1985). For the purposes of this study, only relative measurements of DOM were necessary for the comparison of treatment effects on soluble organic matter. Concentrations of total dissolved Al, Ca, Mn, and Cu in the solutions acidified to pH 1 with 1N HCl were measured using Inductively Coupled Plasma Emission Spectrometry (ICP).

To characterize the soil samples, exchangeable Al, Mn, Cu, and Ca were determined using a 1N KCl extractant solution (Thomas, 1982). Soil pH was determined using a pH combination electrode with Ag/AgCl reference electrode following McLean (1982).

B. Treatment Effects on Bioavailability of Aluminum

An implicit requirement of the metal toxicity hypothesis is that acid precipitation must increase the concentrations of the bioavailable species of the mobilized metals in the soil solution. This enhanced bioavailability should result in the increased uptake of the metals by the plants and be reflected by an increase in the concentrations of the metals in plant tissues. To determine if the bioavailability of Al is enhanced by acid precipitation, selected plant species and soils were treated with artificial precipitation of either pH 3.5 or 5.0, and the concentrations of Al in tissues from these plants were determined. Concentrations of foliar Ca were also measured to determine if Ca uptake was affected by acid precipitation.

Tree seedlings principally served as biomonitors of the effects of treatment pH on the bioavailability of Al. Red spruce (*Picea rubens* Sarg.) and loblolly pine (*Pinus taeda* L.) were chosen for this use in the spruce-fir and the oak-hickory forest soils, respectively. The red spruce was of particular interest because it is a species that is experiencing dieback in the northeastern United States (Siccama *et al.*, 1982) and has experienced a growth decline over the last 20 to 25 years in the Great Smoky Mountains (McLaughlin *et al.*, 1987). Loblolly pine was chosen to maintain a consistency in the use of a coniferous species in all of the soil types in this study.

The effect of treatment pH on Al concentrations in plant tissue was examined in field and greenhouse studies. Field studies were used to examine the treatment effects on metal bioavailability under natural forest conditions. Greenhouse studies allowed for the examination of treatment effects under more controlled conditions (increased soil homogeneity and elimination of plant-plant interactions) and permitted the use of a third treatment pH.

1. Field Studies.

Seedlings of selected tree species were planted on the field plots that were treated in the study of the effects of precipitation pH on Al chemistry. Two-year old red spruce seedlings were obtained from the Maine State Nursery, Passadumkaeg, Maine, and planted on the GSMNP plots in May, 1984 . Two-year old loblolly pine seedlings were obtained from the Environmental Sciences Division, ORNL, and planted on the ORNL plots in late March, 1984. The seedlings had a one-year equilibration period in the field soil before the artificial precipitation treatments commenced. Seedlings were treated contemporaneously with the soils that were examined in the field studies of soil solution Al. Twenty-four seedlings, of the appropriate species, were chosen randomly from a group of seedlings that were of similar size and vigor. These were planted on each plot in two circular patterns (16 seedlings in 2.5-m diameter circle and 8 in a 1-m diameter circle). The soil that was collected from the plots in the study of soil solution chemistry, was sampled in the intermediate area, with no samples taken within 25 cm of the seedlings. See Appendix A. 9 for a plan view of the spacing of the seedlings and the soil samples.

Seedlings and soils received the same artificial precipitation treatments (pH 3.5 or 5.0) that were administered to the field plots during the soil solution chemistry study. See the Treatment Effects of Soil Metal Chemistry section for the description of precipitation treatments. The whole seedlings were harvested at the close of the treatment period and prepared for elemental analysis.

Addtional plant species, that were indigenous to the field plots, served as additional biomonitors of the effects of treatment pH on the bioavailability of the metals. Tissue samples from these plants were collected at the close of the treatment period and analyzed for selected elements. Leaf tissue from fern (*Dryopteris sp.*) (n = 10) were collected from the spruce-fir forest field plots. Leaf tissue of hog peanut (*Amphicarpa*

bracteata (L.) Fernald) (n = 10) and Carolina buckthorn (*Rhamnus Caroliniana* Walt.) (n = 10) were collected from the oak-hickory forest plots at the MBW and WBW sites, respectively. This tissue was prepared for elemental analysis in the same manner as the red spruce and loblolly pine tissue.

2. Greenhouse Studies.

Soil from the zone of fine roots and overlying litter was collected adjacent to the plots at all of the three field sites. The soil was seived, mixed by hand, placed in 2-L pots, and covered with litter from the specific field site and planted with seedlings of the appropriate tree species. The red spruce and loblolly pine seedlings were obtained from the same sources as the seedlings that were planted in the field plots. The seedlings were grown in a greenhouse for 10 weeks. The 45 plants in each soil type that were the most uniform in size and vigor were then selected and randomly divided into three treatment groups. An additional thirty red spruce were later used in a follow-up experiment on the effects of treatment pH on metal bioavailability and rhizosphere chemistry. These seedlings were stored out-of-doors in a stand of short leaf pine for 14 months. They were then transplanted in 6-L pots which were prepared for the rhizosphere chemistry portion of the experiment. The specific pot preparation is described below in the Rhizosphere Chemistry section.

Seedlings were treated with artificial rain of pH 3.5, 4.1, or 5.0. The first and last pH values represent the extremes in rainfall pH and the second represents the mean in rainfall pH recorded at the Walker Branch Watershed, ORNL, during 1983 (G. M. Lovett, Oak Ridge National Laboratory, 1984, pers. comm.). The artificial precipitation also contained neutral salts at the mean concentrations recorded in the same study. Appendix A. 4 describes the chemistry of the artificial precipitation in detail. Rain treatments (2.5 cm per event) were applied over a one hour period , two or three times

a week using a rainfall simulator (Shriner, 1979). The frequency of treatment was such to prevent water stress to the plants. Red spruce seedlings were treated in two different experiments for 28 (initial study) and 46 weeks (follow-up study). Loblolly pine seedlings that were potted in Melton Branch and Walker Branch soils were treated for 28 and 30 weeks, respectively.

3. Treatment Effects on Seedling Growth and Physiology.

Effects of treatment pH on the growth of the different seedlings were monitored in the pine and initial spruce greenhouse experiments and in the spruce field experiment. Growth effects were not determined in the loblolly pine field experiments because of heavy deer(?) browse at both sites just prior to the end of the treatment period. The effect of treatment pH on selected physiological parameters in red spruce was monitored in the initial greenhouse red spruce experiment.

Measurements of stem height and diameter of the greenhouse pine and spruce (initial experiment) and field spruce seedlings were made at the start and the end of the treatment periods to monitor for effects of treatment on seedling growth.

At the end of the treatment period, the seedlings were harvested and partitioned into large (> 0.5 mm) and fine roots, old and new (initiated during treatment) needles, and old and new (initiated during treatment) stems. Needle and stem fractions were rinsed in distilled water. Roots were washed in a 5% Tween 40 (Polyoxyethylene 20 sorbitan monopalmitate) solution on a shaker table for fifteen minutes, followed by six rinses in distilled water. Roots of both tree species were then partitioned into the two size fractions. Plant tissues were dried at 75° C for 48 hours, weighed, and stored in polyethylene bags until they were prepared for chemical analysis.

Transpiration and net photosynthetic rates of the red spruce (initial greenhouse experiment) were measured at week 22 of the treatment period using a portable gas-

exchange system with a 0.25-L chamber (Model LI 6000 Photosynthetic System, Li-Cor, Inc. Lincoln, Nebraska). Measurements were made on new growth on the distal portions of two upper branches on each of ten plants per treatment. Only new needle growth with complete elongation was used.

4. Treatment Effects on Plant Tissue Concentrations of Al.

Evidence suppports the relationship between tissue concentrations and bioavailability (solution concentrations) of Al. Schier (1985) found that the concentrations of Al in both needles and roots of red spruce increased with increased concentrations of Al in hydroponic solutions. Lord (1982) found that foliar concentrations of Al correlated with root concentrations of Al in red spruce growing on Camel's Hump, Green Mountains, Vermont. These studies thus support the use of either needle or root tissue as a bioassay for Al bioavailability. Roots of red spruce contain greater concentrations of Al than do the needles (Schier, 1986 and Lord, 1982); however, the roots were not chosen as the tissue for analysis in this investigation because of considerations of potential metal contamination. Root-associated aluminum has been found as a precipitate on the root surface (Rasmussen,1968) and in the apoplast (Schaedle *et al.*, 1986). In those studies, the total concentrations of Al in the root analyses did not represent only biologically-incorporated Al and, therefore, did not accurately reflect Al bioavailability. It is also questionable as to whether root washing techniques are adequate to remove all of the particle contaminants from the surface of, or cracks in, the roots or the particles associated with any external mycorrhizal tissue that is attached to the root. Indeed, in this study, the washing technique did not adequately remove all particulate contaminants. For this reason, the roots were not chosen as the tissue to monitor for the effects of treatment on the bioavailability of Al.

5. Tissue Preparation and Elemental Analysis.

Plant tissues were prepared for analysis using a dry ashing at 400°C for 48 hours, followed by ash dissolution in 20% HNO_3 (Baes and McLaughlin, 1986). Samples of NBS standard Pine Needles were included in each set of samples to monitor the per cent recovery of Al. The solutions of plant tissue digests were analyzed by ICP at the Institute of Ecology, University of Georgia.

C. Treatment Effects on Rhizosphere Chemistry of Aluminum

The soil solution chemistry of Al in the rhizosphere and the bulk soil were compared to determine the influence of the plant on the soil solution chemistry of Al. This relationship was compared among treatments to determine the effects of precipitation pH on this relationship. The tree seedlings that were treated in the field (spruce) and in the greenhouse (loblolly pine and red spruce--follow-up experiment) in the bioavailability studies were used. The treatment of these seedlings was described previously in the Treatment Effects on Bioavailability of Al methods section.

1. Rhizosphere Collection and Preparation.

Rhizosphere soil was considered to be the soil that adhered to the fine roots of the plants following a light shaking (as done by Smiley, 1974). Following the treatments with artificial precipitation, the plants were dug up or unpotted, and the rhizosphere and bulk (nonrhizosphere) soil were collected. Soil water was collected from these soil samples using centrifugation and the soil solution chemistry of Al was determined using the previously-described speciation methods. Two types of preparation of the rhizosphere and bulk soil were used--equilibration with artificial precipitation treatment solutions while the plant was still in the pot, or with distilled, deionized water after the soil was collected. In the greenhouse studies, the soil was collected after

a 24-hour equilibration period following the watering of the plants with the artificial precipitation on the rainfall simulator. The soil was then collected, centrifuged, and the soil solution collected. In the field study, the soil was stored in polyethylene bags at 4°C for one week following collection. The soil was then placed in 25 mL beakers, wetted with distilled, deionized water, drained for one hour, and then equilibrated in the beaker for 24 hours. The soil was then centrifuged and the equilibrium soil solution was collected.

2. Studies.

a. Field study: red spruce. Effects of treatment on the rhizosphere chemistry of Al were examined in the red spruce that were grown on the GSMNP field plots. Two weeks after the end of the field treatments, the seedlings were carefully dug up by hand. The rhizosphere soil was collected in the field, placed in polyethylene bags, and stored in the laboratory at 4° C until the soil solution was extracted. No bulk soil was collected in the field, so the comparison was only of the effect of treatment on the rhizosphere chemistry of the seedlings. Soil solution chemistry of Al in these rhizosphere samples was determined using the equilibration with distilled water method as described above.

b. Greenhouse studies. In the greenhouse experiments, bulk and rhizosphere soils were collected which permitted the comparison of both treatment and plant effects on the soil solution chemistry of Al in the rhizosphere. Soils were collected at end of the treatment periods of each type of seedling. Techniques used in the preparation and examination of the soils varied between experiments due to refinements that were made during the course of this study. Descriptions of the methods of preparation used in the different rhizosphere experiments follow:

Red spruce (follow-up experiment). In this experiment, a portion of the potting soil was isolated from the roots to better differentiate rhizosphere and non-rhizosphere

soil. Three year-old spruce seedlings were potted in soil from the GSMNP field site in 6- L pots. Polyethylene tubes (5-cm diameter by 10-cm height) with fiberglass mesh (7 mesh/cm) glued to the bottom were used to isolate a portion of the soil in the pot from the plant roots. During the planting of the seedlings, a tube was filled with soil and inserted into the soil in each pot. The tube was positioned such that the top of its soil was situated flush with top of the soil in the pot (Appendix A. 10). Fiberglass mesh prevented the penetration of plant roots into the soil that was in the tube and permitted water drainage. The soil was collected after a 48-hour equilibration following the final treatment (week 46). The nonrhizosphere soil was removed from the tube and the rhizosphere soil was collected from the fine roots by shaking the plant.

Pine seedlings. Soil was collected at 24 hours following the final treatment with artificial precipitation (week 30). Bulk soil, which contained some roots, was collected from the top 4 cm of soil in each pot using a push tube that was used to collect soil samples from the field plots. The plant was then depotted and the rhizosphere soil was collected from the fine roots after it was separated from the nonrhizosphere soil by shaking. Samples were then centrifuged and the soil solution was collected.

D. Statistical Analysis of the Data

Data from the different studies are presented as mean and standard error of the mean. The data from the different studies were statistically analyzed by analysis of variance using a microcomputer program (Statview, D. Feldman and J. Gagnon, 1984). Statistical comparisons of chemical parameters were made among treatments in the individual laboratory, greenhouse, and field experiments. Comparisons were also made between rhizophere and bulk or among nonrhizosphere soils in the greenhouse experiments. The chosen level of statistical significance was $p \leq 0.05$; however, it is also noted in the text when parameters differed at $p \leq 0.10$.

III. RESULTS

A. Laboratory Equilibration Study

1. Solution Chemistry.

a. Solution pH. For the different soils, over the 15 weeks of the study, the ranges in mean pH (as calculated from mean H^+ activities) of the soil water extracts that were collected through day seven following dosing with the pH 5.0 treatment were: Great Smoky Mountains-Collins Gap soil (pH 3.04-3.73), Great Smoky Mountains-Indian Gap soil (pH 3.06-3.75), Adirondack Mountains-unhealthy site soil (pH 3.36-4.36), and Adirondack Mountains-healthy site soil (pH 3.54-4.09) (Appendixes B. 1-6). Solution pH in all four soils decreased over time following treatment and also decreased in time-comparable samples over the course of the experiment.

Effects of treatment pH on the pH of solution extracts are presented for soils from the Adirondack Mountains-healthy site and the Great Smoky Mountains-Collins Gap site, with the latter soil being somewhat representative of the response of the Great Smoky Mountains-Indian Gap and the Adirondack Mountains-poor site soils to treatment pH (Fig. 2). The pH 3.5 treatment lowered solution pH in the Great Smoky Mountains soils and the Adirondack Mountains-poor site soil during all three monitoring periods. while it only decreased solution pH in the Adirondack Mountains-healthy site soil during week 15. Depending upon the monitoring period and soil type, the duration in which the pH 3.5 treatment reduced solution pH ranged from hour one to day one or up through day seven.

b. Dissolved organic matter. For the different soils, the ranges in absorbance values of DOM (correlative with DOM concentrations) in soil water extracts that were collected through day seven following dosing with the pH 5.0 treatment were: Great Smoky Mountains-Collins Gap soil (0.07-0.21), Great Smoky Mountains-Indian Gap

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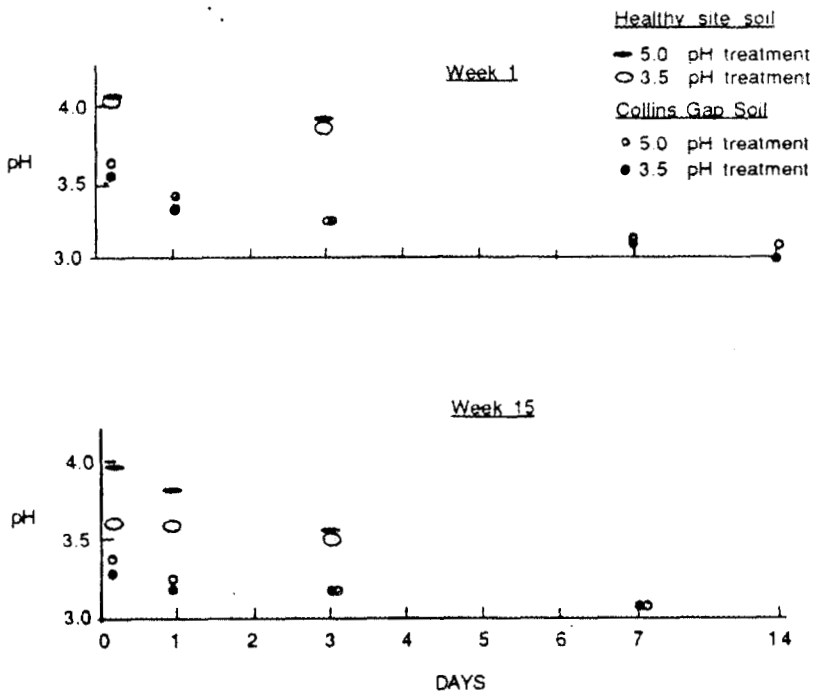

Fig. 2. Effect of treatment pH on pH of soil water in soil samples: Adirondack Mountains-healthy forest site and Great Smoky Mountains-Collins Gap site, weeks 1 and 15 of the study. Dosing a day 0.

soil (0.07-0.23), Adirondack Mountains-unhealthy site soil (0.13-0.32), and Adirondack Mountains-healthy site soil (0.20-00.37) (Appendixes B. 1-6).

Following treatment, DOM absorbance values in solutions of all four soils increased from hour one to day one and then decreased through the end of each monitoring period. The pH 3.5 treatment reduced DOM absorbance values in solutions of all soils during all monitoring periods for which there were data. This effect of treatment pH on DOM is represented by the Great Smoky Mountains-Collins Gap soil (Fig. 3).

c. Monomeric Al.

Total monomeric Al (TMAl). The pH 3.5 treatment affected TMAl concentrations in the soil water extracts of the soils in two manners. It tended to significantly decrease concentrations of TMAl immediately following treatment dosing through day three and significantly increased concentrations of TMAl from day three to the end of the specific monitoring period ($p \leq 0.05$; unless otherwise stated, all differences due to treatment that are subsequently mentioned in the Results chapter were statistically significant at $p \leq 0.05$.) (Figs. 4-7). Depending upon the soil, the pH 3.5 treatment significantly decreased concentrations of TMAl in all four of the soils by up to 33% from hour one, or day one, through day three during weeks 10 or 15. By weeks 10 or 15, the acidic treatment also significantly increased concentrations of TMAl in all soils by up to 60% at different times from day three through the end of the monitoring period. The magnitude of the latter treatment effect increased in all four soils with increasing duration of treatment and was less for the Adirondack Mountains soils than the Great Smoky Mountains soils. Individual data are presented in Appendixes B. 1-6.

Nonlabile monomeric Al (NLMAl). Effects of treatment on the concentration of NLMAl varied both among soils and monitoring periods (Figs. 4-7). However, the pH 3.5 treatment significantly reduced concentrations of NLMAl in solutions from all four soils at different times from hour one through day three. The Adirondack Mountains-

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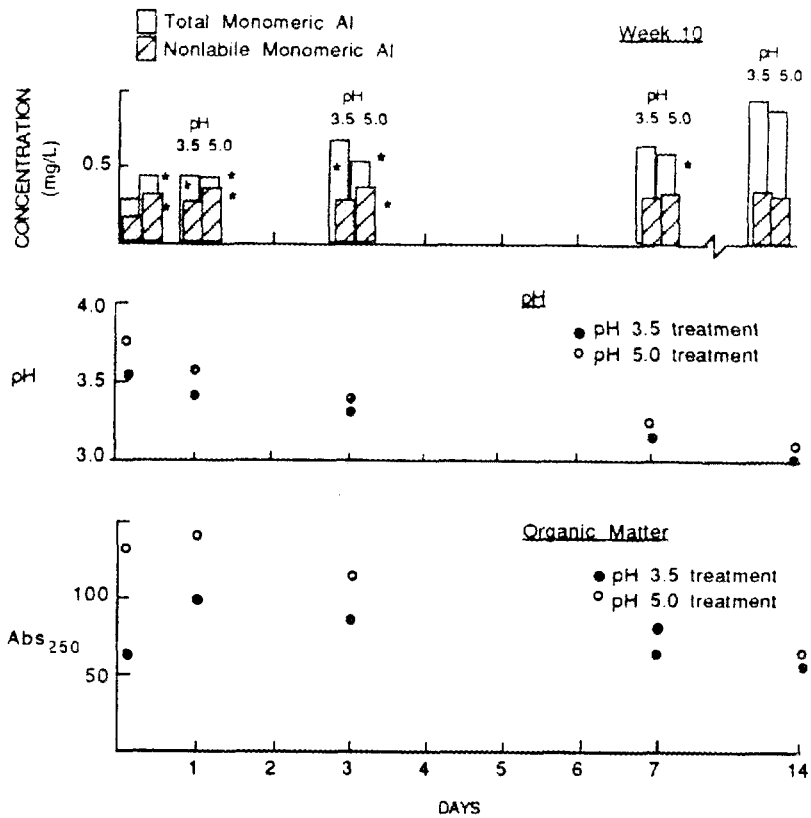

Fig. 3. Effects of treatment pH on solution pH, DOM, and Al parameters in Collins Gap soil, Great Smoky Mountains during week 10 of laboratory equilibration study. Asterisks indicate significant differences ($p \leq 0.05$) between treatments for indicated parameter. Asterisks within rectangle indicate significant difference in LMAl.

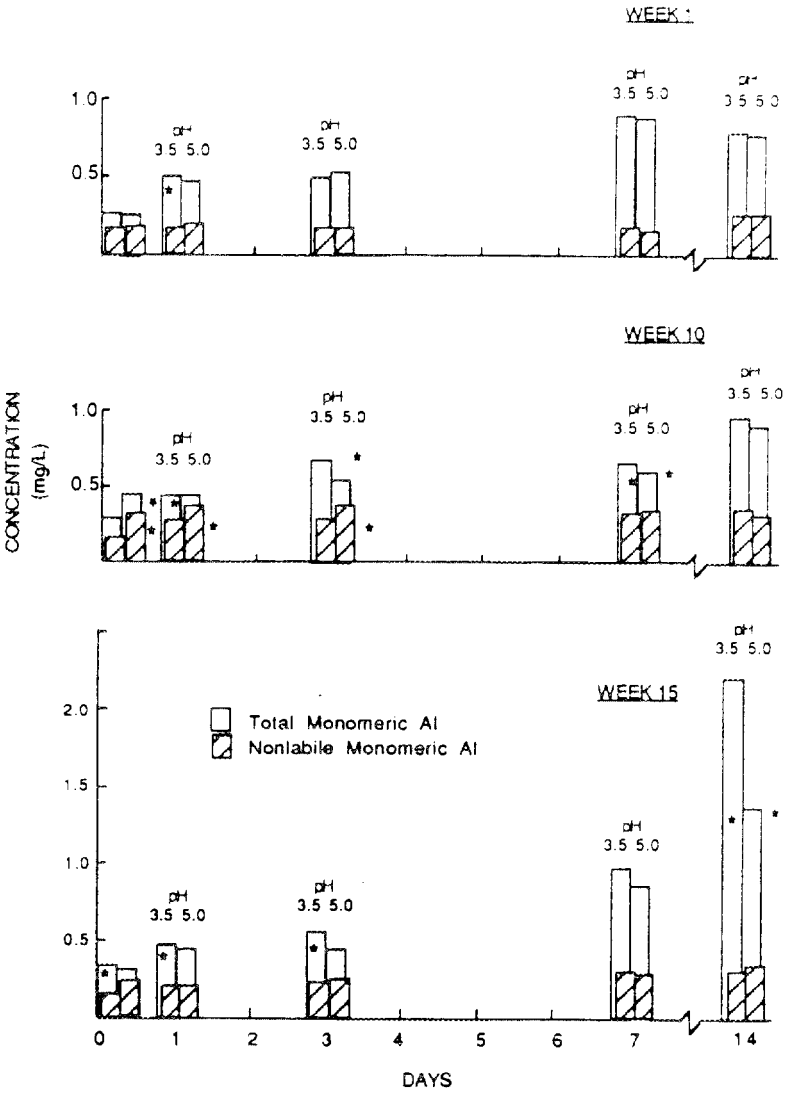

Fig. 4. Aluminum chemistry in soil water extracts from Collins Gap soil, Great Smoky Mountains, as affected by duration and pH of treatment. Dosing at day 0. Asterisks indicate significant differences ($p \leq 0.05$) between treatments for indicated parameter. Asterisks within rectangle indicate significant difference in LMAl.

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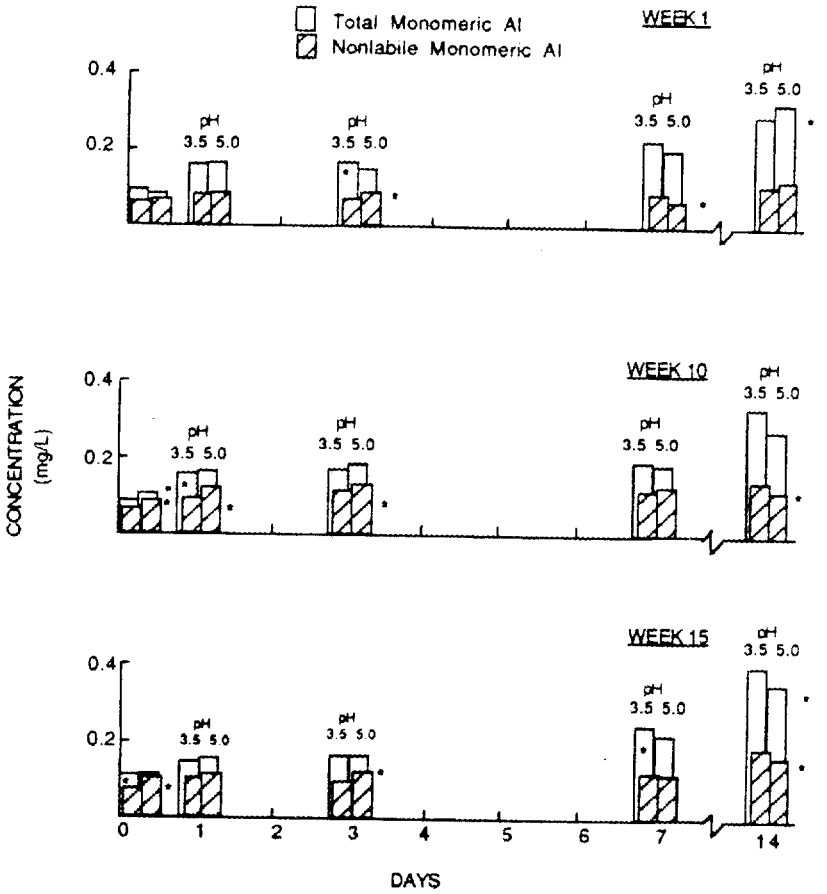

Fig. 5. Aluminum chemistry in soil water extracts from Indian Gap soil, Great Smoky Mountains, as affected by duration and pH of treatment. Dosing at day 0. Asterisks indicate significant differences ($p \leq 0.05$) between treatments for indicated parameter. Asterisks within rectangle indicate significant difference in LMAI.

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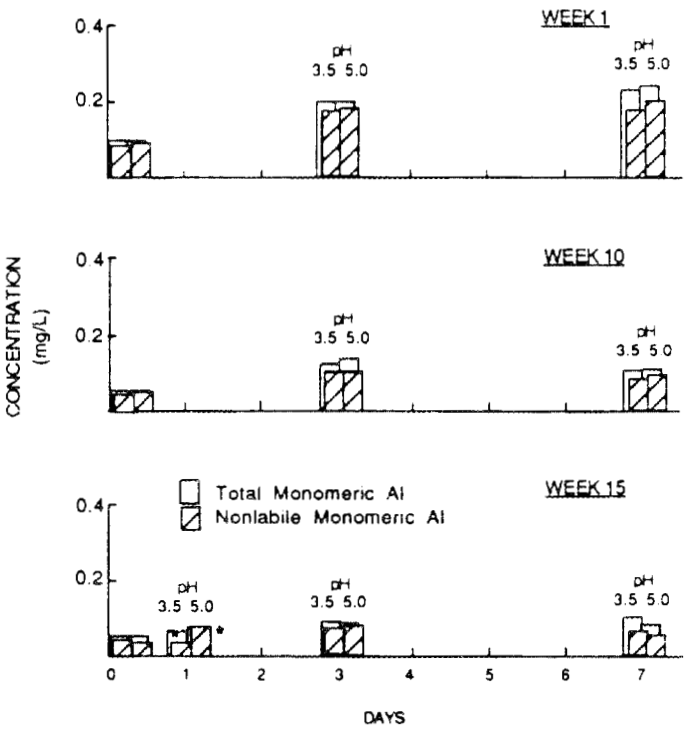

Fig. 6. Aluminum chemistry in soil water extracts from healthy forest location soil, Adirondack Mountains, as affected by duration and pH of treatment. Dosing at day 0. Asterisks indicate significant differences ($p \leq 0.05$) between treatments for indicated parameter. Asterisks within rectangle indicate significant difference in LMAl.

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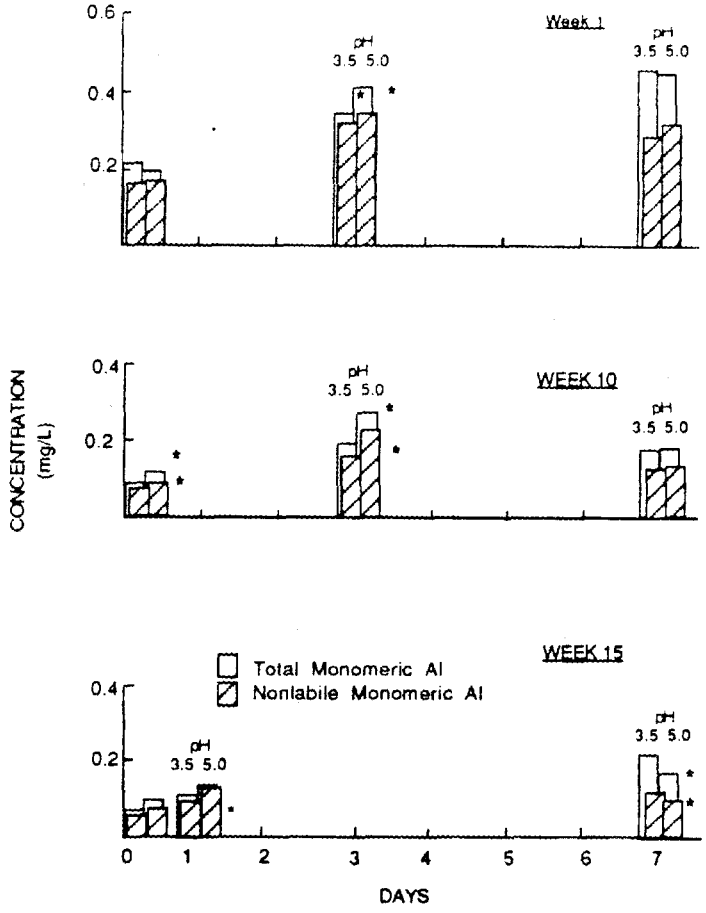

Fig. 7. Aluminum chemistry in soil water extracts from unhealthy forest location soil, Adirondack Mountains, as affected by duration and pH of treatment. Dosing at day 0. Asterisks indicate significant differences ($p \leq 0.05$) between treatments for indicated parameter. Asterisks within rectangle indicate significant difference in LMAl.

healthy site soil was the soil that was least affected by treatment; the pH 3.5 treatment only significantly reduced the concentration of NLMAl during week 15. This effect of was present in the other three soils by week 10.

Labile monomeric Al (LMAl). The pH 3.5 treatment significantly increased concentrations of LMAl in solutions of the Great Smoky Mountains soils (up to 90%) at different times during all three monitoring periods, with the effect most evident in the Collins Gap soil (Figs. 4-7, LMAl = TMAl - NLMAl). For the Adirondack Mountains soils, the pH 3.5 treatment only significantly increased the concentration of LMAl in the healthy site soil at day one of week 15. The pH 3.5 treatment significantly decreased the concentration of LMAl in the Adirondack-unhealthy site soil at day three, of the initial week of treatment.

NLMAl/TMAl. Acidic treament affected NLMAl/TMAl values in soil water extracts of the soils to differing degrees, with the greatest effect occurring in the Great Smoky Mountains soils. The pH 3.5 treatment decreased solution NLMAL/TMAl values in all four soils by week 10 or 15. NLMAl/TMAl values in solutions of both Adirondack soils were only significantly decreased by acidic treatment at day one during week 15. Depending upon the soil and monitoring period, the acidic treatment significantly decreased NLMAL/TMAl values in solutions of the Great Smoky Mountain soils (up to 60%) at hour one through day three.

d. Relationships of solution chemistry parameters. Relationships between treatment pH, solution pH, DOM, and solution Al in the soils are presented using the Collins Gap soil (week 10) as an example (Fig. 3). Under both pH treatments, DOM and solution pH decreased from day one on following dosing. Over time following treatment dosing, concentrations of NLMAl increased under the pH 3.5 treatment and decreased slightly under the pH 5.0 treatment. Concentrations of TMAl increased and NLMAl/TMAl values decreased correspondingly over time. Concentrations of LMAl increased in both

treatments with time. Correlation coefficients for the different solution parameters from day one through day 14 are presented in Table 1. Notable effects are that the LMAl-NLMAl, NLMAl-pH, and NLMAl-DOM relationships were altered under the pH 3.5 treatment.

e. Total dissolved Al, Ca, Mn, and Cu. The pH 3.5 treatment significantly affected concentrations of total dissolved Al in three of the soils, and the effects varied with soil and monitoring period. The pH 3.5 treatment significantly decreased concentrations of total dissolved Al in solutions of two soils during the week following the initial treatment, and increased it in one soil during this initial week and week 15 (Table 2). The pH 3.5 treatment significantly increased solution concentrations of Ca and Mn in only the Adirondack Mountains soils during week 15. Solution concentrations of Cu in all of the soils were not affected by treatment pH (Appendixes B. 7 and 8).

2. KCl-Extractable Soil Chemistry.

The pH 3.5 treatment did not significantly affect concentrations of extractable Al or Cu in any of the soils (Table 3), but did significantly decrease the concentration of extractable Ca in the Great Smoky Mountains-Indian Gap soil by week 15. There was no significant effect of treatment on extractable Ca/Al in any of the soils. The pH 3.5 treatment significantly decreased concentrations of extractable Mn in two of the soils (Appendixes B. 9 and 10).

B. Rhizosphere and Plant Tissue Chemistry.

1. Greenhouse Study: Red Spruce.

a. Rhizosphere chemistry.

Soil solution chemistry. Results of the pH 5 treatment are considered to be representative of effects of the plant on the examined parameters of soil chemistry

Table 1. Effect of Treatment pH on Correlation Coefficients of Solution Variables for Great Smoky Mountains-Collins Gap Soil, Week 10.

	TMAI	NLMAI	NLMAI/TMAI	$[H^+]$	DOM
TMAI		0.89[1], -0.95[2]	-0.92,-0.99	0.94, 0.98	-0.60, -0.86
NLMAI			-0.67, 0.94	0.98, -0.98	-0.77, 0.91
NLMAI/TMAI				-0.74, -0.99	0.50, 0.94
LMAI	0.99, 0.99	0.81, -0.96	-0.94, -0.98	0.89, 0.99	-0.48, -0.87
$[H^+]$					0.67, -0.93

[1]pH 3.5 treatment
[2]pH 5.0 treatment

Table 2. Effects of Treatment pH on Concentrations of Total Dissolved Al, Ca, Cu, and Mn in Solutions from the Laboratory Equilibration Study of Spruce-Fir Forest Soils.

Treatment	pH 3.5				pH 5.0			
Element	Al	Ca	Mn	Cu	Al	Ca	Mn	Cu
				mg/L				
Adirondacks-healthy site								
Week 0, Day 7	23[1]*	100a[3]	3.1	0.20	39*[4]a	90a	4.4a	0.61
	2[2]	18	0.1	0.11	2	18	1.0	0.30
Week 15, Day 7	18*	72b*	3.5*	0.22	12*b	44b*	2.1b*	0.93
	2	4	0.2	0.09	1	5	0.3	0.14
Adirondacks-unhealthy site								
Week 0, Day 7	32*a	9a	4.4a	0.13a	48*	82a	4.2a	0.27
	4	3	0.2	0.00	7	2	0.2	0.05
Week 15, Day 7	19b	61b*	3.1b*	0.33b	27	47b*	2.1b*	0.21
	3	6	0.5	0.20	5	2	0.3	0.03
Smoky Mountains-Indian Gap								
Week 0, Day 7	25a*	65a	3.0a	0.24	18*	59	2.7a	0.11
	1	1	0.1	0.07	6	3	0.1	0.05
Week 15, Day 7								
	12b	47b	1.9b	0.11	14	45	1.8b	0.14
	1	1	0.1	0.02	1	8	0.4	0.05
Smoky Mountains-Collins Gap								
Week 0, Day 7	30a	129a	6.6a	0.42	32a	121a	6.3a	0.14
	3	2	0.4	0.21	1	3	0.1	0.04
Week 15, Day 7	17b	51b	1.9b	0.12	21b	55b	2.2b	0.17
	2	2	0.1	0.08	5	10	0.4	0.05

[1]mean (n=3)

[2]standard error of the mean

[3]Probability of statistically significant effect of time at $p \leq 0.05$ is indicated when letters within a column for a given soil type are different.

[4]Probability of statistically significant effect of treatment pH at $p \leq 0.05$ is indicated with *.

Table 3. Effects of Treatment pH on Concentrations of 1N KCl-Extractable Elements in Solutions from the Laboratory Equilibration Study of Spruce-Fir Forest Soils.

	Al	Ca	Mn	Cu	Ca/Al[1]
			mg/100g soil		
Adirondacks-healthy site					
Initial	2.3[2]a[4]	294	11.0	0.14	58a
	0.2[3]	5	0.8	0.02	10
Week 15: Day 7					
Treatment pH 3.5	7.7b	270	9.5	0.22	15b
	0.5	21	0.8	0.11	4
Treatment pH 5.0	6.9b	285	10.4	0.14	18b
	0.5	14	0.5	0.05	5
Adirondacks-unhealthy site					
Initial	7.1a	267	12.6a	0.15	17a
	0.6	36	2.2	0.02	
Week 15: Day 7					
Treatment pH 3.5	22.5b	213	7.1b	0.12	4b
	1.2	6	0.5	0.02	2
Treatment pH 5.0	20.4b	242	8.6b	0.17	5b
	0.8	53	1.2	0.05	2
Smoky Mountains-Indian Gap					
Initial	41	137a	4.1a	0.15	1.5
	2	3	0.6	0.05	0.2
Week 15: Day 7					
Treatment pH 3.5	46	111b	2.7b	0.12	1.1
	2	2	0.06	0.02	0.1
Treatment pH 5.0	45	119c	3.3c	0.15	1.2
	2	3	0.1	0.03	0.2
Smoky Mountains-Collins Gap					
Initial	83	90	3.2a	0.08	0.5
	3	18	0.3	0.05	0.1
Week 15: Day					
Treatment pH 3.5	85	66	1.5b	0.12	0.3
	5	5	0.2	0.03	0.1
Treatment pH 5.0	64	68	1.7b	0.09	0.5
	12	21	0.5	0.02	0.1

[1]calculated from meq Ca/meq Al

[2]mean (n= for week 15, n=7 for week 0)

[3]standard error of the mean

[4]Probability of statistically significant effect ($p \leq 0.05$) of time/treatment is indicated when letters within a column for a given soil are different.

under non-acidic precipitation conditions. Mean concentrations of TMAl, NLMAl, and total dissolved Al, and DOM absorbance values were all significantly greater, each by at least 50%, and solution pH was significantly lower ($p \leq 0.10$) in soil solutions of the rhizosphere soil than in those of the nonrhizosphere soil (Table 4). Although the LMAl concentration was 58% higher in the rhizosphere soil than that in the nonrhizosphere soil, this difference was not statistically significant. Individual data are presented in Appendix B. 11.

Due to high variability in chemistry among solution samples, it cannot be determined if concentrations of total dissolved Ca, Mn, Fe, and Cu differed between the rhizosphere and nonrhizosphere soils (Appendix B. 12).

KCl-extractable soil chemistry. In seedlings that received the pH 5.0 treatment, there were no statistically significant differences in concentrations of extractable Al, Cu, or Ca, or in extractable Ca/Al values between rhizosphere and nonrhizosphere soils (Table 5). The concentration of extractable Mn was significantly lower by 63% in rhizosphere soil than that in nonrhizosphere soil. Individual data are presented in Appendix B. 13.

Treatment effects on solution chemistry. There were no significant effects of treatment pH on TMAl concentrations in soil solutions of the nonrhizosphere soil. The pH 3.5 and 4.1 treatments decreased NLMAl concentrations by 25% and 32% ($p \leq 0.10$) with respect to the effect of the pH 5.0 treatment, and the pH 3.5 treatment significantly increased the concentration of LMAl by 100% compared with the effect of the pH 5.0 treatment. Mean absorbance values of DOM decreased with decreasing pH of treatment, but the differences were not statistically significant. There were no significant effects of treatment pH on concentrations of total dissolved Al, Ca, Mn, or Cu.

Although the difference was not statistically significant, TMAl concentrations in rhizosphere soil solutions were approximately 25% greater under the pH 3.treatment

Table 4. Effects of Treatment pH on Selected Chemical Parameters of Soil Solution of Rhizosphere of Red Spruce Seedlings: Greenhouse Study.

	TMAl	NLMAl	LMAl	Total Al	NLMAl/TMAl	pH[1]	DOM[2]
		mg/L					
Nonrhizosphere Soil							
pH 3.5	0.61[3]a[5]	0.31cd	0.55f	29.08h	0.55j*	3.37k*	0.215m
	0.06[4]	0.09	0.06	2.89	0.08	0.02	0.015
pH 4.1	0.45a	0.28c	0.17g	24.90h	0.69j*	3.56l*	0.243m
	0.09	0.02	0.07	1.34	0.08	0.04	0.019
pH 5.0	0.67a	0.41d	0.26g	25.77h	0.66j*	3.48kl*	0.294m
	0.09	0.05	0.09	4.38	0.10	0.11	0.047
Rhizosphere Soil							
pH 3.5	1.28b	0.70e	0.58f	33.14hi	0.57j	3.26l	0.548n
	0.26	0.11	0.22	1.55	0.06	0.05	0.131
pH 4.1	0.97b	0.76e	0.23g	28.23h	0.79j	3.45k*	0.483n
	0.09	0.10	0.12	1.96	0.09	0.04	0.023
pH 5.0	1.03b	0.61e	0.41fg	39.14i	0.64j	3.32kl*	0.456n
	0.12	0.04	0.07	2.70	0.07	0.06	0.070

[1]mean pH calulated from mean $[H^+]$

[2]absorbance at 255 nm

[3]mean (n = 10, in all cases except Total Al where n = 4)

[4]standard error of the mean

[5]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column are different.

*indicates significant plant (pH) and treatment effect (NLMAl/TMAl) at $p \leq 0.10$.

Table 5. Effects of Treatment pH on Selected KCl-Extractable Elements in Rhizosphere and Nonrhizosphere Soils of Red Spruce Seedlings: Greenhouse Study.

Treatment	Al	Ca	Cu	Mn	Ca/Al
		mg/100g soil			(meq)
Nonrhizosphere Soil					
pH 3.5	76a[1]	157c	0.15f	2.49h	0.94j*
	5[2]	15	0.01	0.14	0.09
pH 4.1	58ab	187c	0.15f	2.88h	1.46k*
	19[3]	19	0.01	0.33	0.12
pH 5.0	63b	192c	0.15f	2.91h	1.37k*
	3	10	0.01	0.39	0.17
Rhizosphere Soil					
pH 3.5	72ab	167c	0.13fg	1.43i	1.04j*
	5	21	0.01	0.20	0.18
pH 4.1	65ab	192c	0.12g	1.35i	1.34k*
	3	20	0.01	0.36	0.12
pH 5.0	66ab	195c	0.17f	1.05i	1.32k*
	4	13	0.02	0.14	0.11

[1]mean (n = 10)
[2]standard error of the mean
[3]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column are different.
* indicates significant effects at $p \leq 0.10$.

than under either of the other two treatments. The concentration of LMAl was significantly reduced by more than 50% under the pH 4.1 treatment compared with the effects of the pH 3.5 treatment. Mean absorbance values of DOM increased with decreasing pH of treatment, which was the reverse of the relationship that occurred in the nonrhizosphere soil solution. The concentration of total dissolved Al was significantly reduced under the pH 4.1 treatment compared with the effects of the pH 5.0 treatment. There were also no apparent effects of treatment on concentrations of total dissolved Ca, Mn, or Cu.

Treatment effects on KCl-extractable chemistry. The pH 3.5 treatment significantly increased the concentration of extractable Al by 27 and 19% and decreased the concentration of extractable Ca by 19 and 23% in the nonrhizosphere soil in comparison with the pH 4.1 and 5.0 pH treatments ($p \leq 0.05$). Extractable Ca/Al was also significantly decreased by 30% under the pH 3.5 treatment.

There was no significant effect of treatment pH on the rhisozphere concentration of extractable Al. Although the concentration of extractable Ca was reduced by 15% under the pH 3.5 treatment relative to that under the other two treatments, this difference was not statistically significant. The pH 4.1 treatment significantly reduced the concentration of extractable Cu (28%) with respect to the effect of the pH 5.0 treatment. Although not statistically significant, concentrations of extractable Mn increased with decreasing treatment pH. Exchangeable Ca/Al was significantly lower ($p \leq 0.10$) under the pH 3.5 treatment than under the other two treatments.

b. Plant parameters.

Physiological, growth, and biomass parameters. There were no treatment effects on the rates of CO_2 assimilation and transpiration of red spruce in the initial greenhouse experiment (Appendixes B. 14 and 15). During the 28-week treatment period, two flushes of new needle growth occurred in all seedlings of the three treatment groups.

The first occurred at one month and was synchronous across all treatments. The second occurred in the pH 3.5 treatment group at 18 weeks and in the pH 4.1 and 5.0 treatment groups at 22 weeks. Chlorosis was present to varying degrees in the needles of terminal shoots in all treatment groups by weeek 20. The degree of chlorosis by treatment decreased in the following order: pH 4.1 > pH 5.0 > pH 3.5 (Appendix B. 16).

Height growth increment during the treatment period decreased with decreasing pH of treatment (Table 6). There was no effect of treatment on diameter growth increment. The individual data are presented in Appendix B. 17.

The pH 3.5 treatment increased biomass of new needles by 40% and new wood by 85-100% and decreased fine roots by 20% compared with effects of the other treatments. Although fine root biomass decreased with decreasing treatment pH, there was no apparent stunting of fine roots--indicative of Al toxicity--in any treatment group. The pH 3.5 treatment increased the ratio of shoot biomass to root biomass by 45% relative to that under the other treatments. The ratio of new needle biomass to new wood biomass (twigs) decreased with decreasing treatment pH (pH 3.5: mean = 1.87 g, s e = 0.25; pH 4.0: 2.52 g, 0.14; pH 5.0: 2.77 g, 0.28; pH 3 < pH 4.5, $p \leq 0.05$).

Comparisons of biomass or growth parameters between treatments were not made in the follow-up greenhouse experiment of red spruce. Unlike the initial greenhouse experiment using red spruce, the different treatments did not produce chlorosis or differences in phenology of bud break in the seedlings. There was also no new needle growth in the seedlings during the treatment period.

Foliar elemental chemistry: red spruce (follow-up study). Since there was no new needle growth during the treatment period, the needles that were produced prior to treatment were harvested and analyzed for concentrations of Al and other elements. There were no significant effects of teatment on concentrations of Al, Ca, and Mn, and Ca/Al in the foliage of the seedlings (Table 7). Contrary to the results of the field study,

Table 6. Effects of Treatment pH on Growth and Biomass (g) Parameters of Red Spruce Seedlings Treated in the Greenhouse (Initial Red Spruce Experiment).

Treatment	$\Delta Ht/Ht_{in}$[1]	Needles-1[2]	Needles-2[3]	ΣNeedles	Wood-1[2]	Wood-2[3]	ΣWood
pH 3.5	0.15a[6]	2.42[4]c	2.45d	5.02f	1.38h	1.15i	2.53k
	0.02	0.27[5]	0.50	0.50	0.12	0.23	0.27
pH 4.1	0.18b	2.74c	0.74e	3.51g	1.26h	0.26j	1.36l
	0.01	0.20	0.18	0.18	0.10	0.06	0.07
pH 5.0	0.21b	2.89c	0.45e	3.33g	1.16h	0.12j	1.27m
	0.03	0.32	0.21	0.30	0.12	0.06	0.12

Treatment	(ΣWood+ΣNeedles)/Roots	ΣRoots	Fine Roots	FineRoots/ΣRoots	ΣWt
pH 3.5	3.82n	5.28p	1.47q	0.28r	23.1s
	0.36	0.82	0.21	0.02	2.6
pH 4.1	2.57o	5.90p	1.88q	0.30r	20.7s
	0.15	0.53	0.30	0.03	2.0
pH 5.0	2.65o	5.83p	1.98q	0.33r	20.9s
	0.16	0.22	0.26	0.03	1.49

[1] $\Delta Ht/Ht_{in}$ = Height growth increment/Height initial
[2] biomass increment of first flush of foliage
[3] biomass increment of second flush of foliage
[4] mean (n=10)
[5] standard error of mean
[6] Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column are different.

Table 7. Mean Concentrations of Selected Elements in Needle Tissue of Red Spruce (Follow-up Experiment) Grown in Greenhouse as Affected by Treatment pH.

Treatment	Al	Ca	Mn	Cu
		mg/Kg		
pH 3.5	130[1]a[3]	28447b	7149c	14e
	6[2]	2858	629	1
pH 4.1	133a	28394b	6585d	16e
	13	2556	394	1
pH 5.0	134a	30083b	7487c	22f
	8	2942	777	1

[1]mean (n = 10)
[2]standard error of the mean
[3]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column are different.

both acidic treatments significantly reduced the foliar concentration of Cu by approximately 30%. The individual data are presented in Appendix. 18.

2. Field Study: Spruce-Fir Forest Field Plot Species.

a. Treatment effects on rhizosphere chemistry. There were no statistically significant effects of treatment on the soil solution chemistry of TMAl, NMAl, LMAl, DOM, or pH in the rhizosphere soils of the red spruce seedlings that were treated on thefield plots at the spruce-fir forest site (Table 8). There was also no significant effect of treatment on concentrations of extractable Al, Ca, Cu, or Mn in the rhizosphere soils. Individual data are presented in Appendixes B. 19 and 20.

b. Treatment effects on growth and biomass of red spruce seedlings. There were no effects of treatment pH on any measured parameter of growth or biomass in the red spruce seedlings that were treated on the field plots (Table 9). There was also no apparent stunting of the fine roots, chlorosis, or any other visible symptoms that would indicate differential effects of treatment pH on the seedlings. Individual data are presented in Appendixes B. 21-23.

c. Foliar elemental chemistry of red spruce and fern. There was no effect of treatment on foliar concentrations of Al in red spruce seedlings or fern (Table 10). Foliar concentration of Ca in red spruce was not affected by treatment. However, the pH 3.5 treatment significantly increased the foliar concentration of Ca in fern by 40%. Foliar Ca/Al in red spruce was not affected by treatment, while the pH 3.5 treatment increased this parameter in fern by 40%. The pH 3.5 treatment significantly increased foliar concentrations of Cu in red spruce and fern by 50 and 40%, respectively, and also significantly decreased foliar concentrations of Mn in red spruce and fern by 20 and 50%, respectively. Individual data are presented in Appendixes B. 24 and 25.

Table 8. Effects of Treatment pH on Selected Chemical Parameters of Equilibrium Soil Solution and Soil of Rhizosphere of Red Spruce Seedlings: Field Plots in Great Smoky Mountains.

Solution Chemistry

Treatment	TMAl	NLMAl	LMAl	NLMAl/TMAl	pH	DOM [1]
		mg/L				
pH 3.5	0.88[2]	0.44	0.52	0.47	3.53	0.26
	0.10[3]	0.07	0.08	0.05	0.08	0.06
pH 5.0	0.90	0.42	0.56	0.51	3.48	0.35
	0.11	0.08	0.13	0.09	0.10	0.05

1N KCl-Extractable Chemistry

Treatment	Al	Ca	Cu	Mn	Ca/Al(meq)
		mg/100 g soil			
pH 3.5	46.05[2]	44.73	0.08	2.34	0.53
	3.93[3]	8.61	0.01	0.56	0.25
pH 5.0	46.64	55.47	0.09	2.63	0.53
	4.79	11.47	0.01	0.59	0.18

[1]Absorbance at 255 nm.
[2]mean (n=10)
[3]standard error of the mean

Table 9. Effects of Treatment pH on Growth and Biomass (g) Parameters of Red Spruce Seedlings Treated in the Field.

	$\Delta Ht/Ht_{in}$[1]	$\Delta Diam/Diam_{in}$[2]	Needle[3]	Wood[3]	Fine Roots	ΣRoots	Root/Shoot
Treatment							
pH 3.5	0.07[4]	0.12	0.74	0.16	0.22	1.00	0.26
	0.01[5]	0.02	0.04	0.02	0.02	0.05	0.05
Treatment							
pH 5.0	0.08	0.13	0.64	0.14	0.23	1.05	0.26
	0.01	0.01	0.02	0.01	0.02	0.03	0.06

[1] $\Delta Ht/Ht_{in}$ = Height growth increment/Height initial

[2] $\Delta Diam/Diam_{in}$ = Diameter growth increment/Diameter initial

[3] tissue biomass produced during treatment

[4] mean (n=16)

[5] standard error of mean

Table 10. Effects of Treatment pH on Concentrations of Selected Elements in Foliage of Red Spruce Seedlings and Fern: Great Smoky Mountains Field Plots.

Treatment	Al	Ca	Mn	Cu	Ca/Al
		mg/Kg			(mol)
Red Spruce					
pH 3.5	216[1]a[3]	4111a	1937a	22a	13a
	8[2]	331	218	2	2
pH 5.0	222a	4639a	2491b	14b	16a
	9	593	394	1	3
Fern					
pH 3.5	1811c	24913c	3476c	30c	13b
	274	2714	626	3	3
pH 5.0	1749c	17731d	6800d	23d	8b
	203	735	462	1	1

[1]mean (n = 10)

[2]standard error of the mean

[3]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column for a given species are different.

3. Greenhouse Study: Loblolly Pine.

a. Rhizosphere chemistry.

Soil pH. In the greenhouse study, under the pH 5 treatment, the plant significantly decreased the soil pH (both in H_2O and 1 N KCl) of the rhizosphere in soils from both Melton Branch Watershed (MBW) and Walker Branch Watershed (WBW) field sites by approximately 0.15-0.20 pH unit (Table 11). In both soil types, pH (in H_2O) of the bulk soil decreased significantly with decreasing treatment pH. This pattern of decreasing soil pH with decreasing treatment pH was present in rhizosphere soil in the soil from the WBW field site, but not in the soil from the MBW field site. Individual data are presented in Appendixes B. 26 and 27.

KCl-extractable elemental chemistry. The concentration of extractable Al was greater in the WBW soil than in the MBW soil (Tables 12 and 13). Under all pH treatments, concentrations of extractable Al in the former soil were significantly greater, by at least 55%, in the rhizosphere soils than in the bulk soils. In the MBW soil, there was no difference in this parameter between the bulk and rhizosphere soils.

The pH 3.5 treatment significantly increased the concentration of extractable Al by 65% in the rhizosphere soil in the WBW soil. The concentration of extractable Al in the bulk soil of this soil type increased under the pH 3.5 treatment, but the effect was not statistically significant. In the MBW soil, there was no effect of treatment on the concentration of extractable Al in either bulk or rhizosphere soils. Individual data are presented in Appendixes B. 28 and 29. The concentration of extractable Ca was at least 75% greater in the MBW soil than in the WBW soil. Under the pH 5.0 treatment, there was no difference in concentrations of extractable Ca between bulk and rhizsophere soils in either of the two soil types. The pH 3.5 treatment significantly decreased the concentration of extractable Ca by 15% in rhizosphere soil relative to that in bulk soil in the MBW soil, but had no effect in the WBW soil.

Table 11. Effects of Treatment pH on Bulk and Rhizosphere Soil pH of Greenhouse Loblolly Pine Seedlings Grown in Walker Branch and Melton Branch Soils.

Soil	Treatment pH	Bulk Soil pH		Rhizosphere Soil pH	
		H_2O	1 N KCl	H_2O	1 N KCl
Walker Branch Watershed Soil					
	pH 3.5	5.61[1]a	4.94d	5.53a	4.83d
		0.09[2]	0.11	0.04	0.04
	pH 4.1	5.72ab	4.99d	5.64bc	4.92de
		0.04	0.04	0.04	0.04
	pH 5.0	5.83b	5.09de	5.69c	4.96e
		0.06	0.05	0.04	0.03
Melton Branch Watershed Soil					
	pH 3.5	5.91a	5.22d	5.90ac	5.17de
		0.06	0.06	0.05	0.04
	pH 4.1	6.06ab	5.34d	5.92c	5.21e
		0.05	0.05	0.03	0.03
	pH 5.0	6.11b	5.34d	5.91c	5.20e
		0.05	0.05	0.03	0.02

[1]mean (n=10)
[2]standard error of the mean
[3]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column for pine grown in a given soil type differ.

Table 12. Effects of Treatment pH on Selected 1N KCl-Extractable Elements in Bulk and Rhizosphere Soil of Loblolly Pine Seedlings Grown in Greenhouse: Melton Branch Soil.

Treatment	Al	Ca	Mn	Ca/Al
		mg/100g soil		
Bulk Soil				
pH 3.5	0.26[1]a[3]	306b3	0.69d	2044f
	0.03[2]	13	0.15	280
pH 4.1	0.32a	293bc	0.76d	1653f
	0.04	7	0.11	243
pH 5.0	0.23a	274bc	0.74d	2245f
	0.03	9	0.11	265
Rhizosphere Soil				
pH 3.5	0.27a	258c	1.34e	1631f
	0.03	14	0.15	234
pH 4.1	0.29a	279bc	1.34e	1635f
	0.05	5	0.20	270
pH 5.0	0.24a	275bc	1.19e	1825f
	0.02	8	0.12	135

[1]mean (n = 10)
[2]standard error of the mean
[3]Probability of statistically significant difference between compared parameters within a given column at $p \leq 0.05$ is indicated when letters within a column differ.

Table 13. Effects of Treatment pH on Selected 1N KCl-Extractable Elements in Bulk and Rhizosphere Soil of Loblolly Pine Seedlings Grown in Greenhouse: Walker Branch Watershed Soil.

Treatment	Al	Ca	Mn	Ca/Al
		mg/100g soil		
Bulk Soil				
pH 3.5	0.53[1]a[3]	170	1.26d	723g
	0.11[2]	8	0.14	186
pH 4.1	0.42a	161	1.20d	638g
	0.05	9	0.09	114
pH 5.0	0.39a	160	1.08d	794g
	0.06	6	0.11	120
Rhizosphere Soil				
pH 3.5	1.09b	155	1.85e	263h
	0.17	6	0.12	54
pH 4.1	0.66c	159	1.55ef	311h
	0.06	5	0.09	59
pH 5.0	0.69c	153	1.37f	342h
	0.05	5	0.11	26

[1]mean (n = 10)
[2]standard error of the mean
[3]Probability of statistically significant difference between compared parameters within a given column at $p \leq 0.05$ is indicated when letters within a column differ.

The concentration of extractable Mn was greater in the WBW soil than in the MBW soil and was significantly greater by 25 and 60% in rhizosphere soils compared with bulk soils in the WBW and MBW soils, respectively. In the WBW soil, the pH 3.5 treatment significantly increased the concentration of extractable Mn by 30% in rhizosphere soil. There was no effect of treatment on the concentration of extractable Mn in either bulk or rhizosphere soils in the MBW soil.

Extractable Ca/Al was at least 100% greater in the MBW soil than in the WBW soil. In the WBW soil, extractable Ca/Al in rhizosphere soil was significantly lower by 55% than that in bulk soil. In both MBW and WBW soils, there was no effect of treatment on exchangeable Ca/Al in either bulk or rhizosphere soils.

Soil solution chemistry.

i. Monomeric Al. Across all treatments of the loblolly pine seedlings that were grown in the MBW and the WBW soils, concentrations of TMAl and NLMAl in the rhizosphere soil solution were significantly greater than those in the bulk soil solution by at least 50% and 20%, respectively (Tables 14 and 15). The individual data are presented in Appendixes B. 30-33.

There were no statistically significant effects of treatment pH on concentrations of TMAl or NLMAl in either bulk or rhizosphere soils of either soil type. However, in the WBW soil, the pH 3.5 treatment increased the TMAl concentration in the rhizosphere by 30% relative to the effect of the pH 5.0 treatment ($p \leq 0.10$).

In the MBW soil, under the pH 5.0 treatment, the concentration of LMAl in rhizosphere soil was significantly greater, by an order of magnitude, than that in bulk soil, but did not differ between rhizosphere and bulk soils in the WBW soil. The pH 3.5 treatment significantly increased the LMAl concentration in the bulk soil by 600% and decreased the LMAl concentration in the rhizosphere by 40% in the MBW soil and increased the LMAl concentration in the rhizosphere by 166% in the WBW soil.

Table 14. Effects of pH of Treatment on Soil Solution Chemistry in Bulk and Rhizosphere Soil: Loblolly Pine Seedlings--Walker Branch Watershed Soil.

Treatment	TMAl	NLMAl	LMAl	NLMAl/TMAl	pH	DOM
		mg/L				
Bulk Soil						
pH 3.5	0.32[1]a[3]	0.25c	0.11e	0.74g		
	0.04[2]	0.04	0.04	0.05		
pH 4.1	0.27a	0.20c	0.07e	0.80g		
	0.03	0.02	0.02	0.08		
pH 5.0	0.30a	0.22c	0.09	0.81g		
	0.04	0.02	0.03	0.09		
Rhizosphere Soil						
pH 3.5	0.56b	0.31d	0.32f	0.56h	4.64i	0.064k
	0.05	0.04	0.06	0.04	0.08	0.006
pH 4.1	0.46b	0.30d	0.11e	0.74g	5.05j	0.080k
	0.05	0.05	0.03	0.04	0.11	0.006
pH 5.0	0.43b	0.31d	0.12e	0.74g	5.02j	0.078k
	0.05	0.04	0.02	0.05	0.11	0.005

[1]mean (n=10)

[2]standard error of the mean

[3]Probability of statistically significant difference between compared parameters within a given column at $p \leq 0.05$ is indicated when letters within a column differ.

Table 15. Effects of pH of Treatment on Selected Soil Solution Parameters in Bulk and Rhizosphere Soil: Loblolly Pine Seedlings--Melton Branch Watershed Soil.

Treatment	TMAl	NLMAl	LMAl	NLMAl/TMAl	pH	DOM
		mg/L				
Bulk Soil						
pH 3.5	0.066[1]a[3]	0.048c	0.018e	0.77e	5.45g	0.030i
	0.010[2]	0.004	0.008	0.05	0.11	0.004
pH 4.1	0.055a	0.052c	0.003f	0.93f	6.07h	0.043ij
	0.003	0.003	0.001	0.03	0.17	0.006
pH 5.0	0.064a	0.061c	0.003f	0.92f	6.10h	0.055j
	0.010	0.002	0.001	0.06	0.17	0.010
Rhizosphere Soil						
pH 3.5	0.114b	0.092d	0.022e	0.83f	5.56g	0.038i
	0.012	0.007	0.008	0.05	0.17	0.002
pH 4.1	0.142b	0.092d	0.048g	0.73f	6.02h	0.061j
	0.030	0.017	0.024	0.08	0.10	0.010
pH 5.0	0.131b	0.093d	0.038g	0.74f	6.15h	0.049j
	0.016	0.010	0.008	0.04	0.08	0.006

[1]mean (n=10)

[2]standard error of the mean

[3]Probability of statistically significant difference between compared parameters within a given column at $p \leq 0.05$ is indicated when letters within a column differ.

In the MBW soil, the pH 3.5 treatment significantly reduced NLMAl/TMAl values in the soil solution of the bulk soil by approximately 15% compared with effects of the pH 4.1 and 5.0 treatments. There was no effect of treatment on NLMAl/TMAl in the rhizosphere soil. The NLMAl/TMAl value of rhizosphere soil was less than that of bulk soil under the pH 4.1 and 5.0 treatments, but was approximately equal to that of bulk soil under the pH 3.5 treatment.

In the WBW soil, there was no effect of treatment on NLMAl/TMAl in the soil solution from the bulk soil. In the rhizosphere, however, the pH 3.5 treatment significantly lowered NLMAl/TMAl by approximately 25% compared with effects of the other treatments ($p \leq 0.01$).

ii. Solution pH and dissolved organic matter. In the MBW soil, the pH 3.5 treatment significantly decreased the values of both solution pH (approximately 0.5 pH unit) and DOM absorbance by at least 20% in rhizosphere soil solutions. Soil solution pH decreased with decreasing treatment pH in both bulk and rhizosphere soils in the MBW soil and in bulk soil in the WBW soil. (Data for the WBW bulk soil were misplaced.)

b. Growth and biomass parameters of loblolly pine seedlings. In both soil types, the pH 3.5 and 4.1 treatments increased growth increment in height (ΔHt) and ΔHt/initial height of the pine seedlings by at least 40% ($p \leq 0.01$) (Table 16). There were no significant treatment effects on growth in diameter of seedlings that were potted in either soil type or in new needle or new wood biomass in seedlings that were potted in the MBW soil. In seedlings that were grown in the WBW soil, new wood biomass was at least 24% greater under the pH 3.5 (not statistically significant) and pH 4.1 ($p \leq 0.025$) treatments than under the pH 5.0 treatment. Both acidic treatments significantly increased new needle biomass in seedlings that were grown in the WBW soilby at least 33% ($p \leq 0.005$). There was a similar pattern in seedlings that were

Table 16. Mean Growth and Biomass Increment Parameters of Greenhouse Seedlings of Loblolly Pine as Affected by pH of Treatment.

Treatment	ΔH[1]	$\Delta H/H_{in}$[2]	ΔD[3]	$\Delta D/Din$	New wood	New needles	Roots	Root/Shoot
						g tissue		
Walker Branch Watershed Soil								
pH 3.5	33.16[4]a[6]	0.69c	0.46	0.67	6.24ef	20.72g	18.34a	0.44ab
	1.96[5]	0.05	0.02	0.04	0.56	1.14	1.32	0.03
pH 4.1	32.98a	0.69c	0.50	0.73	7.00e	25.73g	17.90a	0.42a
	2.10	0.05	0.02	0.04	0.59	2.96	1.10	0.03
pH 5.0	23.40b	0.45d	0.49	0.72	5.11f	15.67h	20.11a	0.53b
	2.46	0.05	0.02	0.04	0.51	0.95	1.34	0.05
Melton Branch Watershed Soil								
pH 3.5	31.39i	0.59k	0.44	0.66	5.58	19.26	14.22a	0.33c
	1.57	0.03	0.03	0.04	0.75	1.07	1.24	0.03
pH 4.1	34.01i	0.64k	0.47	0.61	6.26	20.35	18.23ab	0.41cd
	2.27	0.05	0.03	0.04	0.75	1.07	1.86	0.03
pH 5.0	22.41j	0.43l	0.49	0.69	4.67	16.65	18.22b	0.50d
	1.92	0.04	0.02	0.04	0.46	0.87	0.96	0.05

[1]growth increment in height during treatment period

[2]in=initial

[3]growth increment in diameter during treatment period

[4]mean (n=15)

[5]standard error of the mean

[6]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicted when letters within a column for pine grown in a given soil type are different.

grown in the MBW soil; however, the differences were not statistically significant.

In seedlings that were grown in the MBW soil, the pH 3.5 treatment significantly lowered root biomass by 20% ($p \leq 0.025$). Both pH 3.5 and 4.1 treatments lowered root biomass in seedlings that were grown in the WBW soil by up to 30%; although this effect was not statistically significant.

The pH 3.5 and 4.1 treatments decreased root/shoot values in seedlings that were grown in both soils. The pH 3.5 treatment significantly decreased this parameter in seedlings that were grown in the MBW soil to a greater degree than that which occurred in those that were grown in the WBW soil (34% versus 17%, respectively). Decreases in root/shoot values were due to increases in shoot biomass and decreases in root biomass. Individual data are presented in Appendixes B. 34 and 35.

c. Foliar elemental chemistry. In at least one of the two soil types, acidic treatments significantly decreased foliar concentrations of Ca, Mn, Cu, and Al in the loblolly pine seedlings (Table 17). In seedlings that were potted in the MBW soil, the two acidic treatments significantly lowered foliar concentrations of Al by at least 40% compared with the pH 5.0 treatment, but had no statistically significant effect on foliar concentrations of Al in seedlings that were grown in the WBW soil. There were no statistically significant effects of treatment on foliar concentrations of Ca in seedlings that were grown in the MBW soil; however, both acidic treatments significantly reduced Ca concentrations in seedlings that were grown in the WBW soil by 23%. Individual data are presented in Appendixes B. 36 and 37.

Acidic treatments increased foliar Ca/Al in seedlings that were grown in the MBW soil (pH 3.5 treatment, $p \leq 0.05$). Conversely, in seedlings that were grown in the WBW soil, the pH 3.5 treatment lowered Ca/Al by 25% compared with the effect of the pH 5.0 treatment; however, this difference was not statistically significant ($p \leq 0.25$).

The pH 4.1 treatment significantly reduced foliar concentrations of Mn in

Table 17. Mean Concentrations of Selected Elements in Foliar Tissues of Loblolly Pine Grown in Greenhouse in Walker Branch Watershed and Melton Branch Watershed Soils as Affected by Treatment pH.

	Ca	Mn	Cu	Al	Ca/Al	Mn/Al
		mg/Kg			mol/mol	
Walker Branch Watershed						
pH 3.5 treatment	10127[1]a[3]	2083cd	10.81ef	275g	32h	8a
	679[2]	62	0.25	14	8	1
pH 4.1 treatment	10089a	1865c	9.51e	176g	47h	11b
	188	54	0.09	9	8	2
pH 5.0 treatment	12908b	2448d	11.44f	280g	44h	9ac
	410	75	0.15	21	8	2
Melton Branch Watershed						
pH 3.5 treatment	10584i	1136jk	11.16l	89n	89p	3b
	962	95	0.71	11	13	2
pH 4.1 treatment	9393i	961j	10.06l	97n	81pq	10bc
	814	53	0.78	15	15	2
pH 5.0 treatment	10119i	1331k	15.03m	171o	49q	8c
	1024	114	0.78	28	11	2

[1]mean (n=10)

[2]standard error of the mean

[3]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column for a given soil type are different.

seedlings that were grown in both soil types by approximately 25%. The pH 3.5 treatment also decreased the concentration of Mn with respect to the effect of the pH 5.0 treatment; however, this difference was not statistically significant. Foliar Mn/Al of seedlings that were grown in the MBW soil increased with decreasing treatment pH. Conversely, in the WBW soil, the pH 3.5 treatment reduced this parameter relative to that of seedlings under the pH 4.1 treatment.

In both soil types, foliar concentrations of Cu in seedlings were significantly reduced by at least 20% under the pH 4.1 treatment compared with the effects of the pH5.0 treatment. The pH 3.5 treatment also significantly reduced Cu concentrations in seedlings that were potted in the MBW soil by 50%.

To better assess Al and Ca uptake by the plant, it is desireable to consider the dilution of accumulated elements due to differential needle growth in the seedlings among the different treatments. Total needle content of the examined elements in new foliage is presented in Table 18. In the MBW soil, acidic treatments significantly reduced foliar Al content by 37% and increased foliar Ca content (pH 3.5 by 33%, $p \leq 0.05$; pH 4.1 by 20%, $p > 0.25$) in the pine seedlings. Although the pH 3.5 treatment increased foliar content of Al (28%) in needles of the seedlings that were potted in the WBW soil, this difference was not statistically significant ($p > 0.25$). Individual data are presented in Appendixes B. 38 and 39.

4. Field Study: Oak-Hickory Forest Field Plots.

At both of the oak-hickory forest field sites, there were no visible effects of treatment on the health of the loblolly pine seedlings that were planted on the field plots or any of the indigenous plants of the field plots.

There was no effect of treatment pH on foliar concentrations of Al, Ca, or Cu, or Ca/Al in loblolly pine at either the MBW or the WBW field sites (Table 19). There

Table 18. Mean Content of Selected Elements in Foliar Tissues of Loblolly Pine Grown in Greenhouse in Walker Branch Watershed and Melton Branch Watershed Soils as Affected by Treatment pH.

	Ca	Mn	Cu	Al
	total mg element/total foliage			
Walker Branch Watershed				
pH 3.5 treatment	189[1]	38	0.20	4.94
	20[2]	4	0.02	0.71
pH 4.1 treatment	219	40	0.21	4.02
	18	4	0.01	0.75
pH 5.0 treatment	186	35	0.17	3.87
	18	4	0.01	0.82
Melton Branch Watershed				
pH 3.5 treatment	218a[3]	24	0.23	1.79a
	7	3	0.02	0.23
pH 4.1 treatment	196ab	19	0.19	1.77a
	29	2	0.01	0.21
pH 5.0 treatment	164b	22	0.25	2.48b
	14	3	0.02	0.11

[1]mean (n=10)

[2]standard error of the mean

[3]Probability of statistically significant treatment effect at $p \leq 0.05$ is indicated when letters within a column for a given soil type are different.

Table 19. Mean Concentrations of Selected Elements in Foliar Tissues of Selected Plant Species Grown on Field Plots at Melton Branch Watershed and Walker Branch Watershed Field Sites as Affected by Treatment pH.

	Ca	Mn	Cu	Al	Ca/Al (mol)
			mg/Kg		
Walker Branch Watershed					
Loblolly pine					
pH 3.5 treatment	4331	90	0.66	168	2.7
	322	14	0.09	13	0.7
pH 5.0 treatment	471	110	0.64	167	2.7
	35	14	0.02	7	0.3
Carolina buckthorn					
pH 3.5 treatment	1814	19	7.19	88	21.2
	102	1	0.28	10	1.8
pH 5.0 treatment	1681	18	7.10	84	21.9
	79	2	0.28	9	2.3
Melton Branch Watershed					
Hog peanut					
pH 3.5 treatment	3960	141	1.68	28	140
	180	11	0.08	1	9
pH 5.0 treatment	4024	142	1.49	28	148
	316	17	0.10	3	9
Loblolly pine					
pH 3.5 treatment	842	114*[3]	0.79	139	8.9
	76	21	0.05	25	2.2
pH 5.0 treatment	818	169*	0.79	162	5.6
	30	13	0.04	22	0.7

[1]mean (n=10)

[2]standard error of the mean

[3]presence of asterisk (*) indicates that two compared means are significantly different ($p \leq 0.05$).

was likewise no effect of treatment pH on foliar concentrations of Al, Ca, or Cu, or Ca/Al in either Carolina buckthorn or hog peanut that were treated on the WBW or MBW field plots, respectively. At the MBW site, the pH 3.5 treatment significantly reduced the foliar concentration of Mn in loblolly pine by 33%. The pH 3.5 treatment likewise reduced the foliar concentration of Mn in loblolly pine at the WBW site by 15%, although this difference was not statistically significant. Tissue chemistry data for the different plant species are presented in Appendixes B. 40-43.

C. Field Studies: Soil Chemistry.

1. Spruce-Fir Forest.

a. Solution chemistry.

Monomeric Al. Most of the monomeric Al in the soil solution of both treatment plots was in the labile form, as the mean NLMAl/TMAl values ranged between 0.14-0.40 and 0.07-0.23 during the sampling periods in May and October, respectively (Figs. 8 and 9). NLMAl/TMAl tended to decrease during each six-day sampling period. Concentrations of LMAl increased and those of NLMAl remained relatively constant between hours 72 and 144 and hours 24 and 72 of the May and October sampling periods, respectively. This increased concentrations of TMAl and decreased NLMAl/TMAl values. Individual data are presented in Appendixes B. 44 and 45.

There were no statistically significant effects of treatment pH on concentrations of TMAl, LMAl, or NLMAl at any sampling time during the May sampling period (Fig. 8). Between hours 72 and 144, concentrations of LMAl and TMAl increased by approximately 1.5 and 2.2 times in the pH 3.5 and 5.0 treatment plots, respectively; only the increases in TMAl and LMAl in the pH 5.0 treatment plot were statistically significant. Concentrations of NLMAl remained relatively constant over the 144-hour sampling period.

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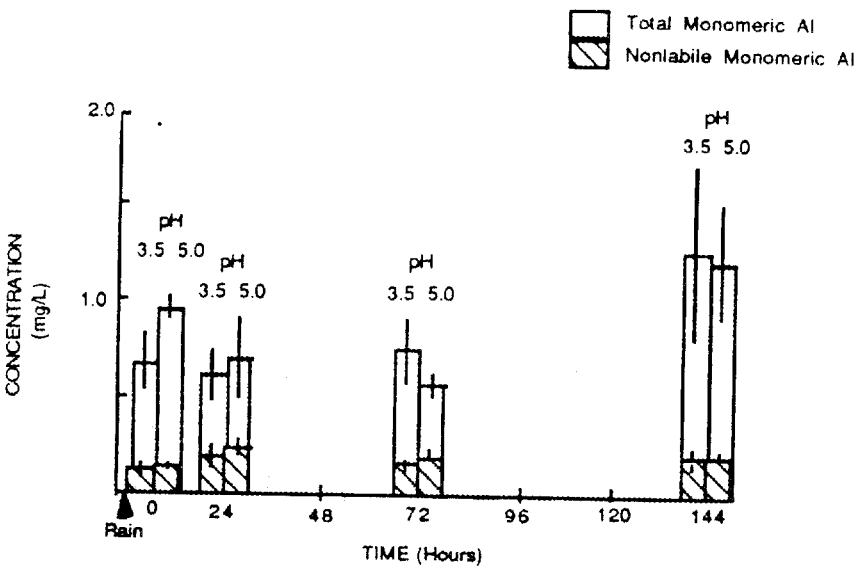

Fig. 8. Effects of treatment pH on soil solution Al parameters over time: spruce-fir forest, May, 1985. Error bar = 2 times standard error.

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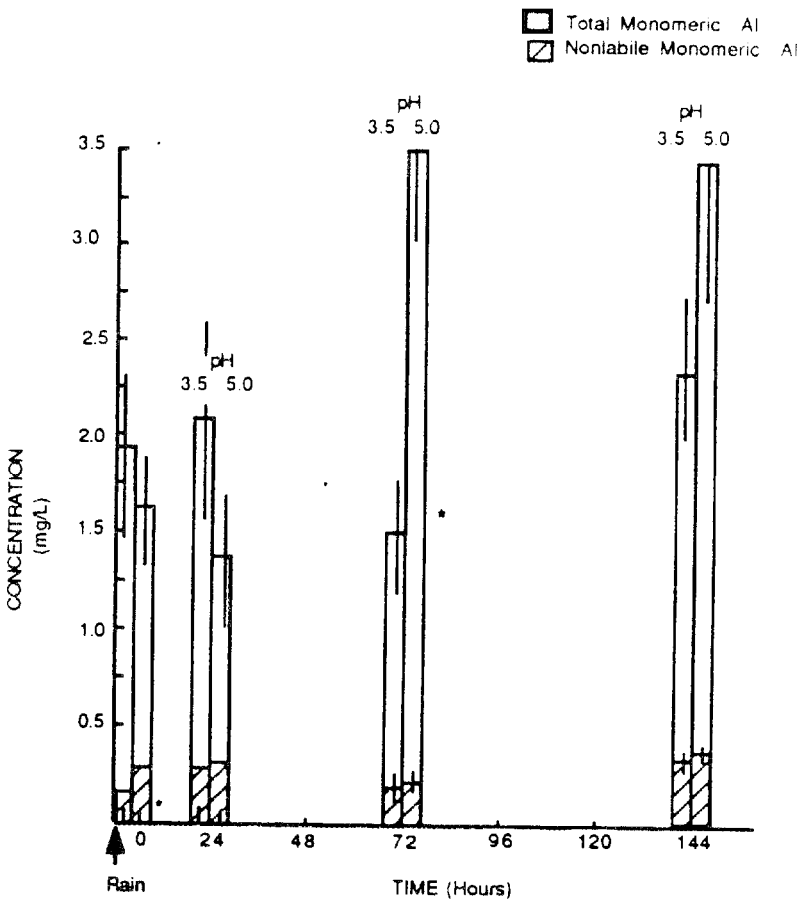

Fig. 9. Effects of treatment pH on soil solution Al parameters over time: spruce-fir forest, October, 1985. Error bar = 2 times standard error. Asterisks indicate significant differences ($p \leq 0.05$) between treatments for indicated parameter.

In both treatment plots, concentrations of TMAl were approximately two-fold higher during the October sampling period than those during the May sampling period (Fig. 9). Concentrations of NLMAl were similar between the two sampling periods. However, when time- and treatment-comparable NLMAl/TMAl values are compared between May and October, in seven of eight cases, the values are at least 30% lower in October samples than in May samples (Appendixes B. 44 and 45).

Treatment effects were evident in the October solution samples. Concentrations of TMAl were approximately 20 and 55% greater in the pH 3.5 treatment plot than in the pH 5.0 treatment plot at hours one and 24, respectively; however, these differences were not statistically significant. In the pH 5.0 treatment plot, concentrations of TMAl and LMAl were approximately 135-140 and 50-55% greater than those in the pH 3.5 treatment plot at hours 72 ($p \leq 0.05$) and 144, respectively. In samples that were collected at hour one, the concentration of NLMAl was significantly reduced by approximately 50% in the pH 3.5 treatment plot. At that time, NLMAl/TMAl values were 0.08 and 0.21 for the pH 3.5 and 5.0 treatments, respectively.

Total dissolved Al, Ca, Mn, and Cu. Concentrations of total dissolved Al were from 25-100 and 8-100 times greater than concentrations of TMAl during the May and October sampling periods, respectively (Appendix B. 46). In samples that were collected at 72 hours following treatment during the October sampling period, total dissolved Al was significantly greater in the pH 5.0 treatment plot than in the pH 3.5 treatment plot (pH 5.0: mean = 47 mg/L, s.e. = 6; pH 3.5: mean = 30 mg/L, s.e. = 3).

There were no effects of treatment pH on concentrations of total dissolved Ca or Mn at hour 72 during the October sampling period. Copper was not detected in the solutions. Individual data are presented in Appendix B. 46.

Solution pH and dissolved organic matter. Soil solution pH of samples that were collected during October was slightly lower than that of time-comparable samples that

were collected during May (Appendix B. 47). During the May and October sampling periods, solution pH increased following hour one in both treatment plots. There was no effect of treatment on soil solution pH in May or October.

Absorbance values of dissolved organic matter did not vary over the sampling period in May (Appendix B. 47). There was also no effect of treatment on DOM values during this period. However, during the sampling period in October, the pH 3.5 treatment significantly lowered DOM values in samples that were collected at one hour following treatyment dosing by approximately 50%.

b. KCl-extractable elemental chemistry. In the soils of both treatment plots, concentrations of extractable Al were significantly greater by 20-30% in soil samples that were collected during October compared with those that were collected during May (Table 20). During October, concentrations of extractable Cu were also significantly greater by 30 and 60% in soils of the pH 3.5 and 5.0 treatment plots, respectively. Concentrations of extractable Ca were lower by 10 and 20%, and those of extractable Mn, by 42 and 44%, in the pH 3.5 and pH 5.0 treatment plots, respectively, in the samples that were collected in October compared with those that were collected in May. The differences for the samples from the pH 5.0 treatment plot were statistically significant, while only the difference in Mn was such for the pH 3.5 treatment plot.

There were no effects of treatment on concentrations of any of the examined extractable elements during the May sampling period. The pH 3.5 treatment significantly reduced concentrations of extractable Al in soils that were collected during October. From May to October, none of the other elements were affected by treatment pH. Extractable Ca/Al increased in soils of both plots, but was not affected by treatment. Individual data are presented in Appendix B. 48.

Table 20. Effects of Treatment pH on the Concentrations of 1 N KCl-Extractable Elements from Soil Samples of the Great Smoky Mountains Field Plots: May and October, 1985.

	Al	Ca	Cu	Mn	Ca/Al
		mg/100g soil			meq
May					
Treatment pH					
3.5	48[1]a[3]	47d	0.084f	3.16h	0.43j
(n=10)	5[2]	8	0.005	0.66	0.08
5.0	53a	63d	0.075f	4.16h	0.55j
(n=9)	7	12	0.005	0.90	0.12
October					
Treatment pH					
3.5	61b	40d	0.120g	1.76i	0.35k
(n=10)	36	10	0.015	0.25	0.11
5.0	71c	51e	0.120g	2.33i	0.34k
(n=10)	3	6	0.015	0.45	0.06

[1]mean

[2]standard error of the mean.

[3]Probability of statistically significant treatment effects at $p \leq 0.05$ is indicated when letters within a column are different.

2. Oak-Hickory Forest.

a. KCl-extractable elemental chemistry. At both field sites, there was high variability among concentrations of extractable elements in soil samples of the individual plots (Appendix B. 49). Ranges in concentrations of extractable Al, Cu, Fe, and Mn were similar between sites, while that of extractable Ca was approximately twice as great at the MBW site (Hapludult) compared with that at the WBW site (Paleudult). Comparison of extractable chemistry between the May and October sampling periods is hampered by the limited number of samples (WBW, 8; MBW, 9) taken during the May sampling period. Based upon the number of samples taken, however, the concentration of extractable Cu was approximately twice as great at the MBW site during October compared with May. There was no apparent effect of treatment on any of the examined elements.

b. Solution Chemistry.

Solution pH and DOM. During the May and October sampling periods, soil solution pH within treatment plots at the MBW field site was highly variable among samples collected at each sampling time. The greatest variability at any given time of sample collection following treatment dosing occurred in the pH 3.5 treatment plot, where the smallest range in sample pH was pH 4.1-6.8 (October, hour 72) and the largest range was pH 4.1-8.0 (May, hour 24). In the pH 5.0 treatment plot, the smallest range in solution pH was pH 4.0-5.0 (May, hour 24) and the largest range was pH 4.6-6.7 (October, hour 24).

There was less variation in soil solution pH in samples from the WBW plots. In most cases, the ranges in solution pH of samples collected at any given time following dosing were similar between treatment plots. The greatest variability at any given time of was pH 4.2-6.7 in the pH 5.0 treatment plot (October, hour one). If the latter value (pH 6.7) is not included in the data set, the greatest range in sample pH was 3.8-4.6

(pH 5.0 treatment, October, hour 24). The least variability also occurred in the same treatment plot, where pH values ranged from 4.0-4.2 (May, hour 144). During both May and October sampling periods, there were no significant effects of treatment on DOM absorbance values at either field site . The pH and DOM chemistry data are presented in Appendix B. 51.

Monomeric Al. There was very high variability in concentrations of TMAl within individual plots at both sites during the May and October sampling periods (Appendix B. 51). In the samples from the MBW plots, concentrations of TMAl varied up to 60 fold during a single sampling time, and this variability was particularly present in the pH 3.5 treatment plot. Concentrations of TMAl in samples from the WBW plots varied up to 10-fold during a single sampling time.

In general, concentrations of TMAl in the WBW plots were up to seven times greater than those in the MBW plots during the May sampling period (Figs. 10 and 11). From hours 24 to144 following dosing, apparent temporal patterns in concentrations of TMAl occurred in the different treatment plots (e.g., decreasing TMAl concentrations in the pH 5.0 treatment, MBW plot). However, high variability in concentrations of TMAl among samples makes apparent temporal trends suspect.

At the MBW site, the pH 3.5 treatment reduced concentrations of TMAl by at least 50%. The effects of treatment at hours one and 24 were statistically significant ($p \leq 0.005$ and $p \leq 0.10$, respectively). There was no significant effect of treatment on concentrations of TMAl in the WBW plots.

During the October sampling period, there was also very high variability in concentrations of TMAl among samples from each treatment plot at both sites (Figs. 12 and 13). As in May, concentrations of TMAl were greater at the WBW site, and as in the case of the MBW site, apparent temporal trends in the concentrations of TMAl are suspect because of high sample variability.

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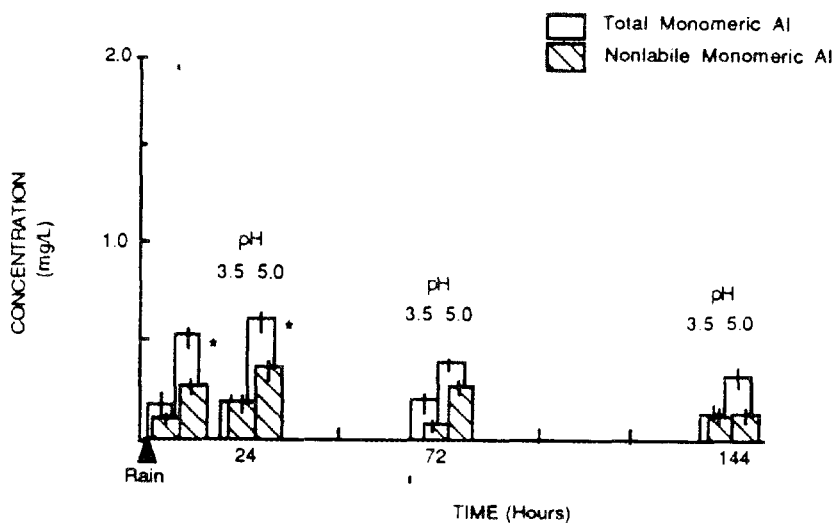

Fig. 10. Effects of treatment pH on soil solution Al parameters over time: oak-hickory forest, Melton Branch site, May, 1985. Error bar = 2 times standard error. Asterisks indicate significant differences ($p \leq 0.05$) between treatment for indicated parameters

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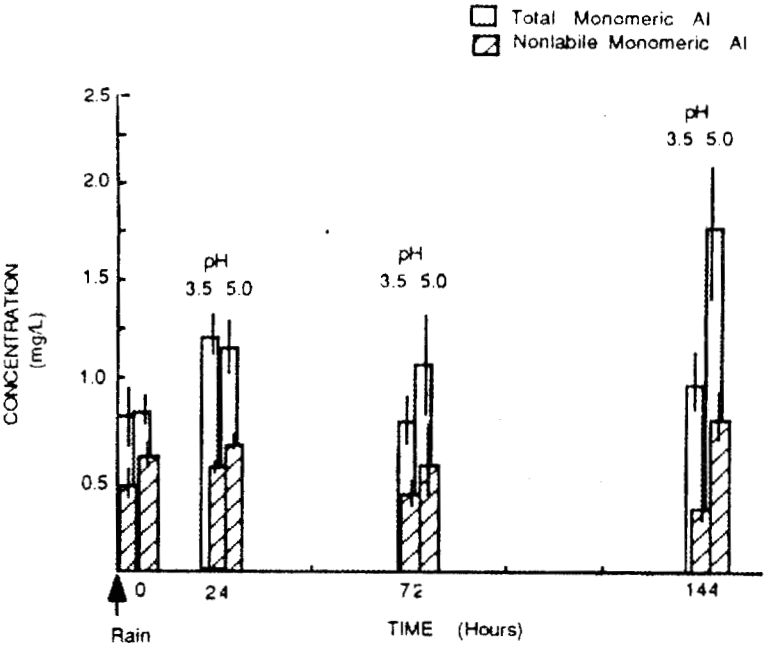

Fig. 11. Effects of treatment pH on soil solution Al parameters over time: oak-hickory forest, Walker Branch site, May, 1985. Error bar = 2 times standard error.

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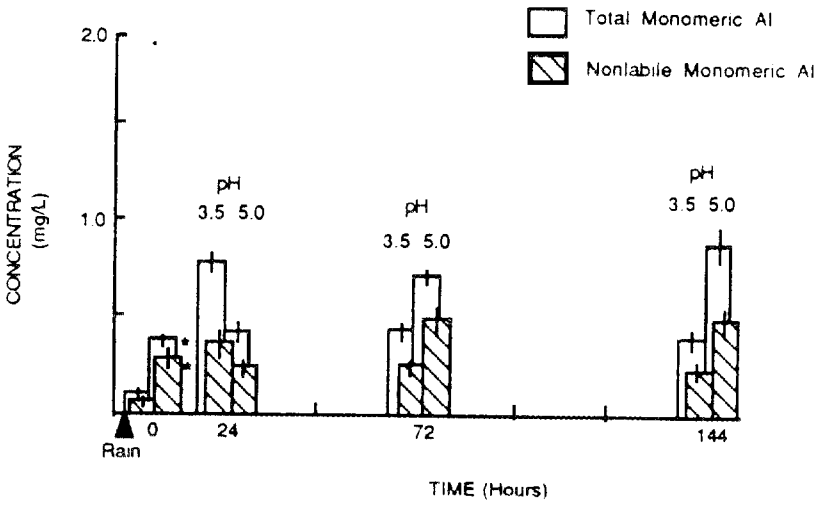

Fig. 12. Effects of treatment pH on soil solution Al parameters over time: oak-hickory forest, Melton Branch site, October, 1985. Error bar = 2 times standard error. Asterisks indicate significant differences ($p \leq 0.05$) between treatments for indicated parameter.

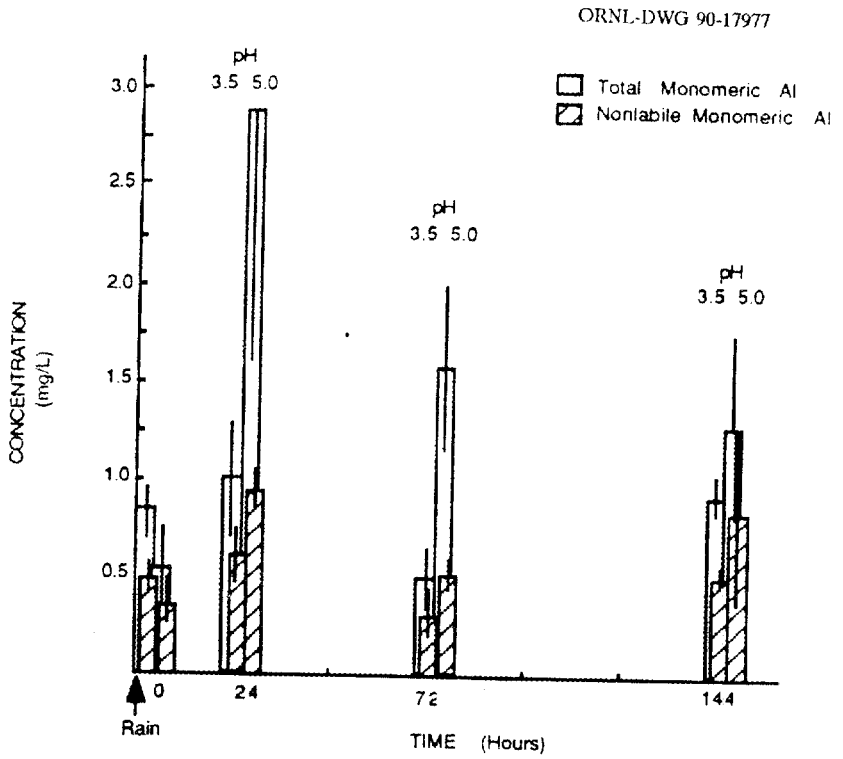

Fig. 13. Effects of treatment pH on soil solution Al parameters over time: oak-hickory forest, Walker Branch site, October, 1985. Error bar = 2 times standard error.

At hour one following dosing, pH 3.5 treatment decreased the concentration of TMAl at the MBW field site ($p \leq 0.10$). Although concentrations of TMAl after hour one following treatment dosing differed between plots by approximately 50%, none of the differences between reatments were statistically significant. Variability in concentrations of NLMAl among samples was much less than that in concentrations of TMAl. During the May sampling period, concentrations of NLMAl in the WBW plots were at least 50% greater than those in the MBW plots (Figs. 10 and 11). At both sites, concentrations of NLMAl were greatest in the pH 5.0 treatment plot. This difference was only statistically significant at hour 144 in the WBW site ($p \leq 0.025$).

Concentrations of NLMAl in the individual plots were similar between the May and October sampling periods. During October, the pH 3.5 treatment significantly reduced the concentration of NLMAl at the MBW site at hour one following treatment dosing (Fig. 11).

NLMAl/TMAl values tended to be greater in soil solution from the MBW site (range 0.42 to 0.96) than in that from the WBW site (range 0.42 to 0.63). These values of solutions at the MBW site were similar between May and October, while those at the WBW site tended to be lower in October than in May. During May and October, there were no significant effects of treatment on NLMAl/TMAl at either oak-hickory forest site.

Total dissolved Al, Ca, Mn and Cu. Concentrations of total dissolved Al were similar between sites (Appendix B. 52). There were no apparent differences in either concentrations of total dissolved Al between May and October or effects of treatment pH on concentrations of total dissolved Al at either field site.

Solution concentrations of Ca, Mn, and Cu were similar between field sites. There were no apparent differences in concentrations of either Ca or Cu at either site between the May and October sampling periods. During the October sampling period,

concentrations of Mn at both sites were decreased by at least 50% in the pH 3.5 treatment plots at one hour following treatment. There were no other apparent effects of treatment. Individual data are presented in Appendix B. 52.

IV. DISCUSSION

A. Hypothesis I

Acidic precipitation will not significantly mobilize Al in the soil zone that contains fine roots, but will significantly alter the speciation of dissolved Al in this soil zone. This alteration will occur as an increase in free ionic Al plus inorganic Al complexes relative to organic Al complexes.

As hypothesized, acidic treatment of the soils in the laboratory equilibration, greenhouse, and field plot studies significantly altered the speciation of soil solution Al. This alteration occurred as an increase in the concentration of inorganic monomeric Al (LMAl) relative to that of organic monomeric Al (NLMAl). Concentrations of LMAl and NLMAl were affected by treatment in the laboratory equilibration, greenhouse, and field studies. Acidic treatment significantly increased soil solution concentrations of total monomeric Al (TMAl) and LMAl in the soils that were treated in the laboratory equilibration and greenhouse studies and decreased concentrations of both parameters in the spruce-fir and oak-hickory forest soils in the field studies. Thus, only results of the field studies support the initial hypothesis that acidic precipitation would not significantly mobilize soil Al. Acidic treatment also significantly decreased the concentration of NLMAl in the laboratory equilibration, greenhouse, and spruce-fir field studies.

Solution chemistry of Al in the examined soils differed both spatially and temporally within soils from a single forest type (e.g., spruce-fir forest) and between forest types (spruce-fir and oak-hickory forests). Differences in solution chemistry are very likely related to spatial and temporal differences in soil solution pH, dissolved organic matter, and exchangeable Ca/Al chemistry among soils. Temporally, the soil

solution chemistry of Al in the different soils varied significantly during the seven-day period following treatment dosing and also with increased duration of treatment.

Effects of H^+-treatments on the soil chemistry of Al are best understood by first considering several soil factors that influence the soil solution chemistry of Al. Solution chemistry of Al is directly related to solution pH, dissolved organic matter, and exchangeable Ca/Al chemistry (Driscoll and Schecher, 1988). These relationships can be used to interpret the patterns in soil solution Al in this study. Results of the laboratory equilibration study will be used to discuss the influence of these three parameters on the soil solution Al. The Al chemistry of the soils that were treated in the field studies, and the effects of acidic treatment on that chemistry, will then be intrepreted in this context.

1. Relationship of Al Chemistry to Soil Parameters.

a. Soil solution pH and Al chemistry.

Solution pH. In the laboratory equilibration study, the pH of solution extracts of all four spruce-fir forest soils decreased over time following treatment during each of the three monitoring periods. Part of this progressive acidification was very likely due to the cumulative effects of enhanced nitrification that were caused by disturbance of the soils during collection. The presence of enhanced nitrification is indicated by the results of a semi-quantitative examination that found that concentrations of solution nitrate in all four soils increased over time following the initial treatment dosing. The general decrease in solution pH for any given time following dosing with increased duration of treatment may be due to the accumulated effects of this endogenous acidification on the soils.

In contrast with these results, soil solution pH at the spruce-fir field site did not significantly decrease during the 144 hours following treatment in either May or

October. Differences in soil solution pH following treatment dosing between the laboratory equilibration and field studies support the proposition that disturbance of the soils caused by soil collection and handling prior to treatment accelerated the rates of nitrification in soils of the laboratory equilibration study.

If the decrease in solution pH was related to nitrification, one would predict that nitrification rates in the Great Smoky Mountains soils were greater than those in the Adirondack Mountain soils, because increases in H^+-activity following dosing were greater in the former soils. This prediction is indirectly supported by the study of Johnson *et al.* (in press), who report that concentrations of soil solution NO_3^- in a spruce-fir forest in the Great Smoky Mountains were at least 10 times greater than those in a similar forest on Whiteface Mountain in the Adirondack Mountains.

Solution pH and LMAl. In the laboratory equilibration study, concentrations of LMAl (which includes Al^{+3}) in solutions of all four soils increased correspondingly with the decrease in solution pH following treatment dosing. This result is in accordance with observations that Al solubility increases with decreasing solution pH (e.g., Driscoll and Schecher, 1988). The general increase in LMAl concentrations in the two Great Smoky Mountains soils with progressive decrease in solution pH over the 15 weeks of treatment further supports the pH-Al solubility relationship.

Acidic treatment decreased solution pH in all spruce-fir soils in the laboratory equilibration study and in the nonrhizosphere soil in the greenhouse study. Such an effect, however, was not present in the bulk soil in the spruce-fir field study. This difference between the field study and laboratory equilibration and greenhouse studies supports the interpretation that natural acidification in the soils of the latter studies was accelerated sufficiently through soil disturbance, as to decrease the capacity of the soil to buffer the soil solution pH under treatment inputs of H^+.

b. Dissolved organic matter and Al chemistry.

Dissolved organic matter (DOM). Decreased solubility of DOM with decreasing solution pH occurred in all four soils during each of the three periods of examination of Al chemistry and was very likely due to the decrease in solubility of organic matter with increased solution acidity. The DOM determination presumably measures dissolved humic and fulvic acids (Kumada, 1985). Weak acid functional groups on these compounds will protonate at low solution pH and serve to buffer solution pH. This protonation decreases the negative surface charge on the organic compounds. Attractive forces between the dissolved organic molecules will thus increase, the molecules will aggregate (Davis and Mott, 1981), and consequently, the solubilities of the organic compounds will decrease (Krug and Issackson, 1984). This mechanism explains the progressive decrease in DOM values with the decrease in solution pH from day one on during all three periods in which solution chemistry was monitored. The increase in DOM values between hour one and day one presumably reflects the time necessary for equilibration of soil organic matter with the treatment solutions. It is reasonable to assume that as concentrations of dissolved organic matter decrease, the organic ligand concentration (i.e., complexation capacity) will correspondingly decrease.

The decrease in DOM with time following treatment dosing may be due, in part, to the loss of dissolved organic matter due to decomposition. This possibility is not, however, supported by the data if the absorbance measurement at 255 nm is primarily a measurement of dissolved humic and fulvic acids as is interpreted from Kumada (1985). Humic matter is quite resistant to breakdown and presumably would not have a half-life of two-weeks, as would be indicated by the rate of decrease in DOM values over time. Indeed, the half-life of humic matter is given by Clark and Paul (1970) as >15 years.

The above-described pH-DOM solubility relationship explains the reduction in DOM values under acidic treatment in the laboratory equilibration, greenhouse, and field

plot studies. This treatment effect was not restricted to soil of the organic soil horizon, as it also occurred in the mineral soil from the Melton Branch Watershed field site in the greenhouse study. The presence of treatment effects could not be determined in the soil from the Walker Branch Watershed field site due to the absence of data. There was, however, no evidence of such an effect of H^+-input on DOM solubility at either oak-hickory forest field site.

These results support the likelihood that buffering of anthropogenic inputs of H^+ by soil organic matter, presumably fulvic/humic acids, is a significant H^+-buffering reaction in forest soils, as has been suggested by Krug and Frink (1983). This buffering mechanism has been neglected in many considerations of H^+-additions by acidic precipitation to forest soils. For example, the conceptual model of soil acidification by acidic precipitation of Reuss and Johnson (1986) considers H^+-cation exchange reactions and purposely does not include H^+-organic anion protonation reactions.

In the Reuss-Johnson model, enhanced Al-mobilization from the exchange complex is dependent upon increased total solution concentration (i.e., ionic strength) of the soil solution. Inputs of strong acid anions and H^+ in acidic precipitation to soils will increase total solution concentration and solubilize exchangeable cations (including Ca and Al). However, H^+-buffering reactions of humic/fulvic acids would decrease the negative charge of organic anions in solution. Therefore, any increase in ionic strength of the soil solution due to the input of strong acid anions would be, at least partially, moderated by this decrease in negative charge of organic anions. Thus, this H^+-buffering mechanism would minimize any increase in total solution concentration (including solution H^+) that is related to anthropogenic inputs of strong acid anions and H^+.

This pH buffering mechanism would decrease the magnitude of H^+-Al exchange

reactions and, consequently, limit the increase in the soil solution concentration of Al that would be predicted by the Ruess-Johnson model. As written, the model is likely applicable to mineral soils with a low content of organic matter. However, in organic-rich soils, such as the organic soil horizons of the spruce-fir forest soils that were examined in this study, it is very likely that model predictions would less accurately describe H^+-soil interactions.

Dissolved organic matter and NLMAl. If the solution concentration of Al remains constant, the inferred decrease in the solubility of organic chelates with decreases in solution pH may lower the solution concentration of organic-Al (NLMAl) through several mechanisms. Precipitation of organic ligands through the protonation-aggregation mechanism which has previously been discussed would decrease the number of ligand sites in solution that would be available to complex dissolved Al and, consequently, decrease the formation of organic-Al complexes. It is very likely that dissolved organic-Al complexes would similarly be directly precipitated from solution by increased concentrations of solution H^+. Additionally, the increased concentration of H^+ would compete with Al^{+3} for the bonding sites of organic ligands and decrease the formation of organically-complexed Al. Associated with the decrease in solution pH, however, is the increased concentration of Al^{+3} that would compete with H^+ for the reduced number of complexation sites that would be available on the dissolved organic chelates. This would serve to minimize the reduction in solution concentration of organic-Al complexes that would be induced by decreased solution pH.

Fulvic-Al complexes are thermodynamically more stable than fulvic-H complexes as evidenced by the presence of fulvic-Al complexes at solution pH values at which the weak organic acid functional groups of fulvic acids would be dissociated (e.g., Schnitzer, 1969). Over changes in solution pH of 3/4 pH unit, as was observed in this study, the stability constants of organic-Al complexes will be lowered somewhat.

However, Al^{+3} will still be more effective, although to a lesser degree, than H^+ in forming complexes with the reduced concentrations of organic ligands (Driscoll and Schecher, 1988). This explains the presence of relatively constant concentrations, rather than decreased concentrations, of NLMAl in the four soils with decreases in solution pH and DOM over time following treatment dosing.

Since Al^{+3} competition with H^+ for ligand bonding sites becomes less effective with decreasing solution pH (Driscoll and Schecher, 1988), the proportion of inorganic monomeric Al to organic monomeric Al in solution should increase under conditions of increased solution acidification. Such a result occurred in the solutions extracted from both of the Great Smoky Mountains soils that were examined in the laboratory equilibration study. Aluminum was solubilized with decreasing solution pH and, once in solution, Al^{+3} apparently less-readily formed complexes with organic chelates. As a consequence, concentrations of LMAl increased and those of NLMAl remained relatively constant. It is possible that additional organic-Al complexes may have formed, but were removed from solution through H^+-induced precipitation of the organic-Al complexes. Thus, the decrease in NLMAl/TMAl with decreases in solution pH follows a pattern predicted from thermodynamic considerations.

c. Exchangeable Al and Ca chemistry.

Exchangeable Al and Ca. Exchangeable Al is important in the metal toxicity hypothesis of forest decline because, due to the relatively rapid nature of Al-exchange reactions, it presumably serves as an immediate source of Al for H^+-Al reactions (Bache, 1986). The exchangeable Ca/Al parameter is a reflection of soil base saturation and directly influences the soil solution concentration of Al through equilibrium and H^+-cation exchange reactions.

Concentrations of exchangeable Al tended to increase and exchangeable Ca/Al decreased in all four spruce-fir forest soils over the course of the study. With the

exception of the Collins Gap soil, this increase in exchangeable Al occurred regardless of treatment pH. The magnitude of increase was less for the soils having greater initial concentrations of exchangeable Al. Increases in exchangeable Al over the course of the study very likely resulted from increased retention of Al that was solubilized through mineralization of Al-containing organic matter and/or dissolution of Al-containing minerals by the exchange complex.

The greater the initial exchangeable Ca/Al value of the soil, the greater the magnitude of decrease over the course of treatment. This decrease in exchangeable Ca/Al was due to decreases in the concentration of exchangeable Ca, as well as, increases in the concentration of exchangeable Al. Leaching may have decreased the concentration of exchangeable Ca. In addition, mineralization of Al-containing organic matter and/or dissolution of Al-containing minerals may have solubilized Al which, in turn, may have displaced Ca from exchange sites.

Exchangeable Al and Ca and LMAl. The examined Great Smoky Mountains soils had much greater concentrations of exchangeable Al and lower exchangeable Ca/Al than did the Adirondack Mountains soils. In the examined soils, LMAl concentrations were greatest in soils having greater concentrations of exchangeable Al and lower exchangeable Ca/Al. A comparison of the Collins Gap and Indian Gap soils further emphasizes the significant influence of exchangeable Al (or exchangeable Ca/Al) on LMAl concentrations. While both soils had a similar range in solution pH, exchangeable Al was greater and exchangeable Ca/Al was lower in the Collins Gap soil. This difference corresponds with the greater concentration of LMAl in the Collins Gap soil; a difference that would be predicted from thermodynamic considerations of the differences in exchangeable chemistry of the two soils.

2. Response of All Soils in Laboratory Equilibration Study to Acidic Treatment.

a. Soil chemistry. Solution chemistry of Al and effects of acidic input on this chemistry differed among the four spruce-fir forest soils. From the results, it is therefore apparent that it is somewhat inappropriate to make generalizations of the effects of non-acidic or acidic precipitation on soil solution chemistry of Al in spruce-fir forest soils from one location to another. This is particularly the case in regard to both the timing and magnitude of effects of precipitation chemistry on soil Al chemistry.

There are, however, common effects of acidic treatment on the soil solution chemistry of Al that can be explained by the solution pH-DOM-exchangeable Al-solution Al chemistry relationships that were described above. In general, the concentration of NLMAl (organic Al complexes) is decreased by acidic addition. The hypothesized mechanism is the decreased solubility of organic chelates (fulvic/humic acids), while the decreased production of organic chelates by decomposition may also serve to decrease NLMAl concentration. Although there is no direct evidence to support the latter mechanism, it cannot, however, be ruled out by interpretations of the available data. Acidic treatment also tends to increase LMAl concentration through the lowering of solution pH which, consequently, solubilizes soil Al. Together, these effects of acidic treatment on LMAl and NLMAl alter the ratio of organic to inorganic monomeric Al in solution.

Effects of acidic treatment on the solution chemistry of Al varied temporally in relation to treatment dosing. Concentrations of NLMAl were reduced immediately following acidic treatment and then tended to increase over time. In comparison, the treatment effects on LMAl concentrations tend to be delayed, but could be present through the duration of soil drying. These temporal differences in effects of acidic treatment on the solution chemistry of Al support the interpretation that the kinetics of H^+-DOM reactions are much more rapid than those of H^+-soil Al reactions. This further

emphasizes the probable importance of protonation of organic anions in H^+-buffering reactions in forest soils that receive acidic precipitation.

b. Implications to forest decline. Three of the four soils in this study were collected at field sites where measurements of radial growth increment in red spruce were made in previous studies. The fourth soil, that from the Collins Gap site, was collected within 1/4 km of such a site and was developed from the same parent material that occurred at that site. It is therefore reasonable to examine the health state of red spruce at these field sites in the context of the soil chemistry of Al that was observed in the laboratory equilibration study. One would anticipate a correlation between the soil chemistry of Al and the health state of the red spruce if Al toxicity is a major stress affecting tree growth at the four field sites.

Based upon the differences in concentrations of LMAl, NLMAL/TMAl, and exchangeable Ca/Al between the soils of the Great Smoky Mountains and the Adirondack Mountains, trees at the sites of soil collection in the Great Smoky Mountains would most likely be exposed to greater concentrations of potentially bioavailable/toxic Al than those that grow at the sites of soil collection in the Adirondack Mountains. Within the Great Smoky Mountains, the concentration of potentially bioavailable/toxic Al would most likely be greater in soils at the Collins Gap site than in those at the Indian Gap site. This prediction is based upon the greater LMAl concentrations and lower exchangeable Ca/Al values in the Collins Gap soil compared with those of the Indian Gap soil. Concentrations of LMAl in both soils, however, are below the level at which red spruce exhibits Al toxicity symptoms (approximately 6.5 mg/L, Thornton *et al.*, 1987).

In the Adirondack Mountains, there would probably be greater concentrations of potentially bioavailable/toxic Al at the site having tree dieback. This prediction is supported by LMAl concentration and exchangeable Ca/Al. However, LMAl concentrations in this soil are well below levels at which red spruce exhibit Al toxicity symptoms.

The effects of acidic treatment on soil solution chemistry of Al supports the hypothesis that acidic precipitation can increase solution concentrations of LMAl and, therfore, enhance the potential bioavailability of Al in all four soils.

Growth decline in red spruce, as is indicated by decreases in radial growth increment of xylem tissue, has been found within 1/4 km of the Collins Gap field site and at the location of soil collection at Indian Gap (McLaughlin *et al.*, 1987). The decline in growth at the Indian Gap site was greater than that at the Collins Gap site. This difference in degree of growth decline between the two sites is the reverse of that which would be predicted based upon the differences in LMAl concentrations and exchangeable Ca/Al between the two soils that were found in this laboratory study.

Growth decline in red spruce, as indicated by decreases in radial growth increment of xylem tissue, has been found at the locations on Whiteface Mountain where the Adirondack Mountains soil samples were collected for this study (A. J. Friedland, University of Pennsylvania, pers. comm., 1988). Growth decline was greatest at the unhealthy forest site and therefore follows the prediction of Al bioavailability that is based upon results of this laboratory study. Needle loss, poor root growth, and reduced mychorrizal infection are dieback symptoms that occur only at the unhealthy forest site. These characteristics, like radial growth decrease, occur in spruce that were grown in the soil that had the greater concentration of LMAl and lower exchangeable Ca/Al. This evidence suggests that Al toxicity is a factor in the forest decline at the unhealthy forest site. The absence of increased LMAl concentrations under acidic treatment, however, does not support the hypothesis that Al toxicity in this soil would be significantly enhanced by acidic precipitation.

Based upon LMAl concentrations and total dissolved Ca/LMAl values of the soils that were observed in this study, it is probable that if Al toxicity is the single cause of forest decline in spruce-fir forests, trees growing at the locations of soil collection in

the Great Smoky Mountains would be more adversely affected by Al than those growing at such locations in the Adirondack Mountains. The presence of dieback symptoms (e.g., poor root development, needle loss) at the unhealthy forest site in the Adirondack Mountains, coupled with the apparent absence (based upon this author's observations) of such symptoms at either site in the Great Smoky Mountains, does not support the likelihood that Al toxicity is the single significant stress in forest decline. The evidence, however, does not rule out Al toxicity as a stress of secondary importance in the decline.

It should be stressed that this comparison between the chemical charateristics of the examined soils and the apparent degree of forest decline at the field sites is quite simplistic. It does not consider differences in stress regimes (natural and anthropogenic) and genotypic variation in response of red spruce to stress between the different geographic locations. This comparison also does not include the actual effects of acidic treatment on the soils as intact ecosystem components under natural conditions. Therefore, caution must be used in the extrapolation of these laboratory results to the level of the ecosystem in any consideration of the problem of forest decline.

3. Aluminum Biogeochemistry of Field Site Soils.

While focusing on effects of acid precipitation on soil chemistry of Al in two types of forest, this study also provides basic information on Al biogeochemistry in the forest ecosystem. Comparison of soil Al chemistry at the field sites with that of other forests, particularly those experiencing forest decline, is of interest to better understand the similarities and dissimilarities in Al biogeochemistry between different forests. Also of interest are temporal variations in dissolved Al forms in the soil solution following an individual precipitation event and between different portions of the growing season. These temporal variations are pertinent to any discussion of Al mobilization by acid precipitation. They are also of significance in any discussion of Al

biogeochemistry of forest ecosystems when one considers plant-Al relationships and pedogenesis.

The following discussion will first consider several aspects of Al biogeochemistry and the effects of acid precipitation on that biogeochemistry of the spruce-fir forest soil--with particular emphasis on the field site study. This will be followed by a similar, but briefer, discussion of soil Al chemistry of the oak-hickory forest field sites. This emphasis is chosen because of the author's interest in forest decline in spruce-fir forests and also because the response of Al chemistry of the spruce-fir forest soil to treatment pH can be related to treatment effects present in the laboratory equilibration study.

a. Spruce-fir forest soils.

Aluminum biogeochemistry.

i. Exchangeable Al chemistry. This author was able to find very few published data of exchangeable Al in organic soil horizons of spruce-fir forests for comparison with that of this field manipulation study. Concentrations of exchangeable Al in the Collins Gap soil are similar to concentrations of exchangeable Al in organic horizons of soils at two other locations in spruce-fir forest in the Great Smoky Mountains and are greater than that of soils from spruce-fir forests on Whiteface Mountain in the Adirondack Mountains, New York, and in the Cascade Mountains, Washington (Johnson *et al.*, in press). In the laboratory equilibration study, concentrations of exchangeable Al in the Collins Gap soil were two times greater than that in the Great Smoky Mountains-Indian Gap soil and 10 to 50 times greater than that in the two Adirondack Mountains soils.

From this, it is apparent that the Great Smoky Mountains soils, including the Collins Gap soil, contain greater concentrations of exchangeable Al than several comparable soils at other locations. As such, the Collins Gap soil represents a spruce-

fir forest soil in which Al may be more bioavailable and potentially toxic to forest plants under non-acidic precipitation conditions. It is also very likely a soil in which Al may be more mobilized by acidic precipitation compared with other spruce-fir forest soils.

ii. Solution Al chemistry. Information on the solution chemistry of Al in forest soils has only entered the scientific literature relatively recently (e.g., Nilsson and Bergkvist, 1983; David and Driscoll, 1984; Driscoll *et al.*, 1985), in part due to an interest in the effects of acid precipitation on forest soil Al. Of this, little pertains to the organic horizon of soils--a horizon of importance in Al biogeochemistry in spruce-fir forests because it may contain the majority of the fine plant roots. That information which is available tends to deal only with concentrations of total dissolved Al. This parameter, which consists of ionic, inorganic and organic complexes, and polymeric Al species, can be used to estimate Al fluxes from a particular ecosystem when collected in lysimeter solutions. However, since ionic Al, the more bioavailable and toxic Al species, makes up only a minor portion of total dissolved Al in this study, the concentrations of total dissolved Al should not be used an indicator of Al bioavailability or toxicity.

Total dissolved Al. Concentrations of total dissolved Al (15-67 mg/L) in soil solution samples in the spruce-fir field study are an order of magnitude greater than the range (up to 4 mg/L, Johnson *et al.*, in press and 1.3-2.6 mg/L, Jones *et al.*, 1983) in Al concentrations in lysimeter-collected solutions in other locations in spruce-fir forest in the Great Smoky Mountains.

Concentrations of total Al in this study are also greater than those reported for soil solutions (up to 15 mg/L, but primarily below 2 mg/L) in coniferous forests in the Solling Mountains, West Germany (Matzner *et al.*, 1982), the Adirondack Mountains, New York (David and Driscoll, 1984), the White Mountains, New Hampshire (Cronan and Schofield, 1979), on Whiteface Mountain, New York (Johnson *et al.*, in press), and

on Camel's Hump Mountain, Vermont (A. J. Friedland, University of Pennsylvania, pers. comm., 1988). These comparisons suggest that either the field site of this study has exceptionally high concentrations of total dissolved Al, or that the differences between this and other field studies are related to methods of soil water collection.

Differences in total dissolved Al between this and other studies are likely due to methods of soil solution collection. Results of the laboratory equilibration study support the conclusion that the comparison of concentrations of total dissolved Al between this and other field studies is not appropriate. In the laboratory equilibration study, concentrations of total dissolved Al in solutions from the two Great Smoky Mountains soils were similar to soil solution concentrations at the spruce-fir field site in this study and were up to 15 times greater than those reported for other field sites in spruce-fir forest in the Great Smoky Mountains. Concentrations of total dissolved Al in the two soils from the Adirondack Mountains (8 to 48 mg/L) were up to 25 times greater than those reported in field studies of similar forest soils in the Adirondack Mountains .

Since most of the total dissolved Al is non-labile with respect to 8-hydroxyquinoline and passed through the 0.4 μm filter, it is likely in a colloidal association which is not readily mobile in soil, but which is mobilized during centrifugation. The above comparisons support the conclusion that differences in concentrations of total dissolved Al between this and other field studies are due to differences in methods of soil solution collection. Therefore, values of total dissolved Al are likely not comparable between this study and field studies in which soil water was collected using lysimeters.

In the laboratory equilibration study, concentrations of total dissolved Al were similar among the soils from the four different spruce-fir forest locations of soil collection. In that study, there was very little change in concentrations of total dissolved

Al during the drying period of the soils following treatment dosing. Thus, this parameter did not illustrate the dynamics of the soil that were displayed by the monomeric Al parameters. Since monomeric Al contains Al^{+3}, it is the dynamics of this dissolved Al fraction, rather than that of total dissolved Al, which would be of greater influence on the bioavailability and toxicity of soil Al. This underscores the difference in any description, and interpretation of ecological significance, of Al chemistry of different soils that would result from only examining total dissolved Al, rather than monomeric Al chemistry. It again should be stressed that, since > 90% of total dissolved Al was resistant to complexation by 8-hydroxyquinoline in this study, the total dissolved Al parameter should not be used in as an indicator of Al bioavailability.

Monomeric Al. Concentrations of inorganic monomeric Al in organic horizon leachates in spruce-fir forests at two other locations in the Great Smoky Mountains (up to 1.6 mg/L as calculated from Johnson *et al.*, in press) were similar to LMAl concentrations found in this field study. The two studies also found similar ratios of organic to inorganic monomeric Al. In the laboratory equilibration study, TMAl concentrations and NLMAl/TMAl values in the two soils from the Adirondack Mountains were similar to those found in lysimeter solutions in similar soils in the northeastern United States by David and Driscoll (1984) and Driscoll *et al.* (1985).

These similarities support the interpretation that the monomeric Al chemistry examined in this study approximates the natural Al chemistry in the organic soil horizon of this spruce-fir forest, and can be used in comparison with the soil solution chemistry of Al of other spruce-fir forests.

Total monomeric Al. There is little published information on the chemistry of total monomeric Al in any forest soil, but that which is available is from spruce-fir forests. Soil solution oncentrations of TMAl measured in this field study (up to 6.5 mg/L) are higher than those measured in a red spruce-balsam fir forest in the

White Mountains of New Hampshire (up to 1.5mg/L, Driscoll *et al.*, 1985) and in a red spruce-eastern hemlock forest in the Adirondack Mountains of New York (up to 1 mg/L, David and Driscoll, 1985)). The TMAl concentrations, however, are apparently within the range in concentrations measured by Johnson *et al.* (in press) at two locations in spruce-fir forest in the Great Smoky Mountains. In that particular study, concentrations of total dissolved Al ranged up to 4 mg/L. Since inorganic monomeric Al was 80-90% of total dissolved Al, the highest TMAl concentrations would therefore have been between 3.2 and 4 mg/L.

Solution concentrations of TMAl in the soils in the laboratory equilibration study are also within the range in TMAl concentrations found in the field in similar soils from their respective geographic locations. For the soil from the Collins Gap site in the Great Smoky Mountains, TMAl concentrations in the laboratory equilibration study are generally similar to concentrations measured in the field study during May and fall at the lower end of the range in TMAl concentrations measured during October. Solution concentrations of TMAl in the Adirondack Mountains soils fall within the range of TMAl concentrations in lysimeter solutions from soils in the Adirondack Mountains (up to 1 mg/L, David and Driscoll, 1984) and the White Mountains (up to 1 mg/L, Driscoll *et al.*, 1984). These comparisons support the conclusion that the chemistry of monomeric Al of the soils examined in the laboratory equilibration study is representative of that which occurs in the field.

Nonlabile and labile monomeric Al. Concentrations of NLMAl and LMAl in the spruce-fir forest soils that were examined in the laboratory, greenhouse, and field studies are comparable to values reported in other studies in spruce-fir forests. In the laboratory equilibration study, concentrations of both LMAl and NLMAl in the Collins Gap soil are similar to those found in the spruce-fir field plots during May. Concentrations of LMAl in the field plots are apparently similar to those measured at two locations in

spruce-fir forest in the Great Smoky Mountains by Johnson *et al.* (up to approximately 4 mg/L, in press). Concentrations of LMAL and NLMAl in the Adirondack Mountains soils in the laboratory equilibration study are also within the ranges in concentrations found in the field in the White Mountains (Driscoll *et al.*, 1985) and the Adirondack Mountains (David and Driscoll, 1984).

Differences in the soil solution chemistry of Al betweeen spruce-fir forest soils are apparent in solution NLMAL/TMAl values of the soils examined in the laboratory equilibration study and in comparisons of solution NLMAL/TMAl values of the spruce-fir field site with that of other spruce-fir forests. In the laboratory equilibration study, Solution NLMAl/TMAl values from the Collins Gap soil were lower than values of the two soils from the Adirondack Mountains which, in turn, were similar to reported field values for soil solutions from organic soil horizons in the Adirondack Mountains (82%, David and Driscoll, 1984) and the White Mountains (> 75%, Driscoll, *et al.*, 1985). NLMAl/TMAl values of soil solutions from the Great Smoky Mountains field site are also lower than those reported for the Adirondack and White Mountains. However, values from the Great Smoky Mountains field site are similar to those (< 20%, estimated from their data) found by Johnson *et al.* (in press).

iii. Short-term variations in soil solution Al chemistry. Results of the laboratory equilibration and field studies demonstrate that significant changes in soil solution chemistry of Al can occur over a relatively short time (< 1 week). In the examined soils, LMAl concentrations tended to increase over time following wetting of the soil. Concentrations of NLMAl also tended to increase immediately following wetting, but remained relatively constant from day one on.

Use of centrifugation, rather than lysimeter collection of soil solution, increases the ability to monitor temporal variations in Al chemistry following a single precipitation event. Lysimeter collection of soil water is restricted to water held at less

than one times gravity (commonly 0.3 to 0.6 bars). When soil drying exceeds this tension, no water can be collected by lysimeters. Thus, soil drying limits the use of lysimeters in studies of temporal variations in soil solution chemistry.

In this field study, use of centrifugation allowed for sufficient soil solution to be collected up to six days following an artificial precipitation event. Variations over such a time period tend not to be considered in discussions of the dynamics or the bioavailability and toxicity of Al in forests. This may, in part, be a function of the common use of lysimeters to collect soil solutions. Alternatively, there may not be an interest in the examination of such short-term dynamics of soil solution Al. As is apparent from the data of this study, the chemistry of soil solution Al can vary quite considerably during a week's time. Such variation underscores the importance of considering changes in soil solution chemistry over such a timeframe, rather than that presented by single weekly or monthly collections, when Al bioavailability is of interest.

The dynamics of soil solution Al in the pH 5.0 treatment plot should be somewhat representative of such dynamics that are present following a non-acidified rainfall event. During the May and October sampling periods, concentrations of TMAl and LMAl increased and NLMAl/TMAl values decreased over time following treatment in this treatment plot. The change in the latter value is due to the increase in concentrations of LMAl coupled with no corresponding increase in NLMAl concentrations. The increase in LMAl concentrations over time following the artificial precipition event is consistent with the enhanced mobilization of Al due to natural acidification within the soil or, alternatively, may reflect the slow kinetics of dissolution of soil Al as the soil equilibrated with the treatment solutions.

Given the dynamic chemical nature of a forest soil, temporal variations in Al chemistry should be expected. Specific mechanisms for the observed temporal variations in Al chemistry cannot be determined by this study. It is very likely,

however, that evapotranspiration, biological activity, and physical-chemical parameters are all involved to some degree.

Elemental uptake by plants is differential, with some elements being preferentially excluded by the plant and concentrated in the rhizosphere. This has been suggested as a mechanism for detoxification of soil solution Al by plants (Marschner, 1986). Transpiration and evaporation will decrease soil water content and further concentrate elements that are excluded during plant uptake in the soil solution of the rhizosphere. Although this author made no quantitative measurement of the volume of soil that could be considered rhizosphere soil, it was obvious, through examination of the organic soil horizon at the field site, that plant roots occupy a large portion of a given volume of that soil. Therefore it should be expected that a significant portion of the soil solution that was collected in this study was influenced by plant roots. Thus, the exclusion of Al by the plant during water uptake would have influenced the soil solution chemistry of a major volume of soil in the soil zone of fine roots.

Several other biological processes may influence the soil solution chemistry of Al. Since Al is biologically cycled (David and Driscoll, 1984), Al should be solubilized during decomposition of organic matter. Mineralization of nitrogen and sulfur forms inorganic acids that could also react with Al-containing minerals and exchangeable Al and consequently release Al^{+3} into solution. Rhizosphere acidification by plants could do likewise.

Since LMAl concentrations tended to increase over time, it is logical to hypothesize that dissolution and/or exchange reactions that were caused by the natural generation of acids is responsible, as this apparently occurred in the laboratory study. Unlike the laboratory study, however, soil solution pH values did not decrease correspondingly during either the May or October sampling intervals. Such a result should be expected due to the pH buffering capacity of the soil, because Al solubilization

will be one of the H^+-consumption reactions. Data on solution concentrations of SO_4^{-2} and NO_3^- would be helpful in determining whether or not natural acidification occurred during the monitored periods; unfortunately, measurement of these chemical parameters was beyond the scope of this study.

If bioavailability and toxicity of Al are assumed to be correlated with LMAl, the trend of increasing LMAl concentrations over time supports the hypothesis that Al bioavailability and potential toxicity would increase in a like manner. This, in turn, suggests that the frequency of precipitation can potentially influence the bioavailability of Al (and possibly other elements). A hypothesis that can be formulated from this information is that Al bioavailibility and toxicity would increase as soils dry and natural acidification occurs. This combination of degree of soil moisture and natural acidification does not seem to have been thus far considered in the problem of forest decline.

iv. Seasonal variations in soil Al chemistry.

Solution Al chemistry. In general, solution concentrations of TMAl and LMAl were greater and solution NLMAl/TMAl values were lower in the October sampling period compared with the May sampling period. Since the study lasted only a single growing season, one cannot determine if these changes were seasonal and/or treatment effects. It is very likely that these effects approximate seasonal effects because the chemistry of the artificial precipitation was similar to that of the ambient precipitation.

The seasonal pattern in TMAl concentrations was similar to the increase in concentrations of total dissolved Al in A horizon leachates in a spruce-fir forest over the course of the growing season that was found by Tyler (1978). Jones *et al.* (1983) also found that concentrations of total dissolved Al in soil solutions at three locations in spruce-fir forest in the Great Smoky Mountains increased during July and August.

This temporal difference should be expected due to the general increase in biological activity (plant and soil microoganisms) as soil and air temperatures increase following the early portion of the growing season. The May sampling period was prior to bud break in the red spruce that were planted on the plots and the soil had not yet warmed to summer temperatures. During the following months, maximum biological activity would have occurred in the forest, with decomposition, nutrient uptake, and acid production, as well as solubilization of inorganic Al, likely occurring at increased rates. Given these considerations, precipitation similarities, and corroborating evidence of other field studies, it is reasonable to suggest that the differences in the soil solution chemistry of Al between May and October were, to a large part, due to seasonal effects.

If such is the case, it likely that bioavailability and potential toxicity of Al would have been greater during the sampling period in October than that in May. Therefore, if Al toxicity is a stress to plants in the examined spruce-fir ecosystem, and if growth phenology of plants on the site evolved in a manner to avoid periods of greatest Al stress, it is likely that fine root growth would preferentially occur during May rather than October. Unfortunately, site-specific data of fine root growth is not available to test this hypothesis.

Exchangeable elemental chemistry. The increase in concentration of exchangeable Al from May to October may be due to the mobilization of Al by mineral weathering and/or decomposition of Al-containing organic matter. Corresponding decreases in concentrations of exchangeable Ca, Mg, and Mn over the same period is interpreted as due to depletion of the exchangeable pools of these cations by biologic uptake. Differences in seasonal patterns of exchangable Al and Ca, Mg, and Mn support the interpretation that preferential exclusion of Al relative to Ca, Mg, and Mn during plant uptake was the mechanism for increased exchangeable Al. Such would also be predicted based upon nutritional and toxicity considerations. Alternatively, it is

possible that Al was supplied to the exchange complex at a greater rate than the other elements. This may have been the case if mineral weathering was primarily of an Al-mineral (e.g., interlayer-Al of vermiculite).

No published data on seasonal variations in soil pools of exchangeable Al in spruce-fir forests could be found. Given the differences in nutritional value among elements, however, such patterns in exchangeable Al and other elements should be present in forests. Plant uptake of nutrient cations, acidification of the rhizosphere, and increased acidification due to mineralization of organic matter will all very likely deplete the soil pool of exchangeable Ca and increase that of exchangeable Al.

Effects of treatment pH on soil Al chemistry.

i. Total dissolved Al. The absence of increased concentrations of total dissolved Al under acidic treatment does not support the prediction of the metal (Al) toxicity hypothesis of forest decline, as was initially presented by Ulrich *et al.* (1979). Under the hypothesis, acidic treatment should have increased concentrations of total dissolved Al. The decrease in concentrations of total dissolved Al under acidic treatment that occurred at 72 hours following treatment during the October monitoring sequence is completely contrary to the prediction of the hypothesis.

The cause of this reduction in concentrations of total dissolved Al under acidic treatment cannot be determined directly from the data of this study and could be due to either decreased or increased solubilization of Al by acidic treatment. Decreased solubilization could be due to Al immobilization caused by reductions in either the solubility of polymeric organic-Al compounds or the production of large soluble organic-Al complexes due to inhibition of decomposition of Al-containing organic matter.

Alternatively, it is possible that through enhanced leaching between the May and October sampling periods, the pH 3.5 treatment may have decreased the soil pool of Al which is part of, or available to become incorporated in, total dissolved Al. This

interpretation is supported by concentrations of exchangeable Al in the soils that were collected during October. Since concentrations of exchangeable Al were decreased by the pH 3.5 treatment, and if exchangeable Al is a source of Al for colloidal Al and/or strongly bound organic-Al complexes in solution, total dissolved Al may have been decreased accordingly by the pH 3.5 treatment.

While the specific mechanism(s) which decreased concentrations of total dissolved Al in solution in the pH 3.5 treatment plot cannot be determined, it is apparent that the acidic treatment did alter the chemistry of total dissolved Al. This alteration occurred in the soluble Al fraction which consists of colloidal Al and strongly bound or occluded Al-organic complexes (David and Driscoll, 1985).

ii. Treatment effects on total and labile monomeric aluminum. As hypothesized, the acidic treatment did not significantly increase soil solution concentrations of TMAl during the May and October sampling periods. There was also no significant enhancement in LMAl concentrations by acidic treatment. Neither of these results support the metal toxicity hypothesis of forest decline. However, the high variability in concentrations of TMAl and LMAl among samples of a given treatment plot may have masked specific treatment effects.

Instances where variability may obscure treatment effects are the hour one and day one collection data from October. Concentrations of TMAl and LMAl were elevated in the pH 3.5 treatment samples by 20-30% and 50-55%, respectively, for the two different times. Although these differences were not statistically significant, evidence from the laboratory equilibration and greenhouse studies of the Collins Gap soil supports the likelihood that these differences may represent real treatment effects. Identical patterns of elevated concentrations of TMAl and LMAl, accompanied by a reduction in NLMAl concentrations, occurred in the pH 3.5 treatment soils in both laboratory and field studies at hour one following treatment. Also, identical patterns of increased

concentrations of TMAl and LMAl, with no reduction in NLMAl concentrations, occurred under acidic treatment in the laboratory equilibration, greenhouse, and field studies at 24 hours following dosing.

During the October sampling period, the decreases in TMAl concentrations at 72 and 144 hours following dosing under the pH 3.5 treatment were related to decreased LMAl concentrations. Such an effect has not been predicted in any hypothesis regarding metal mobilization by acid precipitation. As previously noted, such a treatment effect was also present in total dissolved Al, and as in the case of total dissolved Al, this pattern was not found in this soil in the laboratory equilibration study. Such a pattern did occur, however, in the Adirondack Mountains-unhealthy site soil during the first week of treatment in the laboratory equilibration study.

The cause of decreased LMAl concentrations under acidic treatment can only be hypothesized. Possible mechanisms may include alteration of natural acidification or organic matter decomposition, formation of a less soluble Al-containing mineral phase, or enhanced leaching of soil Al between May and October.

The presence of a treatment effect at hours 72 and 144 , and not at hours one or 24, supports the likelihood that an endogenous soil process was altered. Acidic treatment may have inhibited nitrification in the soil. This would decrease the natural production of nitric acid and result in decreased solubilization of Al by cation exchange reactions or mineral weathering. Unfortunately, nitrate analysis of soil treatment, was precluded from the study by time constraints.

Another possible cause of reduced LMAl concentrations under acidic treatment is the formation of a less soluble Al compound. An alumino-sulfate mineral is a likely choice, as the formation of various Al-sulfate minerals in soils that receive inputs of sulfate via acidic precipitation has been hypothesized (Prenzel, 1983). Under this hypothesis, exchangeable- and mineral-Al is solublized by acidic precipitation and/or

natural acidification. High concentrations of anthropogenic SO_4^{-2} inputs subsequently precipitate the Al^{+3} as an Al-sulfate mineral.

In this field study, SO_4^{-2} concentrations were 31 times greater in the pH 3.5 treatment solution than in that of the pH 5.0 treatment. Due to this, soil solution concentrations of SO_4^{-2} in the pH 3.5 treatment plot may have become great enough to precipitate an Al-sulfate mineral. Since the solubilities of Al-sulfate minerals are lower than that of gibbsite in the pH range of soil solutions in this study (Bache, 1986), subsequent natural acidification would solubilize the Al that is present in vermiculite Al-interlayers [Al(OH)x polymer (Tamura, 1957) with solubility less than gibbsite] and on the exchange complex in the pH 5.0 treatment plot to a greater degree than the Al that is present in the hypothesized Al-sulfate mineral in the pH 3.5 treatment plot.

An alternative hypothesis is that due to the decrease in concentrations of exchangeable Al under the pH 3.5 treatment, there was less Al on the exchange complex to be mobilized by H^+ that was produced by natural acidification. Therefore less Al should be expected to be solubilized. However, the absence of a corresponding effect of the pH 3.5 treatment in the laboratory equilibration study of this soil does not support the hypothesis of enhanced leaching of soil Al due to acidic treatment.

Lastly, it is possible that decomposition was inhibited under acidic treatment and resulted in the decreased production of resin-labile organic-Al complexes that would have been measured as a portion of LMAl. The absence of a corresponding decrease in the concentration of dissolved organic matter, however, does not support this hypothesis.

The above discussion suggests several plausible mechanisms, acting singly or in concert, that may have lowered concentrations of LMAl (and TMAl) at 72 and 144 hours following treatment dosing in the pH 3.5 treatment plot. Inhibition of natural acidification by acidic treatment and induced precipitation of an Al-sulfate mineral are mechanisms favored by this author. But whatever the mechanism, the evidence is clear

that considerations of only simple H^{+}-Al^{+3} interactions are insufficient to describe the effects of acid precipitation on soil Al.

iii. LMAl and potential Al bioavailability. The operationally-defined LMAl fraction should consist of ionic Al, inorganic Al-complexes, and, possibly, resin-labile organic Al-complexes. Inorganic Al species are more toxic to plants than organic-Al complexes (Marschner, 1986) and the activity of Al^{+3} has been correlated with Al toxicity (Adams and Lund, 1966). If Al^{+3} is the only form of dissolved Al of importance in Al toxicity in forests that are experiencing forest decline, it is very likely that the speciation procedures of this study will not adequately provide a level of separation of dissolved Al species to differentiate toxic from nontoxic fractions of monomeric Al.

It is possible that the acidic treatment did alter the concentration of Al^{+3}, but this may not have been detected using the available methods. To determine if such was the case, in addition to using the laboratory Al speciation procedures, it would have been necessary to measure soil solution concentrations of major cations and anions in the soil solution and then use these data in a thermodynamically-based computer simulation program to model Al speciation.

The absence of effects of the pH 3.5 treatment on foliar concentrations of Al in the red spruce and fern, coupled with the apparent lack of toxic effects on the red spruce seedlings under the acidic treatment, supports the conclusion that the LMAl fraction was not an inappropriate parameter to monitor for treatment effects on Al bioavailability.

If the LMAl parameter is an appropriate indicator of bioavailable Al, the importance of the effects of acidic treatment on temporal changes in Al bioavailability is apparent. When LMAl concentrations are integrated over time during the 144 hours following treatment in both May and October, it is evident that plants in the pH 5.0 treatment plot were exposed to concentrations that were equal to, or greater than, those that plants in the pH 3.5 treatment plot were exposed to. The time of greatest potential

Al bioavailability was affected by treatment pH. During October, Al bioavailability would be predicted to be somewhat constant over the 144-hour monitoring period in the pH 3.5 treatment plot. In the pH 5.0 treatment plot, however, Al bioavailablity may have been lower than that in the pH 3.5 treatment plot at hours one and 24 following treatment dosing, but then increased to substantially greater levels at hours 72 and 144.

Again, the importance of duration between precipitation events on Al bioavailability is indicated. Based upon the data, it is hypothesized that over the course of a growing season, soil Al bioavailability will increase as the period between precipitation events increases. There is also the potential that as the duration of soil drying increases, Al bioavailability may be greater in a soil which receives inputs of non-acidic precipitation than in one which receives acidic precipitation. It is hypothesized that this will be the case in soils that have high rates of natural acidification that are depressed by acidic precipitation or in soils in which an Al-sulfate mineral is precipitated by anthropogenic inputs of sulfate.

iv. Nonlabile monomeric Al. As hypothesized, speciation of monomeric Al was affected by acidic treatment, with NLMAl concentrations decreased with respect to those of LMAl. This effect was short-term, being present only in samples collected at one hour following treatment dosing in the October sampling period.

As previously discussed, NLMAl is likely linked to dissolved organic matter. The DOM measurement used in this study reflects solution concentrations of humic compounds (Kumada, 1985), and the NLMAl fraction is interpreted as Al that is complexed by humic compounds (Campbell *et al.*,1983).

During the October sampling period, the pH 3.5 treatment decreased DOM values in soil samples that were collected at hour one following treatment dosing, but not at hours 72 or 144 (hour 24 measurements were not made). Decreases in both DOM

values and NLMAl concentrations at hour one under acidic treatment suggest a linked relationship. Results of the laboratory equilibration study of this soil support the interpretation that decreased solubility of organic compounds that complex Al is responsible for the decreased NLMAl concentrations under acidic treatment. Taken together, the laboratory results and field treatment effects on DOM values support the conclusion that the decrease in NLMAl concentration was due to decreased solubility of these organic-Al complexes caused by H^+-additions.

v. Treatment effects on exchangeable Al. The decrease in concentration of exchangeable Al under the pH 3.5 treatment may be due to either a decrease in the input of Al to, or the enhanced removal from, the exchangeable-Al pool. Decreased input into the exchangeable-Al pool implies the decreased decomposition of Al-containing organic matter. The likelihood of decreased solubilization of Al due to decreased decomposition is uncertain. Reported effects of acidic precipitation on the decomposition of soil organic matter are varied, ranging from enhanced to repressed decompositon rates (Cronan, 1986). A corresponding decrease in concentrations of exchangeable Ca, Mg, and Mn should be found in the pH 3.5-treated soil if decreased decomposition affected the concentration of exchangeable Al. Since this appears to be the case with both Ca and Mn, but not Mg, the hypothesis of decreased inputs of Al to the exchange complex due to reduced decomposition under acidic treatment is partially supported.

Alternatively, the lower concentration of exchangeable Al could be due to the enhanced loss of Al from the exchange complex. For this to happen, H^+ would replace Al^{+3} on exchange sites and thereby increase Al concentrations in the soil solution. Mobilized Al would then be either leached from the organic soil horizon, retained as higher Al concentrations in the soil solution, or taken up by plants. Since the latter two cases are not supported by the field data (soil solution chemistry and plant tissue concentrations of Al, respectively), the likely fate of the mobilized Al would have been

leaching from the soil horizon. Thus exchangeable Al data supports the hypothesis that acidic treatment may have mobilized soil Al during the period between May and October. Unfortunately, there are no field data to test such a hypothesis. The enhancement in LMAl concentrations under acidic treatment in the laboratory equilibration study does support this hypothesis. Enhanced leaching of exchangeable Al under acidic treatment, however, is not indicated by the results of that study.

Bioavailability and toxicity of Al are more related to ionic activity of Al^{+3} in soil solution than solely the concentration of Al^{+3} (Adams and Lund, 1966). The exchange complex theoretically exerts a significant control on the chemistry of dissolved cations through thermodynamic equilibrium reactions (Bache, 1986) and, therefore, should influence the ionic activity of Al^{+3} in solution. Based upon the increase in the concentration of exchangeable Al and the decrease in exchangeable Ca/Al values between the May and October sampling periods, it is thus very likely that the bioavailability of Al was greater in October than in May.

The relationship between the exchangeable chemistry of Al and Ca and the potential bioavailability of Al is supported by the soil solution data which show that the solution Ca/LMAl values were lower in October than in May (May: pH 3.5: 73-237; pH 5.0: 58-221 versus October: pH 3.5: 14-100; pH 5.0: 5-19). If the relationship between the concentration of exchangeable Al (and exchangeable Ca/Al) and the solution concentration of bioavailable Al is valid, then the pH 3.5 treatment would have reduced the bioavailable pool of Al by October relative to that under the pH 5.0 treatment.

Summary. The complexity of soil Al chemistry in an intact system is apparent from the results of the field study. In this field study, some characteristics of solution Al were similar to those that were found in the laboratory eqilibration study. Soil solution concentrations of Al parameters (TMAl, NLMAl, and LMAl), NLMAl/TMAl values, increases in LMAl concentrations over time, and decreases in NLMAl

concentrations under acidic treatment were similar between the laboratory equilibration and field studies. However, a major response to acidic treatment, the decrease in LMAl concentrations during the October sampling period, was not found in the same soil in the laboratory equilibration study. This demonstrates the limitations of manipulations of components of an ecosystem in the laboratory.

This study also demonstrates the potential for acidic precipitation to alter the soil solution chemistry of Al. Acidic treatment significantly decreased NLMAl concentrations and NLMAl/TMAl values, and it may also have increased LMAl concentrations immediately following treatment dosing. Although these effects were short-term and only occurred during the October monitoring period, they support the hypothesis that the bioavailability of Al would also have been altered under acidic treatment during that time. Together, these results support the metal toxicity hypothesis of forest decline. However, the unexpected increases in LMAl concentrations under the nonacidic treatment during hours 72 and 144 of the October monitoring period do not support this hypothesis of forest decline. These results underscore that the relationship between acidic precipitation and soil solution chemistry of Al is not adequately described as a simple H^{+}-Al^{+3} interaction and is more likely a system-level response.

b. Oak-hickory forest soils. Solution pH and concentration of exchangeable Ca are two soil paramters of importance to the soil solution chemistry of Al that differ between the Melton Branch Watershed (MBW) and Walker Branch Watershed (WBW) field sites. Soil pH and exchangeable Ca/Al values are lower in the soil of the WBW site than in that of the MBW site. Differences in these parameters between the two sites reflect differences in the degree of soil development at the two sites. The soil at the WBW is a Paleudult and is therefore more highly weathered than the soil (Hapludult) at the MBW.

Exchangeable elemental chemistry. Absence of effects of the pH 3.5 treatment on the exchangeable pools of Al, Ca, Mn, and Cu demonstrates that the two soils were relatively unaffected by acidic treatment over the duration of the study. This should be expected due to the large soil pools of exchangeable elements compared with the relatively small input of H^+ from the acidic treatment.

Over the course of treatment, the pH 3.5 treatment plots received approximately 2.9 equivalents of H^+ per sample area compared with 0.25 eq in the pH 5.0 treatment plots. This compares with approximately 80 eq and 25 eq of exchangeable Ca^{+2} in the volume of each soil sample (4 cm diameter by 4 cm depth) in the MBW and WBW soils, respectively. If the added H^+ would only replace Ca^{+2} on exchange sites in this volume of soil, the pH 3.5 treatment could have reduced the concentration of exchangeable Ca by approximately10% relative to the effects of the pH 5.0 treatment in the WBW soil, and by approximately 3% in the MBW soil. Given the variability in concentration of exchangeable Ca among samples in the individual treatment plots, such differences due to treatment may not have been detectable.

In reality, many other H^+-buffering reactions very likely occurred in both soils, thereby decreasing both H^+-Ca exchange reactions and Ca loss from the exchange complex. Such reactions could have included H^+-interactions with HCO_3^-, weak organic acid functional groups on soil organic matter, and exchange reactions with other cations (e.g., K, Mg, and Al). This, coupled with the spatial variability in the exchangeable chemistry of the soil, supports the likelihood that effects of treatment pH on exchangeable Ca (or any other cation) were not measurable within the timeframe of the study.

Soil solution Al chemistry. It is likely that pH and exchangeable Ca/Al predominantly influence the soil solution chemistry of Al in these oak-hickory forest soils. Solution pH and exchangeable Ca/Al were lower in the WBW soil than in the MBW

soil, and the concentration of dissolved organic matter did not differ between the soils. Lower values of solution pH and exchangeable Ca/Al will permit greater H^+-Al exchange reactions in the WBW soil. This is supported by greater concentrations of LMAl and NLMAl in this soil compared with those in the MBW soil. Lower NLMAl/TMAl values in the WBW soil are also consistent with the pattern described by Driscoll and Schecher (1988), where this value decreases with decreasing pH of solution.

Differences in the soil solution chemistry of Al between treatment plots were present at both field sites. High variability in Al chemistry among samples in the individual treatment plots, however, makes it difficult to determine if there were any treatment effects on the examined chemical parameters. Therefore, any statistically significant differences in Al chemistry between treatment plots must be interpreted with caution and may be inherent plot effects, rather than treatment effects.

The evidence supports the conclusion that acidic treatment altered the soil solution chemistry of Al in both of the oak-hickory forest soils. It appeared to lower solution concentrations of TMAl (in 13 of 16 cases) and NLMAl (in 14 of 16 cases) over the six-day sampling periods in both May and October. This effect of treatment on TMAl is contrary to that which occurred in the greenhouse study. In that study, acidic treatment increased TMAl concentrations in the bulk soils of both soil types through the enhanced mobilization of LMAl. In the field study, acidic treatment did not mobilize LMAl, and, as a result, concentrations of TMAl did not increase.

The decrease in NLMAl concentration under the pH 3.5 treatment is consistent with effects of treatment on the MBW soil in the greenhouse study, where decreased NLMAl concentration was very likely related to decreased DOM. Probable mechanisms for the reduction in DOM may have been decreased solubility of organic compounds (including organic-Al) and/or decreased production of DOM by decomposition. Either mechanism could have decreased the concentration of organically-complexed Al;

however, there were no apparent effects of treatment pH on DOM absorbance values in the soil solutions of either field site. This lack of effect does not support the likelihood that acidic treatment caused either mechanism to lower NLMAl concentrations at both field sites.

Soil solution Ca chemistry. Values of soil solution Ca^{+2}/Al^{+3} are of importance in the metal toxicity hypothesis of forest decline. Aluminum toxicity to red spruce apparently occurs when molar Ca^{+2}/Al^{+3} values of the soil solution are less than 1.0 (Rost-Siebert, 1984). It is not known what Ca^{+2}/Al^{+3} value is of importance in Al toxicity to loblolly pine; however, it is likely that Ca^{+2}/Al^{+3} can be used as an indicator of the bioavailability of soil solution Al. If this is the case, and if the concentration of LMAl is an approximation of that of Al^{+3}, total Ca/LMAl values in solutions of this study support the conclusion that Al bioavailability would be lower in the MBW soil than in the WBW soil. Greater foliar Ca/Al in the loblolly pine that were treated at the MBW site compared with that in the pine that were treated at the WBW site supports such a conclusion.

Absence of treatment effects on the chemistry of the soil solutions (Ca concentration and Ca/LMAl) suggests that soil Ca was not affected by treatment pH. The absence of any treatment effect on foliar Ca in all of the examined plant species on the field plots likewise supports the interpretation that the soil solution chemistry of Ca was not affected by acidic treatment.

As in the field study in the spruce-fir forest, results of this study support the hypothesis that acidic precipitation can affect the soil solution speciation of monomeric Al. In the case of these oak-hickory forest soils, this treatment effect occurs as a reduction in NLMAl concentration (organic Al). There also appears to have been no enhanced solubilization of LMAl (inorganic Al) under acidic treatment. The results alsoindicate that Al bioavailability in either soil was not enhanced by acidic treatment.

4. Summary of Hypothesis I Research Findings.

Acidic treatment of the soils in the laboratory equilibration, greenhouse, and field plot studies significantly altered the soil solution speciation of Al. This alteration occurred as an increase in the concentration of inorganic monomeric Al LMAl) relative to that of organic monomeric Al (NLMAl). Concentrations of LMAl and NLMAl were affected in the laboratory equilibration, greenhouse, and field studies. Acidic treatment significantly increased concentrations of total monomeric Al (TMAl) and LMAl in the spruce-fir forest soils in the laboratory equilibration study and in the spruce-fir and both oak-hickory forest soils in the greenhouse studies, but not in the soils in the spruce-fir and oak-hickory field studies. Contrary to what is predicted by the metal toxicity hypothesis of forest decline, the acidic treatment reduced concentrations of total monomeric Al (TMAl) and LMAl at the spruce-fir field site. Acidic treatment significantly decreased NLMAl concentrations in the laboratory equilibration, greenhouse, and field studies.

The soil solution chemistry of Al in the examined soils differed both geographically and temporally within soils from a single forest type (e.g., spruce-fir forest) and between forest types (spruce- fir and oak-hickory forests). These differences in solution chemistry are interpreted as being related to differences in soil solution pH, dissolved organic matter, and exchangeable Ca/Al (i.e., base saturation). Temporally, the solution chemistry of Al of the different soils varied significantly over the course of a six-day monitoring period and also with increased duration of treatment.

B. HYPOTHESIS II.

The chemistry of Al in the rhizosphere will differ from that in the nonrhizosphere soil, with the rhizosphere having relatively greater concentrations of

organically-complexed Al. Acidic precipitation will affect the chemistry of Al in the rhizosphere soil less than that in the nonrhizosphere soil.

The plant influence on the measured parameters of rhizosphere chemistry varied with plant species, experimental conditions, soil type, and pH of input solutions. As hypothesized, the plant significantly affected Al chemistry in the rhizosphere soil. Both the loblolly pine and red spruce affected increases in the soil solution concentrations of TMAl and NLMAl. The concentration of LMAl was also increased by the pine. The results support the interpretation that two plant-induced factors--soil acidification and production of organic chelates--are important in causing such effects.

The complex influence of the plant on the effects of acidic treatment on the soil chemistry of Al is evident in comparisons of rhizosphere and nonrhizosphere soils of the different plant species that were examined in this study. Effects of acidic treatment on soil solution Al in the rhizosphere differed between the red spruce and loblolly pine and between soil types in the pine studies. In the greenhouse studies, acidic treatment increased the LMAl concentration in the rhizosphere to a lesser extent than it did in the bulk soil in the loblolly pine that were potted in the soil from the MBW field site; conversely, the reverse occurred in the loblolly pine that were potted in the soil from the WBW field site. In the greenhouse study of red spruce, the concentration of LMAl in both the rhizosphere and nonrhizosphere soils were affected similarly under acidic treatment.

1. Mechanisms of Plant Influence on Soil Chemistry of Al.

It is desireable to first examine the influence of the plant on soil acidity and dissolved organic matter. This will provide a basis for the interpretation of plant and/or acidic treatment effects on the rhizosphere chemistry of Al.

a. Soil acidification. Acidification of the rhizosphere by both loblolly pine and red spruce was apparent, as both species lowered the pH of the soil or soil solution by up to 0.15 pH unit compared with the like parameter in the bulk or nonrhizosphere soil. This plant influence was evident under both nonacidic and acidic treatment conditions. One possible mechanism of this acidification may be the liberation of H^+ by the plant root during ion uptake when the equivalent charge of cations is greater than anions (Kennedy, 1988). A second mechanism may be the production of organic acids by the root (Marschner, 1986). This rhizosphere acidification will increase the solubilization, and consequently, the bioavailability, of cations (both nutrient and nonnutrient--including Al).

In the greenhouse studies, the pH of the rhizosphere soil of loblolly pine and of the rhizosphere soil solution of red spruce tended to decrease in correspondence with the decrease in the comparable pH parameter in the bulk/nonrhizosphere soil that occurred with increased input of treatment-H^+. As in the bulk soil, this increased acidification of the rhizosphere under the acidic treatments may be due to the direct acidification by H^+. An alternative hypothesis is that H^+-acidity is transferred from the plant foliage to the rhizosphere, as has been hypothesized by Ulrich (1983) and found by Flückiger *et al.* (1988). Under this hypothesis, H^+ in precipitation exchanges with basic cations (e.g., Ca^{+2}) in the foliage, acidifying the foliage, and causing the loss of the basic cations through leaching. A corresponding H^+ is given off by the roots to the rhizosphere to maintain the internal pH status of the plant. The role of this hypothesized mechanism in the acidification of the rhizosphere in the studies of loblolly pine and red spruce will be evaluated in the following discussion.

Although loblolly pine decreased the rhizosphere soil pH in the soil from the MBW field site, there was no corresponding difference in the pH of the soil solution between the bulk and the rhizosphere soils. This lack of an effect on soil solution pH

indicates the lack of a significant plant influence on soil solution pH. This contradiction with the effect of the plant on soil pH can be explained by H^+-exchange and/or dissolution reactions. The presence of such pH buffering reactions is indicated by elevated concentrations of LMAl and Ca in the rhizosphere soil solution. This effect cannot be evaluated for the soil from the WBW field site due to the lack of solution pH data for the bulk soil.

Although the pH 3.5 treatment acidified the soil solution of the bulk and rhizosphere soils in the soil from the MBW field site (also in the rhizosphere soil in the soil from the WBW field site), the degree of acidification of the rhizosphere solutions of the plants that were dosed with the pH 3.5 treatment was less than that which occurred in the bulk soil. This result supports the idea that the plant has the ability to buffer the pH of soil solutions. Simple organic acids that are present as root exudates may buffer the soil solution pH of the rhizosphere (Marschner, 1986). Unfortunately, the role of these organic acids in acidification of the rhizosphere soil solution could not be evaluated with the methods used in this study. The lessened acidification of the rhizosphere soil solution under the pH 3.5 treatment supports the hypothesis that under acidic precipitation conditions, the plant will acidify soil solutions via Ulrich's (1983) proposed mechanism to a lesser degree than that of the direct effect of acid precipitation on the soil. Conversely, in red spruce, the degrees to which the rhizosphere and the nonrhizosphere soil solutions were acidified by the pH 3.5 treatment were similar. These results, in turn, support the hypothesis that acidification of the rhizosphere and nonrhizosphere soils are similar under the Ulrich hypothesis.

Thus, the results of the greenhouse studies of both plant species support the hypothesis that acidic precipitation can acidify the rhizosphere. In addition, if the transfer of precipitation-H^+ from the foliage to the rhizosphere by the plant is a viable mechanism, the degree to which it occurs very likely varies among plant species.

b. Production of Dissolved Organic Matter. Red spruce and loblolly pine had different effects on the concentration of DOM in the rhizosphere soil solution. In the greenhouse study, red spruce significantly enhanced the rhizosphere concentration of DOM. In the field plot study, DOM concentration was greater in solution extracts from the rhizosphere soil of red spruce than in soil solutions from the bulk soil samples that were collected during October. It cannot be determined, however, if this difference was real or due to differences in the chemistry of the solutions (artificial precipitation versus DDW, in the bulk and rhizosphere soils, respectively) that were used to wet the two groups of soils. If real, the results indicate the presence of plant-affected increases in concentrations of fulvic/humic acids in the soil solution and are consistent with the results of the greenhouse study of red spruce.

In the greenhouse study of loblolly pine, however, the plant had no apparent effect on the concentration of DOM in the soil from the MBW field site. The absence of DOM data for the bulk soil prevents the evaluation of such a plant effect in the soil from the WBW field site.

The rhizosphere-nonrhizosphere differences in DOM in the red spruce studies can be explained by either of two mechanisms. Elevated DOM values in the rhizosphere indicate the enhanced production of soluble fulvic/humic acids within the rhizosphere. The rhizosphere has greater microbial populations than does nonrhizosphere soil (Marschner, 1986). It is therefore likely that processes of humification are of correspondingly greater intensity in the rhizosphere as compared with nonrhizosphere soil. This author could find no published data, however, which could confirm or refute this hypothesis. Alternatively, DOM may move from the nonrhizosphere soil to the rhizosphere soil through mass flow due to water uptake by the plant. Once in the rhizosphere, DOM would very likely be excluded from uptake by the plant root and, consequently, be concentrated in rhizosphere soil solutions.

Acidic treatment affected rhizosphere DOM differently between the loblolly pine and red spruce. Under acidic treatment, there was no apparent influence of the pine on DOM, as the pH 3.5 treatment reduced the DOM values of the rhizosphere soil solutions in the soils that were collected from the MBW and WBW field sites. This may have been due to the decreased solubility of dissolved organic matter under acidic treatment as was found in the laboratory equilibration study. Alternatively, the pH 3.5 treatment may have inhibited the production of DOM in the rhizosphere.

The increase in DOM concentrations in the rhizosphere of red spruce with decreasing treatment pH indicates a plant-mediated increase in DOM. This increase in DOM in the rhizosphere may have occurred through either (a) an increase in the rate of production of these organic compounds relative to that in the nonrhizosphere soil, (b) a decrease in the rate of decomposition of these compounds relative to that in the nonrhizosphere soil, or (c) an accumulation of DOM that was transported via mass flow from the nonrhizosphere soil to the rhizosphere. Results support the interpretation that acidic treatment increased rates of production of organic compounds within the rhizosphere.

The increase in rhizosphere concentrations of DOM with increasing treatment acidity was not likely due to accumulation of DOM that moved via mass flow from the nonrhizosphere soil to the rhizosphere. Increasing treatment acidity decreased DOM values in soil solutions of the nonrhizosphere soil, with the probable cause being the decreased solubility of fulvic/humic compounds. Due to this reduction in DOM in the nonrhizosphere soil, the movement of DOM from the nonrhizosphere soil to the rhizosphere should have been decreased under acidic treatment and resulted in less, rather than greater, accumulation of DOM in the rhizosphere.

Therefore, it is very likely that acidic treatment affected the rate(s) of production and/or decomposition of DOM in the rhizosphere. It cannot be determined

from the data, however, as to what occurred. Reported effects of acidic treatment on the decomposition rates of soil organic matter are quite variable, but are summarized by Cronan (1985), who states that decomposition of organic matter is relatively unaffected by acid treatment at pH > 3.0. Thus, results of other studies do not support the hypothesis that acidic treatment decreased decomposition rates of rhizosphere DOM.

This leaves the alternative that acidic treatment enhanced the production of DOM in the rhizosphere. This author is not aware of any study of acidic precipitation-plant interactions on the organic chemistry of the rhizosphere that would either support or refute this conclusion. An hypothesis that can be generated from this interpretation is that acidic precipitation either stimulates the production of plant root exudates or enhances the turnover of roots and mycorrhizae. Either effect would presumably increase the organic substrate from which decomposers produce humic compounds and result in increases in the soil concentration of these humic compounds.

2. Effects of Plant and Treatment pH on Exchangeable Al and Ca.

The influence of the plant on exchangeable Al and Ca in the rhizosphere varied with soil type and plant species. While red spruce had no effect on the concentration of exchangeable Al in the rhizosphere compared with nonrhizosphere soil, it did influence the concentration of exchangeable Ca; although this effect differed between the greenhouse and field studies. In the greenhouse study, loblolly pine increased the concentration of exchangeable Al and decreased exchangeable Ca/Al in the rhizosphere compared with the bulk soil--but only in the soil from the WBW field site. The influence of acidic treatment on exchangeable Al and Ca in the rhizosphere also differed with plant species and soil type. Acidic treatment decreased the concentration of exchangeable Ca and Ca/Al in the red spruce study. It also decreased concentrationsof exchangeable Al and Ca/Al values in the loblolly pine greenhouse study--again, only

in the soil from the WBW field site.

The red spruce and loblolly pine studies will be discussed separately in the following discussion of plant and acidic treatment effects on the exchangeable chemistry of the rhizosphere. The red spruce studies illustrate effects of differences in experimental conditions (greenhouse versus field) on this chemistry of the rhizosphere. The loblolly pine studies, in turn, illustrate the influence of differences in soil chemistry on effects of the plant and acidic treatment on the exchangeable chemistry of the rhizosphere.

a. Red spruce.

Plant effects. In the greenhouse study, the red spruce had no effect on concentrations of exchangeable Al or Ca. In the field study, however, the concentration of exchangeable Ca was greater in the rhizosphere soil than in the bulk soil that was collected during October, while the concentration of exchangeable Al was similar between the bulk and rhizosphere soils. Exchangeable Ca/Al was consequently increased in the rhizosphere. If these differences are not artifacts of experimental methods, the evidence supports the interpretation that the plant has an influence on the exchangeable-Ca pool of the rhizosphere. This increase in rhizosphere concentration of exchangeable Ca would have theoretically increased the concentration of Ca relative to that of Al in the rhizosphere soil solution and consequently decreased the potential bioavailability of Al. Unfortunately, it cannot be determined if this occurred because the concentration of Ca in rhizosphere soil solutions was not measured .

It is likely that experimental conditions--greenhouse versus field--influenced the chemistry of exchangeable Ca of the Collins Gap soil in the two studies. In the greenhouse study, concentrations of exchangeable Ca in the bulk and rhizosphere soils were at least twice as great as those that were found in this soil in the field and laboratory equilibration studies.

To prevent excessive soil drying, the greenhouse soils were treated with approximately 2.5 times the volume of treatment solutions and, as a result, received a total input of Ca that was approximately 2.5 times greater than that received by the soils in the field and laboratory equilibration studies. Alternatively, the mineralization rate of organic matter may have been greater in the greenhouse study, because soil temperatures were greater than those in the field and laboratory equilibration studies. Consequently, this may have supplied greater amounts of mineralized-Ca to the exchange complex.

Concentrations of exchangeable Sr and Ba--elements that are chemically similar to Ca--support the likelihood that both the volume of treatment solutions and rate of organic matter decomposition increased the concentration of exchangeable Ca in the greenhouse study. Neither Sr or Ba were components of the artificial precipitation that was used in these experiments. It is assumed that processes of decomposition will affect Ba, Sr, and Ca in similar manners--as would be predicted based upon similarities of chemical attributes (e.g., ionic charge) among the elements. Therefore, any differences in concentrations of exchangeable Sr and Ba between the field and greenhouse studies should be due to differences in soil processes, rather than in total volume of treatment solutions, between the studies. Any differences in exchangeable (Sr, Ba)/Ca values of the soils between the field and greenhouse studies would reflect the influence of differences in the total treatment input of Ca.

Concentrations of exchangeable Sr and Ba were elevated by approximately 50% in the greenhouse soils compared with that in the field rhizosphere soils. This supports the hypothesis that the increase in exchangeable Ca was an effect of soil processes. A comparable 50% increase in the concentration of exchangeable Ca in the greenhouse study would be predicted from these results. However, such an increase is much less than the actual 200-300% increase in concentrations of exchangeable Ca in the soils of

the greenhouse study compared with concentrations in the soils in the laboratory and field studies. The actual increase supports the likelihood that the difference in the concentration of exchangeable Ca between studies was due to differences in treatment dose input of Ca. Taken together, these results support the interpretation that both differences in the treatment input of Ca and mineralization rate of organic matter affected the concentration of exchangeable Ca in the soil of the greenhouse study compared with that of the field study. In addition, the treatment input of Ca had a greater influence in this regard than did the mineralization of organic matter.

This increased addition of Ca in the greenhouse study may have altered the effects of treatment pH on the bioavailability, and plant uptake, of Al through the increase in exchangeable Ca/Al. Soil solution concentrations of Ca were also two to three times greater in the greenhouse study (bulk and rhizosphere soils) than the concentrations that were present in the laboratory equilibration and field (bulk soils) studies. The LMAl concentration may also have been affected by experimental conditions. Mean LMAl concentration ranged from 0.23-0.58 mg/L in the greenhouse soils, and in time-comparable (24 hours following dosing in both May and October) samples in the spruce-fir field plots, the mean concentration ranged from 0.4-1.8 mg/L.

It is very likely that, in the greenhouse study, plant uptake of Ca would have been increased with respect to that of Al. This conclusion is supported by foliar concentrations of Al and Ca. Foliar Ca/Al was greater in the red spruce seedlings of the greenhouse study compared with those of the field study. The foliar concentration of Ca was approximately six times greater, and that of Al was approximately 1/3 lower, in seedlings that were treated in the greenhouse than in those that were treated in the field.

Taken together, these results support the conclusion that the observed differences in Ca and Al chemistry of the plant-soil system between the field and greenhouse studies were due to experimental conditions. As previously mentioned, these

effects were likely related primarily to differences in treatment input of Ca between the studies. As a result of these differences in experimental conditions, the bioavailability of soil Al was probably decreased in the greenhouse study relative to that in the field study. This conclusion is supported by the presence of a lower foliar concentration of Al in red spruce of the greenhouse study than in those of the field study.

Effects of experimental condition may have also altered the response of the examined plant-soil system to acidic precipitation. The magnitude of the effects of acidic treatment on Al chemistry of this system in the greenhouse study was likely decreased due to the enhanced treatment input of Ca. Therefore, it is likely that the greenhouse representation of the plant-soil system was probably more representative of a spruce-fir forest soil with a greater base saturation than that which is present under field conditions at the Collins Gap forest site.

Effects of treatment pH. In the greenhouse study, while the pH 3.5 treatment increased the concentration of exchangeable Al in the nonrhizosphere soil, there was no such treatment effect in the rhizosphere. Exchangeable Al of the rhizosphere was likewise not affected by acidic treatment in the field study. These results support the hypothesis that the plant has a significant influence on the Al chemistry of this spruce-fir forest soil.

In the field and greenhouse soils, exchangeable Ca in the nonrhizosphere and rhizosphere soils decreased in concentration with decreasing treatment pH. These results support the conclusion that acidic treatment enhanced leaching of Ca from both the rhizosphere and nonrhizosphere soils. These differences also support the interpretation that acidic precipitation can affect exchangeable Ca and Al in a manner that should increase Al bioavailability. Concentrations of Al and Ca/Al values in foliage of red spruce in the field and greenhouse studies, however, do not indicate the occurrence of such an effect of treatment. Given the effects of treatment on concentrations of

exchangable Al and Ca, it is hypothesized that the bioavailability of soil Ca and Al would, respectively, decrease and increase over time with prolonged inputs of acidic precipitation to this soil.

b. Loblolly pine.

The effects of the plant and treatment pH on exchangeable Al and Ca differed between the two oak-hickory forest soils. This can be explained by differences in H^+-soil reactions that are related to soil differences in concentrations of exchangeable Al and Ca. The soil from the WBW field site has greater exchangeable Al and lower exchangeable Ca than that from the MBW field site. Based upon these differences in exchangeable chemistry, it is predicted that under acidic precipitation, H^+-Al exchange reactions will be greater in the soil from the WBW field site, and H^+-Ca exchange reactions will be greater in that from the MBW field site.

Exchangeable Al. Under the pH 5.0 treatment conditions, the plant affected increases in the rhizosphere concentration of exchangeable Al in the soil from the WBW field site, but not in that from the MBW field site. This increase in the former soil may reflect either increased Al concentration in the rhizosphere through the preferential exclusion of Al during plant uptake of soil solution or enhanced solubilization of mineral-Al within the rhizosphere. In either mechanism, solution Al will react, in turn, with the exchange complex and consequently increase the concentration of exchangeable Al.

The lack of a plant effect on the concentration of exchangeable Al in the soil from the MBW field site would be predicted based upon the soil pH and concentration of exchangeable Ca. Hydrogen ions preferentially solublize Ca over Al in cation exchange and mineral dissolution reactions, as is apparent in the decrease in exchangeable Ca/Al in soils during soil formation. The greater concentration of exchangeable Ca in the soil from the MBW field site will facilitate greater H^+-Ca exchange reactions than would

occur in the soil from the WBW field site. The solubility of mineral-Al will also be lower in the former soil due to the higher soil pH and will result in lower solution concentrations of Al^{+3} which could react with the exchange complex.

The pH 3.5 treatment increased concentrations of exchangeable Al in the rhizosphere and bulk soils in the soil from the WBW field site. As would be predicted, acidic treatment increased concentrations of exchangeable Al and LMAl in the rhizosphere soil of this soil type. However, the increase in concentration of exchangeable Al in the bulk soil under the pH 3.5 treatment does not correspond to any apparent treatment effect on the concentration of LMAl; although it is possible that treatment effects were too subtle to detect. These results support the possibilities that, if the concentration of exchangeable Al is related to the solution chemistry of Al (e.g., LMAl concentration) treatment effects may have occurred during soil drying at a time other than that at which samples were collected (24 hours following dosing); or the soil chemistry of Al may have been altered prior to the last treatment dosing of the seedlings.

The absence of an effect of acidic treatment on the concentration of exchangeable Al in the soil from the MBW field site may be related to the Ca/Al status of the exchange complex of that soil. Due to the relatively high exchangeable Ca/Al values of this soil compared with that of the soil from the WBW field site, exchangeable Al would be less reactive with H^+-inputs (similarly to the case of rhizosphere acidification). As a result, the concentration of exchangeable Al in the soil from the MBW field site would be less affected by acidic treatment.

Exchangeable Ca. Under nonacidic treatment, concentrations of exchangeable Ca in both oak-hickory forest soils do not appear to have been affected by the plant. This does not support an hypothesis that is based upon the acidification of the rhizosphere by the plant. A decrease in the rhizosphere concentration of exchangeable Ca would be predicted due to the likely enhancement in H^+-Ca exchange reactions during rhizosphere

acidification. It is possible, however, that rhizosphere acidification did mobilize exchangeable Ca which was subsequently removed from solution by plant uptake. The movement of Ca from the nonrhizosphere soil to the rhizosphere via mass flow may have then replenished the rhizosphere pool of exchangeable Ca. Such a mechanism implies a steady-state condition between the exchangeable pool of Ca in the rhizosphere and plant uptake of Ca.

There are several plausible mechanisms for the decrease in the rhizosphere concentration of exchangeable Ca in the soil from the MBW field site under the pH 3.5 treatment. Of these, the decreased replenishment of rhizosphere Ca via mass flow is not indicated by soil solution data, because there was no apparent effect of treatment on the solution concentration of Ca in the rhizosphere. The lack of a decrease in concentration of exchangeable Ca in the bulk soil does not support the hypothesis that acidic treatment enhanced the depletion of exchangeable Ca in the rhizosphere.

The decrease in rhizosphere concentration of exchangeable Ca, however, indicates a plant-induced depletion that is influenced by acidic treatment--specifically, the rhizosphere acidification mechanism that was hypothesized by Ulrich (1983). However, the absence of an increase in the solution concentration of Ca in the rhizosphere of the pH 3.5-treated plants does not support this hypothesis. Although, such an effect may not be apparent due to the small number (four) of examined solution samples and high variability in the concentration of Ca among the samples. In addition, the timing of soil solution collection may have been inappropriate to detect treatment effects on the solution concentration of Ca. Significant treatment effects may have occurred during soil drying following treatment at a time other than that of sample collection or perhaps may have occurred prior to the final treatment dosing.

The lack of a comparable treatment effect in the rhizosphere soil of the soil from the WBW field site may be related to the difference in concentration of exchangeable Ca

between the two soils. Fewer H^+-Ca reactions would be predicted in this soil type based upon the smaller pool of exchangeable Ca. Also, given the difference in the size of the pools of exchangeable Ca in these two soil types, proportional changes in the concentration of exchangeable Ca would be of a lesser magnitude in the soil from the WBW field site than in that from the MBW field site and, consequently, may be less detectable.

Effects of both the plant and treatment pH on exchangeable Ca and Al differed between the two soils. Exchangeable Ca/Al chemistry of the soil from the WBW field site was more influenced by treatment effects on Al, while that of the soil from the MBW field site was more influenced by the effects on Ca. As would be expected based upon pedological classification, exchangeable Ca/Al was lower in the soil from the WBW field site than in that from the MBW field site. Exchangeable Ca/Al in the soil from the WBW field site was lower in the rhizosphere than in the bulk soil and reflected an enrichment in exchangeable Al in the rhizosphere. A similar pattern in exchangeable Ca/Al was also present in the soil from the MBW field site, although the difference was much smaller. In this case, the difference was related to a depletion of exchangeable Ca in the rhizosphere.

The pH 3.5 treatment decreased exchangeable Ca/Al of the rhizosphere soil more in the soil from the WBW field site than in that from the MBW field site. The decrease in exchangeable Ca/Al in the former soil corresponds to increases in exchangeable Al rather than decreases in exchangeable Ca. The reverse is the case in the latter soil, where under the pH 3.5 treatment, exchangeable Ca/Al was lower in the rhizosphere soil than in the bulk soil, and was related to a decrease in the concentration of exchangeable Ca. Through either the decreasing of the concentration of exchangeable Ca or the increasing of that of exchangeable Al, the lowering of exchangeable Ca/Al in the rhizosphere soil under acidic treatment would increase Al bioavailability to plants.

These above-described differences between the two soils demonstrate that both the plant and treatment acidity had a greater effect on exchangeable Al in the soil from the WBW field site than in that from the MBW field site. This reflects the inherent differences in the chemistry of exchangeable Al and Ca between the two soil types. Due to the lower exchangeable Ca/Al in the soil from the WBW field site, exchangeable Al in that soil would probably be more reactive with H^+-inputs from both the plant and acidic precipitation than it would in the soil from the MBW field site. Consequently, Al bioavailability in the former soil would very likely be enhanced to a greater degree by acidic precipitation than would be the case in the latter soil.

3. Effects of the Plant on Soil Solution Chemistry.

Red spruce and loblolly pine increased soil solution concentrations of TMAl, NLMAl, and Ca in the rhizosphere compared with concentrations in the nonrhizosphere soil. Pine also increased the concentration of LMAl, while spruce had no statistically significant effect on this parameter. The rhizosphere-nonrhizosphere differences in concentrations of the Al parameters and Ca can be explained by the apparent plant-induced enhancement of acidification and production of organic matter within the rhizosphere.

Plant-induced solubilization of rhizosphere Al could be due to the complexation of Al with simple organic chelates that were produced within the rhizosphere and/or rhizosphere acidification by the plant. Alternatively, Al and Ca may be concentrated in the rhizosphere soil solution through preferential exclusion of the elements during plant uptake of soil water. It is difficult to differentiate between these mechanisms (acidification versus exclusion) based upon the results of this study, and it is possible that both mechanisms influenced the rhizosphere chemistry of Al and Ca. The decrease in pH of rhizosphere soil or soil solution in both plant species indicates that plant

acidification was a factor that increased concentrations of Al and Ca in the rhizosphere soil solution.

Soil Al may also be solubilized in the rhizosphere through complexation with low molecular weight organic chelates and fulvic/humic acids. Smith (1976) found a number of simple organic acids present in rhizosphere soil of American beech, yellow birch, and sugar maple. Included in this group were citric, malic, malonic, and oxalic acids; all of which form relatively stable complexes with Al (Jardine and Zelazny, 1987). Unfortunately, the effects of these simple organic chelates on Al solubility in the rhizosphere could not be evaluated by the methods that were used in this study. A cursory examination found that simple organic acid (citric, malonic, oxalic, and glutaric acids) complexes of monomeric Al that may be present in the rhizosphere were not efficiently extracted by the oxine extraction step of the Al fractionation procedure of this study.

Elevated DOM values in the rhizosphere soil solution of the red spruce support the hypothesis that increased rhizosphere concentrations of NLMAl are related to the plant-induced production of organic chelates--possibly fulvic/humic acids. This relationship was not apparent, however, in the rhizosphere of loblolly pine in the greenhouse study. Loblolly pine increased NLMAl concentration, but did not correspondingly increase DOM values in the rhizosphere in the soil from the MBW field site.

Two mechanisms for this enhancement in NLMAl concentration without a corresponding increase in DOM are hypothesized. It is possible that rhizosphere DOM had a sufficient capacity to complex an increment of plant-solublized Al^{+3}. Therefore, it may not be necessary for the plant to effect increases in the production of DOM (fulvic/humic acids) to complex Al^{+3} that is solubilized through rhizosphere acidification. Conversely, chelates important in forming organic-Al complexes (NLMAl)

may be low molecular weight organic acids, rather than fulvic/humic acids, and may be ineffectively detected by the DOM measurement. It cannot be determined which, if either, was the case. Increased NLMAl concentrations in the rhizosphere, however, support the interpretation that the plant altered the soil solution chemistry of Al through an enhancement in the formation of organic complexes of Al which, in turn, increased the solution concentration of presumably less bioavailable Al.

Accumulations of Ca (Barber and Ozanne, 1970), S (Barber *et al.*, 1963), and Sr (Barber, 1962) in the rhizosphere of several different plants have been interpreted as being created through the preferential exclusion of the elements at the root surface during plant uptake of the soil solution. Preferential exclusion from plant uptake is one mechanism of Al tolerance of plants (Marschner, 1986). Evidence from this study does not, however, indicate that exclusion was the mechanism that increased soil solution concentrations of Al and Ca in the rhizosphere soils.

Ratios of solution concentrations of selected elements between the rhizosphere and bulk soils do not indicate the presence of preferential exclusion of Al by the loblolly pine. If exclusion by the root is a valid mechanism, Ca and Mn would presumably be preferentially taken up by the plant compared with Al, because Ca and Mn are essential plant nutrients. Solution concentrations of Ca, Mn, and LMAl were all increased in the rhizosphere relative to the bulk soil. These results can support the interpretation that either rhizosphere acidification or exclusion by the root was the mechanism that increased LMAl concentrations in the rhizosphere. However, values of Ca/LMAl or Mn/LMAl did not differ between the soil solutions of the bulk and rhizosphere soils. If Al is preferentially excluded from uptake by the plant with respect to Ca or Mn, the absence of any rhizosphere effect on Ca/LMAl or Mn/LMAl values does not indicate the presence of such preferential exclusion.

A similar comparison of soil solution values of Ca/LMAl and Mn/LMAl between

the rhizosphere and nonrhizosphere soils of red spruce cannot be adequately evaluated due to the high variability in solution concentrations of the elements.

4. Effects of Acidic Treatment on Rhizosphere Chemistry of Al.

a. Red spruce. In the greenhouse study, as in the laboratory equilibration study, acidic treatments increased the concentration of LMAl and decreased that of NLMAl in the nonrhizosphere soil solution. The increased LMAl concentration is interpreted as being due to enhanced Al solubility with decreasing soil solution pH. Decreases in NLMAl concentration and DOM values are attributed to the decreased solubility of organic matter (including organic-Al complexes) by acidic treatment.

Unlike nonrhizosphere soil, or results of the laboratory equilibration study, there were no apparent effects of acidic treatments on rhizosphere concentrations of NLMAl or LMAl. Concentrations of NLMAl would be predicted to decrease with decreased pH of the rhizosphere soil solution due to the H^+-induced decrease in the solubility of organic complexes, as occurred in the bulk soil and in the laboratory equilbration study. The absence of a treatment effect supports the interpretation that this plant-induced effect on soil solution Al may be related to the generation of organic chelates within the rhizosphere.

The DOM parameter includes humic and/or fulvic acids (Kumada, 1985); both of which strongly complex Al (Driscoll and Schecher, 1987). Increased concentrations of DOM in the rhizosphere soil solution should correspond to increased solution concentrations of humic/fulvic acid chelating agents and, consequently, should increase the complexation of solution Al by organic matter. This would counter the predicted decrease in the complexation capacity of the organic chelates for Al that would occur due to the increased protonation of binding sites with decreased solution pH. As a result, through the complexation of a portion of Al^{+3} that is solublized by acidic treatment, the

increase in concentration of inferred organic chelates (DOM) under acidic treatment may minimize any increase in Al bioavailability that is related to Al solublization by acidic treatment.

Based upon the results of two preliminary rhizosphere studies using DDW equilibration of soils (unpublished data, Stam, 1987), if the rhizosphere chemistry of Al in the field plot study had been affected by treatment acidity, effects would have been apparent in the solutions of the DDW-equilibrated soils. The presence of treatment effects on soil solution Al in the bulk soils during the October sampling period, coupled with the absence of treatment effects on the equilibrated solution chemistry of Al in the field rhizosphere soils, supports the interpretation that the plant moderated effects of treatment acidity on the soil solution chemistry of Al.

Although results differed somewhat between the greenhouse and field studies, results of the red spruce studies support the hypothesis that the plant can affect the soil solution chemistry, and therefore the bioavailability, of Al. The plant may have solubilized soil Al through acidification of the rhizosphere. Given this potential ability, and that Al is toxic to plants, the plant should be expected to have mechanisms to minimize the bioavailability of soil solution Al. This could be done through either control of the ionic activity of Al^{+3} in the rhizosphere through the solubilization of other cations (e.g., Ca), detoxification of Al within rhizosphere, through enhanced production of organic chelates, or detoxification within the plant itself. The results of this study are consistent with the first two of these mechanisms.

This ability of the plant to moderate the potential bioavailability of soil Al (as inferred from LMAl concentrations) is apparent in plant-acidic treatment interactions on the soil and foliar chemistry of Al in the greenhouse study and inferred from the results of the field study. Acidic treatment altered both the inorganic and organic chemistry of Al in the nonrhizosphere soil; while the effect on organic-Al was not

apparent in the rhizosphere. This lack of treatment effect indicates the presence of a plant influence on the soil solution Al that is probably related to the generation of organic chelates within the rhizosphere. This moderation of the effects of acidic treatment on soil solution Al very likely minimizes any enhancement in Al bioavailiability . This interpretation is supported by the lack of effects of acidic treatment on foliar concentrations of Al or Ca/Al values.

b. Loblolly pine. The greenhouse study of loblolly pine examined the importance of exchangeable Ca/Al values of soil on the effects of the plant and/or acidic treatment on soil Al chemistry. The response of the two oak-hickory forest soils to acidic treatment differed in both the effects of acidic treatment on soil solution Al and the influence of the plant on these treatment effects.

Acidic treatments affected concentrations of soil solution Al in the bulk soil, but not the rhizosphere soil, in the soil from the MBW field site. Conversely, these effects were reversed in the soil from the WBW field site. The pH 3.5 treatment increased the concentration of LMAl and decreased that of NLMAl in the bulk soil of the soil from the MBW field site. These changes correspond to decreases in solution pH and DOM values and indicate the increased solubility of soil Al, as well as the decreased solubility of organic-Al complexes with decreasing solution pH. There was no corresponding increase in the rhizosphere concentration LMAl under the pH 3.5 treatment. This lack of treatment effect in the soil from the MBW field site suggests that effects of acidic treatment on soil solution Al in the rhizosphere were negligible compared with the effects of the plant on that chemistry.

Effects of acidic treatment on soil Al in the soil from the WBW field site differed from those in the soil from the MBW field site. Acidic treatment did not increase the concentration of LMAl in the bulk soil, as would be predicted from pH-Al solubility relationships. This lack of treatment effect may be real. Alternatively, a treatment

effect may have been obscured by variabilty in LMAl concentrations among solution samples or may have occurred at a time other than that of sample collection. Rhizosphere concentrations of LMAl, however, increased with decreasing treatment pH. The absence of enhanced solubility of LMAl in the bulk soil, associated with the progressive increase in the rhizosphere concentration of LMAl with decreasing treatment pH, corresponds to the increased rhizosphere acidification under increased treatment acidity. This emphasizes the importance of the plant in influencing the soil solution chemistry of Al in the rhizosphere. It also suggests the presence of a plant effect that was induced by acid precipitation as is predicted under the Ulrich hypothesis of acidity transfer from foliage to the rhizosphere. This underscores the very active role of plants in affecting soil Al chemistry that must be considered in any hypothesis of forest decline that involves Al toxicity as a significant plant stress.

The difference in effects of plant-acidity interactions on the rhizosphere soil solution chemistry of Al between the two soils was probably related to soil differences in the chemistry of Ca and Al. Due to differences in the pools of exchangeable Ca and Al between the soils, H^+-Ca interactions will be greater and H^+-Al interactions will be lower in the soil from the MBW field site than in that from the WBW field site. This prediction is supported by the enhanced depletion of exchangeable Ca in the rhizosphere in the former soil under acidic treatment.

5. Plant Influence on Al Bioavailability.

Loblolly pine increased LMAl concentrations by approximately 10 times in the soil from the MBW field site and 1.5-2 times in that from the WBW field site relative to LMAl concentrations in the bulk soils. If these increases are in inorganic Al (the presence of labile organic-Al complexes in the LMAl fraction is uncertain), the enhancement in Al bioavailability would presumably occur. Loblolly pine generally has

a high tolerance to soil solution Al and toxicity levels vary among clones. In a hydroponic study, toxicity symptoms, expressed as a 10% reduction in root growth, occurred at Al^{+3} concentrations of 17 mg/L or greater in an Al-intolerant loblolly pine clone (M. Schaedle, CESF, SUNY-Syracuse, pers. comm., 1989). No response to treatment Al occurred in an Al-tolerant clone at concentrations of Al^{+3} up to 80 mg/L. In this study, measured LMAl concentrations n the rhizosphere were well below toxic levels of Al^{+3} for even the Al-intolerant clone. It is therefore probable that the enhanced solubility of soil Al by the loblolly pine presents no significant toxicity problem to the plant and is relatively inconsequential.

The concentration of LMAl in the rhizosphere of red spruce was also less than levels of Al^{+3} that have been found to produce toxicity symptoms in this species (e.g., approximately 6.5 mg/L, Thornton, *et al.*, 1987). However, the difference between the rhizosphere concentration of LMAl and experimental toxicity levels was much less for red spruce than that for loblolly pine. The concentration of LMAl in the spruce-fir soil of the field plot approached the toxicity level of Al^{+3} that was determined by Thornton *et al.* (1987). Based upon this, it is very likely that under natural conditions, red spruce that are growing in the area of the spruce-fir forest field site may encounter soil solution concentrations of Al that inhibit growth. The plant-induced increase in dissolved organic matter in the rhizosphere may function as a mechanism to decrease the bioavailability of soil solution Al. Such a mechanism may not be important to loblolly pine, given its relatively higher tolerance to Al.

It is important to remember that the soil solution chemistry in the loblolly pine and red spruce studies is only representative of that occurring at 24 hours following the final artificial precipitation treatment. The soil solution chemistry of Al can change dramatically over time following dosing, as was found in the laboratory equilibration and field plot studies. It is very likely that similar dynamics of Al chemistry were present

in the soils that were treated in the greenhouse study. Therefore, interpretations of the effects of the plant and treatment pH on soil solution Al must be done with caution, because it is possible that the influence of a factor that does affect Al chemistry may not have been significant during the chosen sampling period. In addition, the examined plant-soil systems had been treated for up to 46 weeks prior to sample collection. It is possible that a given factor may have had a greater influence on Al chemistry earlier in the study, but that system change with increased duration of treatment may have decreased the influence of the factor. Therefore, extrapolation of the results of the greenhouse studies to the field situation in regard to Al toxicity and forest decline should be done with caution.

6. Summary of Hypothesis II Research Findings.

Plant influence on the measured parameters of rhizosphere chemistry varied with plant species, experimental conditions, soil type, and treatment pH. As hypothesized, the plant significantly affected the rhizosphere chemistry of Al. Both loblolly pine and red spruce effected increases in concentrations of TMAl and NLMAl in the rhizosphere soil solution. Rhizosphere concentrations of LMAl were also increased by the pine. The results support the conclusion that two plant-induced factors--soil acidification and production of organic chelates--were important in causing such effects.

The complex influence of the plant on the effects of acidic treatment on soil Al is evident in the comparisons of the different rhizosphere-nonrhizosphere soils. Effects of acidic treatment on soil solution chemistry in the rhizosphere differed between red spruce and loblolly pine and between soil types in the two studies of loblolly pine. In the greenhouse studies, acidic treatment increased the concentration of LMAl in the rhizosphere to a lesser extent than it did in the bulk soil in the loblolly pine that were potted in the soil from the MBW field site. Conversely, the reverse occurred in the

loblolly pine that were potted in the soil from the WBW field site. In the greenhouse study of red spruce, LMAl concentrations in both the rhizosphere and nonrhizosphere soils were affected similarly under acidic treatment.

C. Hypothesis III.

Acidic precipitation will increase the bioavailability of soil Al through the increase in inorganic forms of dissolved Al.

1. Effects of Treatment pH on Foliar Elemental Chemistry.

If the foliar concentration and content of Al in the examined plant species is an adequate reflection of the bioavailability of soil Al at the root surface, the majority of the data do not support the hypothesis that acidic treatment increased Al bioavailability in the soils of this set of plant-soil experiments. There was no treatment effect on foliar concentration of Al in any of the examined plants that were grown in the spruce-fir forest soil in the field and greenhouse studies. There was likewise no effect of treatment pH on foliar concentration of Al in any of the plants that were examined in either of the oak-hickory forest soils in the field and greenhouse studies.

Foliar Ca/Al values of loblolly pine that were treated in the greenhouse support the interpretation that acidic treatment may have enhanced Al bioavailability in the soil from the WBW field site. The foliar content of Al in loblolly pine that were grown in that soil increased with decreasing treatment pH. Conversely, acidic treatment increased the foliar content of Ca and Ca/Al values in the greenhouse-treated pine that were potted in the soil from the MBW field site. This supports the conclusion that acidic treatment decreased Al bioavailability. These differences in effects of acidic treatment on the foliar chemistry of Al in loblolly pine that were grown in the two oak-hickory

forest soils help emphasize the importance of the Ca/Al state of the soil in the effects of acidic precipitation on the bioavailability of soil Al.

a. Spruce-Fir Forest Soil.

Effects of treatment pH on foliar Al. No effects of acidic treatment on Al bioavailability were apparent in foliar elemental concentrations of red spruce in the field and greenhouse studies. Since red spruce preferentially immobilizes Al in roots compared to foliage (Lord, 1982; Schier, 1985; Thornton *et al.* 1987), it could be argued that foliar concentrations of Al may not be an appropriate parameter to measure for any enhancement in Al bioavailability under acidic treatments. The Al concentration in red spruce foliage, however, is correlated with that in roots (Lord, 1985; Thornton *et al.*, 1987). There also appears to be a correlation between the solution concentration of Al^{+3} and levels of foliar Al (Schier, 1985; Thornton *et al.*, 1987). From this it should be expected that a proportional increase in Al accumulation in foliage will occur for any increased accumulation in root tissue, and thus foliar concentrations of Al should adequately reflect the bioavailability of Al at the root surface.

Thornton *et al.* (1987) reported that an Al concentration as low as 250 µmol (approximately 6.75 mg/L) increased the concentration of Al and decreased that of Ca, as well as Ca/Al values (determined by calculation from the published data), in foliage of red spruce seedlings in a hydroponic study. Unfortunately, the authors did not examine the effect of Al at lower solution concentrations that would approximate the range in LMAl concentration that was found in this study. In this study, the absence of treatment effects on the foliar concentrations of Ca and Al and Ca/Al values in red spruce supports the conclusion that Al bioavailability was not significantly altered under the acidic treatments in the greenhouse and field studies. The lack of a treatment effect on the foliar concentration of Al in fern in the field study also indicates the lack of an effect of acidic treatment on Al bioavailability.

Relationships between soil Al chemistry and foliar Al.

i. Field study. Absence of a treatment effect on the foliar concentration of Al in red spruce seedlings that were treated in the field is consistent with the absence of treatment effects on the examined Al parameters in the rhizosphere of the seedlings. The Al chemistry of both the plant foliage and rhizosphere supports the likelihood that either the acidic treatment did not enhance the concentration of bioavailable Al in the soil solution, or that the plants were able to effectively control the rhizosphere chemistry of Al and minimize its bioavailability.

In regard to the soil solution Al in the field plots, it appears that acidic treatment only affected the timing of elevated LMAl concentrations in the soil solution. The pH 3.5 treatment appeared to increase LMAl concentrations at hours one and 24 following treatment dosing, while the pH 5.0 treatment did so at hours 72 and 144. If anything, the pH 5.0-treated soils may have had a greater concentration of bioavailable Al for a longer period of time than did the pH 3.5-treated soils. Such interpretations of the chemistry of soil Al are limited, however, because soil solution Al was examined only during single weeks in May and October, and no data are available for the five intervening months. Due of this limitation, it is not known how long the conditions of soil solution Al that were found during October existed--whether only a single week, or for most of the growing season following the May sampling period.

ii. Greenhouse study. Absence of a treatment effect on the foliar concentration of Al in red spruce that were treated in the greenhouse is not consistent with the pattern of rhizosphere concentrations of LMAl in red spruce with respect to treatment pH. Based upon differences in LMAl concentration among treatments, the predicted order of folair concentration of Al would be pH 3.5 treatment $\geq$ pH 5.0 > pH 4.1. This order does not correspond with the absence of an effect of treatment pH on the foliar concentration of Al.

Several factors may have influenced this lack of correlation between the soil solution concentration of LMAl in the rhizosphere and foliar concentration of Al.

The LMAl parameter may not be an entirely adequate measurement of bioavailable Al. It is, not doubt, a more appropriate measure of Al bioavailability than are total dissolved Al or TMAl. However, LMAl probably comprises a number of different inorganic Al species (Al^{+3} and $Al(OH)_x$, $Al_y(SO_4)_x$, and AlF_x complexes), among which the bioavailability of Al likely differs. The activity of Al^{+3} would presumably be a better measurement of potential Al bioavailability because it is directly related to Al toxicity (Adams and Lund, 1966). In this study, this parameter could have been determined through the modelling of solution chemistry had concentrations of appropriate cations and anions been measured. Measurement of those parameters was precluded, however, by limited volumes of soil solution.

Alternatively, the measured LMAl concentration only represents soil solution chemistry that was present at 24 hours following the final dosing of the plants; whereas, the foliar concentration of Al reflects the integration of bioavailable Al over the duration of the study. As was seen in the Collins Gap soil in the laboratory equilibration and field studies, the soil solution chemistry of Al can change dramatically over time following a single treatment dosing of the soil, as well as over the duration of any experiment. Therefore, it is likely that a one-time measurement of the solution chemistry of the rhizosphere may not fully elaborate the Al chemistry that is pertinent to Al bioavailability. For a better understanding of such, it would be desireable to examine the effects of acidic treatment on the rhizosphere solution Al-foliar Al relationship over time--both over a week's duration and over the course of weeks--to determine the effects of solution equilibration, soil drying, and cumulative treatment on this relationship.

A third factor that may affect the LMAl-foliar Al relationship is that the scale of

examination of the rhizosphere soil may have been too large to adequately examine the effect of the plant on Al bioavailability. Perhaps the most important plant effect on Al bioavailability occurs closer to the root surface within the rhizoplane (within 2 mm of the root surface, Marschner, 1987). Rhizosphere soil that was collected in this study extended approximately 5 mm from the root surface and would have contained the rhizoplane soil. It is therefore possible that biologically-significant Al chemistry of the rhizoplane may have not been detected due to the inclusion in, and dilution by, the rest of the rhizosphere soil.

The solution Ca/LMAl parameter more accurately reflects the activity of Al^{+3} than does LMAl concentration, and therefore this value is likely to be more indicative of Al bioavailability. The apparent absence of a treatment effect on Ca/LMAl in the rhizosphere soil solution supports the hypothesis that acidic treatment did not increase Al bioavailability.

b. Oak-Hickory Forest Soils.

Effects of treatment pH on foliar Al. Based upon foliar concentrations of Al in all four plant species that were treated in the field plots and in loblolly pine that were treated in the greenhouse, there is little evidence for any increase in Al bioavailability in either oak-hickory forest soil under acidic treatment. In fact, the foliar concentration of Al in the greenhouse-grown pine that were planted in the soil from the MBW field site was decreased under acidic treatment. The foliar Ca/Al value of the seedlings that were grown in that soil was correspondingly increased under acidic treatment.

Foliar Ca/Al values of the greenhouse loblolly pine support the likelihood that Al bioavailability in the soil from the WBW field site may have been increased under acidic treatment. Although the 30% decrease in foliar Ca/Al that occurred under acidic treatment was not statistically significant, such a treatment effect would be predicted

based upon the lower exchangeable Ca/Al status of this soil compared with that from the MBW field site.

In the greenhouse study, differences in needle growth of pine seedlings among treatments may have influenced foliar concentrations of Ca and Al under the different treatments. Greater growth under pH 3.5 and 4.1 treatments may have served to dilute foliar concentrations of Al and Ca. Therefore, elemental content of foliage should provide a better estimate of total foliar incorporation of Al and Ca. The foliar content of both Al and Ca display patterns which correspond to differences in effects of acidic treatment on Al and Ca between the two soils. The pH 3.5 treatment increased the foliar content of Al (although the effect was not statistically significant) in seedlings that were grown in soil from the WBW field site (low exchangeable Ca/Al) and decreased it in seedlings that were grown in the soil from the MBW field site (high exchangeable Ca/Al). Decreasing treatment pH increased the foliar content of Ca in seedlings that were grown in the MBW soil, but had no effect on that of seedlings that were grown in the WBW soil. Such treatment effects would be predicted by the Ruess and Johnson model (Ruess and Johnson, 1986) of effects of acidic precipitation on the soil solution concentrations of Ca and Al.

This evidence supports the interpretation that the artificial acidic precipitation enhanced Al bioavailability. It is important to note that this enhancement was soil-dependent and was likely related to the exchangeable Ca/Al state of the soil. This underscores the importance of considering other soil factors (including Ca), in addition to soil Al, when examining the hypothesis that acidic precipitation can cause forest decline by mobilizing soil Al.

Relationships between soil Ca/Al and foliar Ca/Al. In the field plot studies, loblolly pine seedlings that were treated at the MBW field site had greater foliar concentrations of Ca than those that were treated at the WBW field site. This difference

is not unexpected, because it corresponds to differences in the concentration of KCl-extractable Ca between the two oak-hickory forest soils.

Foliar concentrations of Al in loblolly pine at the two field sites do not correspond to differences in concentrations of KCl-extractable Al or soil solution LMAl between the two soils. The soil at the WBW field site had greater concentrations of extractable Al and LMAl than did that at the MBW field site, while foliar concentrations of Al in pine seedlings were similar between the two soil types. If bioavailability of Al is directly related to KCl-extractable Al or LMAl, one would predict that foliar concentrations of Al would be greater in seedlings grown at the WBW site. Since this is not the case, these results support the interpretation that the plant has the ability to limit uptake and/or transport of soil Al to foliar tissues.

In the greenhouse study, foliar concentrations of Al in pine that were potted in the soil from the WBW field site under the different treatments do not correspond with the patterns in soil concentrations of LMAl or exchangeable Al and Ca, or values of exchangeable Ca/Al. Differences in foliar Ca/Al values between treatments parallel differences in exchangeable Ca/Al values under the different treatments (foliar Ca/Al: pH 4.1 > 5.0 > 3.5; exchangeable Ca/Al: pH 4.1 > 5.0 > 3.5). The inverse relationship occurred in pine that were grown in the soil from the MBW field site. In this case, differences in foliar concentrations of Al among treatments parallel differences in exchangeable Ca/Al values of the soil under the treatments. While these patterns do not establish linked relationships between foliar Al and exchangeable Al or exchangeable Ca/Al of the soils, they point to the likely the importance of the chemistry of the exchange complex in determining the potential for enhanced bioavailability of soil Al under acidic precipitation.

Results of the greenhouse and field studies support the hypothesis that the plants that grow at the WBW field site would be exposed to greater concentrations of

bioavailable, and potentially toxic, Al than those that grow at the MBW field site. As previously discussed, however, loblolly pine has a great tolerance of Al. Absence of effects of the acidic treatment on foliar concentrations of Al and Ca and Ca/Al values in all of the examined plant species that grew on the field plots supports the hypothesis that acidic treatment did not increase Al bioavailability.

A model of acidic precipitation effects on xylem tissue Ca/Al and Mn/Al. Results of the greenhouse study of loblolly pine can be used to form a conceptual model to predict temporal changes in the Ca-Al and Mn-Al chemistry of xylem tissue of trees in response to soil acidification. This model stresses the influence of soil base saturation (as represented by exchangeable Ca/Al values) on the effects of acidic input on soil Al. In a given soil with a moderate base saturation, acidic addition will preferentially mobilize Ca over Al. This will result in a specific bioavailability and rate of plant uptake of Ca which, in turn, will be reflected by a certain concentration of Ca in xylem tissue. Over time, the soil pool of Ca that is available for mobilization by H^+-inputs will decrease and greater H^+-Al reactions will occur. This will increase the bioavailability and plant uptake of Al, and consequently increase the concentration of Al and decrease the Ca/Al value in new xylem tissue. A similar response to H^+-input is predicted for Mn-Al chemistry based upon the results of the greenhouse studies.

This conceptual model supports the hypothesis of Shortle and Smith (1988), who argue that, over time, plant sequestering of Ca in tissues causes a natural decrease in the soil concentration of bioavailable Ca. The bioavailability of Al correspondingly increases (presumably through H^+-Al reactions) and it results in decreased Ca/Al values in root tissue. From their argument, one can infer that this would likely decrease the Ca/Al value in xylem tissue of the tree bole. This would produce a pattern of decreasing Ca/Al values in new xylem tissue over time; a pattern that could occur without any input of acidic precipitation.

As has been found in this study, enhanced H^+-input affects the bioavailabilities of Ca and Al. The relative degrees to which Ca and Al are affected depends upon the Ca/Al state of the soil at the time of H^+-input. If exchangeable Ca/Al is relatively high (e.g., base saturation > 20%, Ruess and Johnson, 1986) acidic precipitation will mobilize more Ca than Al and result in increased bioavailability and plant uptake of Ca. This initial effect of acidic precipitation should be reflected in the increased concentration of Ca, as well as increased Ca/Al in new xylem tissues--as occurred in foliage of the pine that were grown in the soil from the MBW field site in the greenhouse study. With time, the H^+-enhanced depletion of soil Ca would result, and H^+-Al reactions would increase. The bioavailability of Al would correspondingly increase and be reflected in decreased Ca/Al in new xylem tissues--as occurred in foliage of the pine that were grown in the soil from the WBW field site in the greenhouse study.

If the status of soil Ca/Al was initially low (e.g., base saturation < 20%, Ruess and Johnson, 1986), initial inputs of acidic precipitation would enhance the bioavailability of Al relative to that of Ca. As a result, there would be no initial increase in Ca/Al values in new xylem tissue--only a decrease. Natural or anthropogenic acidification of the soil would produce similar patterns of decreases in xylem Ca/Al. It is likely, however, that the patterns induced by natural and anthropogenic acidification may differ in several respects which are dependent upon the initial exchangeable Ca/Al status of the soil. Natural soil acidification at a relatively constant rate would likely decrease Ca/Al in xylem tissue in a gradual manner due to the gradual depletion of bioavailable Ca in the soil. Inputs of anthropogenic acidity will represent an increment of H^+-input to the forest soils that would be added to the natural background of acidity that is produced by natural acidification. Consequently, the initial input of anthropogenic-H^+ to forest soils would very likely mobilize soil Ca and effect an increase in xylem Ca/Al values. In addition, since inputs of anthropogenic acidity would

likely enhance the rate of soil acidification, it should be expected that the resultant increase in xylem concentration of Al and decrease in xylem Ca/Al would be more dramatic than that in the case of natural acidification.

It is difficult to differentiate the effects of acidic precipitation on Al concentrations or Ca/Al values in xylem tissues from those of natural acidification. Baes and McLaughlin (1984, 1986) found that xylem concentrations of Al in several coniferous species at several sites in eastern Tennessee have increased since 1950. Similar results for Al have been found in red spruce and sugar maple in the Green Mountains of Vermont (Sherbatskoy, 1984) and in red spruce near a coal-burning generator in New Brunswick, Canada (Arp and Manasc, 1988). Bondietti *et al.* (1989) also report decreased Ca/Al values in xylem tissue formed since 1950 in the trees that were studied by Baes and McLaughlin (1986). Data of Arp and Manasc (1988) show a similar pattern. These results could be used as evidence to support hypotheses that either natural or anthropogenic acidification of forest soils is reflected by the patterns in xylem chemistry of the trees. However, the temporal coincidence of the decrease in xylem Ca/Al that occurred in trees at the locations of the three different studies--all of which are impacted by acidic precipitation--supports the hypothesis that these trends in xylem chemistry reflect anthropogenic acidification of the forest soils.

The data of Arp and Manasc (1988) and Baes and McLaughlin (1986), moreover, display a pattern which further supports anthropogenic acidification as the cause of the decreases in Ca/Al in xylem tissue of trees in the respective studies. In both studies, the xylem tissue concentration Ca increased prior to decreasing, as would be predicted from the above-presented model of acidic precipitation and xylem elemental patterns. The xylem tissue concentration of Ca also appears to have increased prior to increases in the xylem tissue concentration of Al in trees in the Great Smoky Mountains (although this is difficult to determine from the figure presented in Baes and McLaughlin, 1986).

In the greenhouse study, the pattern of effects of acidic treatment on foliar Mn/Al values of loblolly pine follows that of Ca/Al. These effects of acidic treatment can be used to further evaluate the findings of the above-mentioned field studies. Data of Arp and Manasc (1988) display an initial increase, that is followed by a decrease, in the concentration of Mn from older to younger tissues in red spruce. The increase in Mn occurred prior to the increase in the xylem concentration of Al. Data of Baes and McLaughlin (1986) display a similar pattern in xylem concentrations of Mn and Al of red spruce and eastern hemlock in trees in which xylem concentrations of Al have increased since 1940. In 25 of 31 examined spruce and hemlock, Mn concentration increased prior to the increase in Al concentration. In the other six trees, the initial increase in concentration of Mn was contemporaneous with the increase in that of Al. In the majority of these trees, Mn concentration decreased following the initial increase. These patterns further support the hypothesis that the bioavailability of Al was increased and that of Ca and Mn was decreased by anthropogenic inputs of acidity to the respective forests.

2. Effects of Treatment pH on Biomass and Growth.

Patterns of growth and biomass allocation in both red spruce and loblolly pine provide supportive evidence that acidic treatment did not increase either the bioavailability or toxicity of soil Al in any of the three examined soils under either greenhouse or field conditions. Treatment affected growth and biomass allocation in red spruce and loblolly pine in only the greenhouse studies. Reduction in fine root biomass in both plant species under acidic treatment could be interpreted as being due to enhanced Al toxicity. The patterns of multiple treatment effects, however, more strongly indicate that nitrogen fertilization was a factor that influenced biomass allocation.

In the greenhouse studies of red spruce (initial study) and loblolly pine, several treatment effects on biomass parameters could be interpreted as resulting from Al toxicity that was induced by the pH 3.5 treatment. Acidic treatments altered the growth and biomass parameters of loblolly pine and red spruce. This alteration was expressed as a shift to increased production of above-ground tissues in both plant species, as indicated by the decreased ratios of both fine root/total root biomass and root/shoot biomass with decreasing treatment pH.

Death of fine roots, decreased root growth, and altered root morphology are common symptoms of Al toxicity in the genus *Picea* (e.g., Thornton *et al.*, 1987; Matzner *et al.*, 1986; Rost-Siebert, 1985). Decreased root growth is also a symptom of Al toxicity in loblolly pine (M. Schaedle, CESF, SUNY-Syracuse, pers. comm., 1989). Therefore, measured decreases in root biomass in red spruce and loblolly pine could be used to support the hypothesis that acidic treatment caused Al toxicity to roots. The pH 3.5 treatment, however, produced no visible signs of altered root morphology or excessive root death in the seedlings--symptoms that are indicative of Al toxicity.

Further evidence that does not indicate that Al toxicity was the cause of reduced root growth is that reduction in root growth was greater in pine that grew in the soil from the MBW field site as compared with those that grew in the soil from the WBW site. The reverse pattern would be predicted if Al toxicity was a factor because concentrations of LMAl (and presumably Al^{+3}) were greater in soil solutions of the WBW site soil than in those of the MBW site soil. In addition, LMAl concentrations were at least an order of magnitude less than the Al^{+3} concentration that produced toxic symptoms (reduced root growth) in loblolly pine in several hydroponic studies (M. Schaedle, CESF, SUNY-Syracuse, pers. comm., 1989).

Several other plant parameters do not support the likelihod that the alteration in fine root biomass that occurred under the most acidic treatment was due to enhanced Al

bioavailability/toxicity, but rather was due to nitrogen fertilization. If the fine roots were adversely affected under the most acidic treatment, decreased translocation of nutrients and water to the shoot and impaired shoot growth should have occurred as is implicit in the metal toxicity hypothesis of forest decline. The increase in shoot biomass in both red spruce and loblolly pine under the pH 3.5 treatment does not indicate that root function was impaired by that treatment. Accelerated bud break in red spruce under the pH 3.5 treatment also indicates a beneficial effect of acidic treatment. Also, the degree of chlorosis in terminal shoot needles of red spruce was less under the pH 3.5 treatment compared with that under the pH 5.0 treatment, and further indicates a beneficial effect of acidic treatment.

Thornton *et al.* (1987) reported that in a hydroponic experiment, a solution concentration of 250 µmol Al decreased the concentration of Ca and Ca/Al (as calculated from their data) in red spruce foliage. In this present study, acidic treatments did not produce such effects on the concentration, or content, of Ca or Ca/Al values in red spruce foliage. The increase in foliar content of Ca in loblolly pine that were potted in the soil from the MBW field site that occurred with decreasing treatment pH argues against the presence of Al toxicity. The acidic treatment, however, significantly decreased foliar concentrations of Ca in pine seedlings that grew in the soil from the WBW field site. This evidence supports the hypothesis that plant uptake of Ca was reduced. The foliar content of Ca was not affected, however, which does not indicate a reduction in Ca uptake by the plant due to Al toxicity. Transpiration rates of red spruce seedlings were also not affected under acidic treatment.

The preceeding results do not support the proposition that acidic treatment reduced uptake of nutrients or water by either red spruce or loblolly pine. Taken together, the results of this study do not indicate any deleterious effect of the most acidic treatment on root growth and function, or of any enhanced deleterious effect of Al on

these parameters, in either red spruce or loblolly pine.

The lack of an enhancement of Al toxicity under acidic treatment is also indicated by results of field studies of either tree species. There was an absence of treatment effects on growth, biomass allocation, and timing of bud break of red spruce that were treated on the field plots. There were also no treatment effects on concentrations of Al and Ca, and Ca/Al values in foliage of either of the examined tree species.

The patterns of altered growth in both red spruce and loblolly pine under acidic treatment support the findings of Troughton (1980), who reported that under conditions of increased nitrogen input, carbon allocation within plants is altered such that less root biomass and greater shoot biomass are produced. In these experiments, N inputs were increased by 8 and 30 times with decreasing treatment pH from pH 5.0 to 4.1 to 3.5. The relationship between patterns of plant growth and N concentrations of the different treatments supports the proposition that effects of treatment on plant biomass were a response of the plants to N fertilization, rather than an effect of Al toxicity.

Results of the greenhouse pine study support the hypothesis that acidic treatment affected a growth-enhancing factor other than (or in addition to) N fertilization. Acidic treatments increased new shoot production and root/shoot ratios to a greater degree in seedlings that grew in the soil from the WBW field site compared with that of the pine that grew in the soil from the MBW field site. These results suggest an interaction between treatment acidity and soil type and can be used to support the hypothesis that treatment acidity increased the bioavailability of certain nutrient cations through dissolution or exchange reactions. Under this hypothesis, H^+-inputs mobilize nutrient cations (e.g., Ca and Mn), the bioavailability and plant uptake of these nutrients increases, and plant growth is consequently enhanced. Such an effect is likely if a solubilized nutrient is limiting plant growth. The absence of treatment effects on foliar concentrations of Ca and Mn do not support the likelihood that either of these two

nutrients were the elements important in this regard.

As occurred with the chemistry of the examined elements in the rhizosphere and foliage, effects of treatment pH on growth and biomass allocation in red spruce also differed between the greenhouse and field experiments. These differences in response to treatment pH underscore that caution should be used in the extrapolation of results of greenhouse studies to the field situation.

3. Summary of Hypothesis III Research Findings.

If the concentration and content of Al in foliage of the examined plant species are an adequate reflection of the bioavailability of soil Al at the root surface, the majority of the data do not support the hypothesis that the bioavailability of Al was increased by acidic treatment in any of the three soils that were examined in this set of plant-soil experiments. There were no effects of treatment on the concentration or content of Al in the foliage of any of the examined plants that grew in the spruce-fir forest soil in either the field or greenhouse studies. There was also no effect of treatment on foliar concentration of Al in any of the examined plants that were grown in either oak-hickory forest soil in the field or greenhouse studies.

Foliar Ca/Al values of loblolly pine that were treated in the greenhouse indicate the possible enhancement of Al bioavailability in the soil from the WBW field site under acidic treatment. The foliar content of Al in loblolly pine that were potted in that soil increased with decreasing treatment pH. Conversely, acidic treatment increased the foliar content of Ca and Ca/Al values in loblolly pine that were potted in the soil from the MBW field site, and these results indicate the absence of increased Al bioavailability in that soil under acidic treatment. These differences in effects of acidic treatment on the foliar concentration of Al emphasize the importance of the status of soil Ca/Al in influencing the effects of acidic precipitation on soil Al.

Acidic treatments decreased root/shoot values of red spruce and loblolly pine that were treated in the greenhouse. The evidence supports the interpretation that nitrogen fertilization due to the increased treatment inputs of nitrogen with decreasing treatment pH, rather than Al toxicity, was the cause of such treatment effects. Effects of treatment pH on growth and biomass allocation in red spruce and foliar concentrations of Ca and Al in loblolly pine and red spruce differed between the field plot and greenhouse studies. These results underscore the uncertainty that is present in the extrapolation of results of greenhouse studies to the field situation.

D. Summary of Hypothesis Evaluation.

Evaluations of the major hypotheses of this work based upon the results of the different studies are summarized in Table 22.

E. The Influence of Hierarchial, Temporal, and Spatial Scales on Soil Al Chemistry.

This study has examined the response of an ecosystem parameter (Al biogeochemistry) to a simulated anthropogenic perturbation (acidic precipitation) at three hierarchial levels within the ecosystem: that of a single component--the soil, the interaction of components--plant and soil, and of multiple interacting components within the ecosystem under nearly natural conditions. The influence of the increased complexity of the examined system on the soil solution chemistry of Al is apparent as one increases the number of interacting components of the manipulated system. The plant alters the soil solution chemistry of Al compared with such chemistry of the nonrhizosphere soil. The solution soil chemistry of Al in the intact system, in turn, is more complex than that which is present in the simple plant-soil system of the greenhouse study.

Certain aspects of the soil chemistry of Al, and the effects of acidic treatment on

Table 22. Summary of the Evaluation of the Major Hypotheses Tested in this Study.

Hypothesis 1. Acid precipitation will not significantly mobilize soil Al.

a. Field studies. Supported by the results of all field studies during both May and October.

b. Greenhouse studies. Supported by the results of oak-hickory forest--WBW site soil.

c. Laboratory equilibration study. Supported by LMAl concentrations in soils of the Adirondack Mountains-unhealthy forest site (9 of 9 monitoring times), Adirondack Mountains-healthy forest site (8 of 9 monitoring times), Great Smoky Mountains-Indian Gap site (11 of 15 monitoring times), and Great Smoky Mountains-Collins Gap site (7 of 15 monitoring times).

Acid precipitation will significantly alter the soil solution speciation of Al through increases in LMAl/NLMAl.

a. Field studies. Supported by results of spruce-fir forest site study (October). Not supported by the oak-hickory forest site studies.

b. Greenhouse studies. Supported by the results of the studies the of oak-hickory forest (MBW site soil) and spruce-fir forest soil.

c. Laboratory equilibration study. Supported by LMAl/NLMAl in soils of the Adirondack Mountains-unhealthy forest site (0 of 9 monitoring times), Adirondack Mountains-healthy forest site (2 of 9 times), Great Smoky Mountains-Indian Gap site (5 of 15 times), and Great Smoky Mountains-Collins Gap site (8 of 15 times).

Hypothesis 2. The rhizosphere will have relatively greater concentrations of organically-complexed Al than will the nonrhizosphere soil.

a. Greenhouse studies. Although the absolute concentrations of NLMAl were increased in the rhizosphere, they were not increased relative to LMAl concentrations, and therefore the hypothesis is not supported by the results of the loblolly pine potted in either of the oak-hickory forest soils and red spruce.

Acid precipitation will affect the rhizosphere chemistry of Al less than that of the nonrhizosphere soil.

a. Greenhouse studies. Supported by the rhizosphere concentration of LMAl in loblolly pine (soil with relatively high Ca/Al). Not supported by that of loblolly pine (soil with low exchangeable Ca/Al) or by that of red spruce.

Hypothesis 3. Acid precipitation will increase the bioavailability of Al.

a. Field studies. Not supported by foliar concentrations of Al and Ca/Al in all examined species at the spruce-fir forest and oak-hickory forest sites.

b. Greenhouse studies: Not supported by foliar concentrations of Al in the red spruce and the loblollly pine potted in both oak-hickory forest soils. Supported by foliar content of Al in loblolly pine potted in the soil with relatively low exchangeable Ca/Al values.

that chemistry, in the intact system can be explained from the results of the laboratory study (e.g., solution NLMAl/TMAl, decreased solubility of NLMAl under acidic treatment, and increases in TMAl concentration over time following the artificial wetting of the soil). Certain dynamics of importance to the Al biogeochemistry (including Al bioavailability and toxicity) of the system, however, would not be predicted from the results of the laboratory manipulation of the soil component of the system. Such an example is the increase in LMAl concentrations under the artificial non-acidic precipitation at hours 72 and 144 following treatment dosing during the October monitoring period of the field study. Differences in treatment effects on plant growth and foliar concentrations of Al, Mn, and Cu between the field and greenhouse studies further emphasize the potential for error that is inherent in the extrapolation of results of a greenhouse or laboratory study on an ecosystem component(s) to the intact system.

In addition to examination of an ecosystem parameter at several different levels of system complexity, this study has incorporated several aspects of temporal and spatial scales in the examination of Al biogeochemistry. The influence of time on the soil solution chemistry of Al is apparent in the laboratory equilibration study, as well as in the field studies. Seasonal differences in soil solution Al have been noted by investigators (e.g., Tyler, 1981); however, the temporal dynamics of soil solution Al at a shorter time scale have not received attention. This may be the first study to examine the dynamics of soil solution Al over a time interval as short as a week.

Major changes in concentrations of certain dissolved Al parameters (e.g., LMAl) that will very likely affect Al bioavailability are possible during such a period. This temporal scale of examination allows a view of certain dynamics of soil Al chemistry that probably have a biological significance that is at least as great as that of such dynamics which would be determined based upon once-a-month sampling of the soil solution. This underscores the importance of the choice of an appropriate time scale for an examination

of an ecosystem parameter which will permit the monitoring of biologically-relevant (i.e., bioavailability or toxicity) dynamics of an ecosystem parameter. A less appropriate temporal scale of examination may completely miss certain dynamics that are important to ecosystem functioning.

This study also illustrates differences in an ecosystem parameter that can occur at different spatial scales of examination. Examination of Al chemistry at the scale of the rhizopshere (cm), field plot (m), and geographic location (km) emphasizes the influence of environmental heterogeneity on soil Al chemistry; an influence that is of implicit biological importance.

Examination of the chemistry of the rhizosphere indicates major differences in the biological/chemical environment of the soil that can occur at very small spatial scales (cm). These studies of rhizosphere chemistry point to the significant differences in soil Al chemistry that can occur at such spatial scales; differences that are very likely of importance to soil organisms (e.g., invertebrates, fungi), as well as plant roots.

This study of effects of the plant on rhizosphere chemistry of Al may be the first to examine solution chemistry of any chemical parameter in the rhizosphere. Judging from the literature--articles and abstracts--surveyed by this author, this very likely is the first to attempt to examine speciation of dissolved Al in the rhizosphere soil solution. Results of this study illustrate the significant influence of the plant on the soil chemistry of Al, as well as on that of soil pH, Ca, Mn, and Cu. An interaction between the plant and acidic precipitation on this soil chemistry, which has only recently been considered to be of importance to forest trees exposed to acidic precipitation, is also apparent.

Geographic variability in soil chemistry of Al is apparent in results of the laboratory study of the different spruce-fir forest soils. This variability is very likely

related to environmental factors--physical and biological--which influence soil development at different forest locations. Climate and length of growing season differ between the Adirondack and Great Smoky Mountains. It is probable that microclimatic differences occur between each of the two field sites in either group of mountains. Soil parent material differs, and plant communities are also likely to differ, between the different locations.

Through differences in these combined factors, it is probable that soil development differs between the different sites, as is indicated by differences in soil chemistry among the four soils. It is also very likely that Al bioavailability varies among forest sites. Effects of acidic treatment on Al chemistry of the four soils also differs among the soils. Differences in effects of acidic treatment on soil Al chemistry among the soils underscore that caution should be used in extrapolation of a soil charateristic (in this case, Al chemistry) of a certain type of forest from one geographic location to another.

E. A Modified Metal Toxicity Hypothesis of Forest Decline.

Although results differed somewhat among the laboratory equilibration, greenhouse, and field studies, this study has demonstrated that acidic precipitation can alter the soil chemistry of Al. There is evidence that potentially bioavailable species of Al can be solublized by acidic precipitation, as has been predicted under the metal toxicity hypothesis of forest decline. The magnitude of change, however, does not appear to be sufficient to significantly enhance the bioavailability, and potential toxicity, of Al in the examined soils.

The active role of the plant in affecting the soil solution chemistry of Al was apparent in the examination of the rhizosphere chemistry of Al. This factor should be considered in any hypothesis of forest decline that invokes the toxicity of soil metals--

Al and/or heavy metals. In this regard, it is also desireable to consider acidic precipitation-soil interactions as acidic precipitation-rhizosphere soil interactions due to the abundance of rhizosphere soil in the soil zone that contains the majority of the fine plant roots in many forests; a factor which has been essentially ignored in considerations of acidic precipitation-soil reactions.

Given that the findings of numerous studies of the effects of a single pollutant (e.g., ozone, H^+, SO_2, and others) on a component of the ecosystem (e.g., the soil, the plant, or soil micro-organisms) have been inconclusive as to linking specific pollutants with a specific occurrence of forest decline, it will probably be more fruitful, more appropriate, to consider forest decline as being a multiple stress syndrome of the whole ecosystem.

Firstly, it is unlikey that a single pollutant will only affect a single component of the given forest ecosystem. Acidic precipitation will interact with leaves of vegetation (both trees and herbaceous growth), soil inorganic matter, soil microorganisms, soil organic matter, mycorrhizae, tree roots, and many other components of the forest. Each will be affected to some extent, however small, if the H^+ in precipitation interacts with the surface chemistry of the component. Ozone will interact with foliar surfaces of both trees and herbaceous growth, as well as any lichens, fungi, and algae that grow on plant surfaces. Inputs of anthropogenic heavy metals to a forest may increase the bioavailability and toxicity of the heavy metals to plants, mycorrhizal fungi, and soil microorganisms. The metals may also replace nutrient cations on the exchange complex and cause the enhanced leaching of the nutrients from the soil.

These examples are mentioned to illustrate that a single pollutant has the potential to affect more than a single component of an ecosystem. Additionallly, in each of the above-mentioned cases, each direct interaction between a pollutant and ecosystem component has the potential to further affect other components of the ecosystem through

energy and nutrient flow linkages.

Secondly, given that many forests are exposed to multiple pollutants, as well as natural stresses (e.g., temperature, moisture) it seems appropriate to consider forest decline as a system-level response to multiple stresses. The concept of predisposing, inciting, and contributing stresses (Manion, 1981) seems very applicable when considering forest decline.

If Al toxicity is a factor in forest decline, it is more likely that it is one of a number of stresses that affect the plants and soil micorooganisms of the ecosystem. Given the multiple stress regime of many forests, and from the findings of this study, a modified hypothesis of forest decline can be developed that includes Al (and heavy metal) toxicity as a significant stress to forest trees, but not as the initiating stress of forest decline. The hypothesis is as follows:

In a given forest, trees are exposed to the natural stress regime. Due to this, the ratio of gross photosynthesis to respiration will very likely not be optimal. Interaction of an anthropogenic stress with the tree (e.g., ozone damage, or nutrient leaching by acidic precipitation) will further reduce the photosynthetic efficiency of the tree. When the combined impact of all stresses is sufficient, the whole-plant physiology of the tree will become altered. One such effect may be the decreased allocation of photosynthate to the roots. If this occurs, the transfer of carbon to the rhizosphere and mycorrhizae may correspondingly decrease. This would decrease both plant exudates and rhizosphere-produced organic compounds that complex dissolved metals and decrease metal bioavailability. A decrease in carbon allocation to mycorrhizal fungi would limit fungal growth and decrease the function of the mycorrhizal fungi in reducing metal toxicity to plants.

As a consequence, bioavailability of soil metals will increase and result in

increased metal uptake by the plant. The ability of the plant to detoxify metals through complexation with organic compounds (e.g., citric acid, Chamura and Koike, 1960) once inside plant roots may also be reduced by decreased allocation of carbon to the roots. Thus, not only would plant uptake of metals increase, but the ability of the plant to detoxify metals within root tissues may be correspondingly decreased. Plant tissues would then be exposed to greater concentrations of metals, which could further impair tissue function and growth (e.g., root growth and function). Included in this hypothesis, is the prediction that soil solution concentrations of a metal at which toxicity symptoms are expressed by the plant would decrease as the plant's ability to detoxify the metal becomes reduced.

Thus, it is hypothesized that as a result of the plant being stressed by a factor that would alter carbon allocation to the roots, the toxicity of soil metals would be increased. This enhanced toxicity of soil metals could occur with, or without, any enhanced solubilization of the soil metals by acidic precipitation. Metal toxicity would likely be enhanced to a greater degree by acidic precipitation due to the possible alteration of the soil solution chemistry of Al by acidic precipitation, as well as the enhanced solubilization of Al within the rhizosphere due to the apparent transfer of acidity from plant foliage to the soil.

G. Acidic Treatment and Soil Manganese and Copper.

Analytical methods that were used in these studies permitted examination of effects of artificial acidic precipitation on two heavy metals--copper and manganese. Both of these metals were affected by acidic treatment and present contrasting examples of effects of acidic addition on soil heavy metals.

1. Manganese.

a. Soil chemistry. Results of several of the studies support the conclusion that acidic treatment enhanced leaching of Mn in the spruce-fir forest soils. In the laboratory equilibration study, the pH 3.5 treatment reduced the concentration of exchangeable Mn in soil from Indian Gap in the Great Smoky Mountians. While exchangeable Mn was not significantly affected by acidic treatment at the Collins Gap spruce-fir field site, decreased foliar concentrations of Mn in both red spruce and fern indicate the pesence of effects of acidic treatment on the soil chemistry of Mn.

b. Rhizophere chemistry. Effects of the plant on exchangeable Mn varied among the different experiments. Red spruce in the field study and loblolly pine in the greenhouse study increased concentrations of exchangeable Mn in the rhizosphere relative to those in the bulk soil. This could have been done through exclusion of Mn at the root surface during water uptake by the plant. Alternatively, plant-induced acidification of the rhizosphere may have solubilized of mineral-Mn, thereby increasing the concentration of Mn that was available to react with the soil exchange complex. The enhanced mineralization of Mn-containing organic matter within the rhizosphere also may have increased the soil solution concentration of Mn that was available to react with the exchange complex.

In the greenhouse study, red spruce decreased the concentration of exchangeable Mn in the rhizosphere soil compared with that in the nonrhizosphere soil. This depletion may have been due to the rate of plant uptake of Mn exceeding the rate of supply of Mn to the exchange complex through either the input of dissolved Mn into the rhizosphere from the nonrhizosphere soil via mass flow or diffusion, or the mineralization of Mn-containing organic matter within the rhizosphere. Alternatively, in the rhizosphere, ionic Mn may have formed complexes with organic matter rather than have reacted with the exchange complex, and consequently may have been less

extractable with 1N KCl.

In the greenhouse study, the slight reduction in concentration of exchangeable Mn in the nonrhizosphere soil of red spruce under the pH 3.5 treatment supports the conclusion that acidic treatment solubilized Mn. In the rhizosphere, however, concentrations of exchangeable Mn increased with decreasing treatment pH. Taken together, these results support the interpretation that the acidic treatments solubilized Mn in the nonrhizosphere soil, and, once solublized, it moved via mass flow to the rhizosphere, where it may have been preferentially concentrated, at least in part, in the exchangeable form.

c. Foliar Mn. Foliar elemental data support the argument that the pH 3.5 treatment decreased Mn bioavailability. Acidic treatment reduced foliar concentrations of Mn in red spruce, fern, and loblolly pine in the field studies and in red spruce in the greenhouse studies.

Possible mechanisms for lower foliar concentrations of Mn under the pH 3.5 treatment are leaching of Mn from foliage, immobilization of Mn within soil, and accelerated leaching of Mn from soil. The occurrence of foliar leaching cannot be evaluated in these studies. Immobilization of soil Mn could be due to several mechanisms. In the greenhouse study, acidic treatments increased exchangeable Mn in the rhizosphere of red spruce. This may represent an immobilization of Mn that decreased its bioavailability. However, absence of a similar treatment effect on exchangeable Mn in the rhizosphere of red spruce that were treated in the field study does not indicate the presence of such a mechanism at the field site. In the greenhouse study, the elevated concentration of DOM in the rhizosphere of red spruce under acidic treatment may have decreased Mn bioavailability through the enhanced complexation of Mn with fulvic/humic acids. The presence of such a mechanism is not indicated, however, by results of the field study, where, although the acidic treatment lowered

rhizosphere DOM values, the foliar concentration of Mn was still reduced.

Soil Mn has been found to be more readily mobilized by soil acidification in comparison with other soil metals (Tyler, 1978, Hanson *et al.*, 1982). Occurrence of such mobilization in this study is indicated by decreases in concentrations of exchangeable Mn that occurred under acidic treatment in the spruce-fir soils in the laboratory equilibration study and in the bulk soil of red spruce in the greenhouse study. In the greenhouse study, however, acidic treatment increased the rhizosphere concentration of exchangeable Mn. As previously mentioned, these results suggest that acidic treatment solubilized Mn in the nonrhizosphere soil and, once in solution, it was transported to the rhizosphere. If Mn bioavailability is correlative with exchangeable Mn, increased bioavailability and plant uptake of Mn would be predicted from such results. Since foliar concentrations of Mn suggest that this did not occur, it may be that 1N KCl-extractable Mn does not represent the fraction of soil Mn that is the most bioavailable.

From the results of these studies, it is apparent that acidic treatment of the soils decreased the bioavailability of Mn. The exact mechanism for decreases in foliar concentrations of Mn in plants of the different studies, however, cannot be determined from results of the studies.

2. Copper.

a. Soil chemistry. There is little evidence in any of the studies that acidic treatments solubilized soil Cu. The only occurrence of an increase in the concentration of total dissolved Cu under acidic treatment was in the Adirondack-healthy site soil in the laboratory equilibration study. Foliar concentrations of Cu in fern and red spruce in the field study, however, do provide indirect evidence that the solubility of Cu was increased under acidic treatment.

The plant appears to have had a lesser effect on the soil chemistry of Cu than it had on that of Mn. In the field and greenhouse studies, exchangeable Cu was not affected by red spruce under nonacidic treatment. The effect of pine could not be determined, because exchangeable Cu was not detectable in either of the two oak-hickory forest soils that were used in the greenhouse study.

Acidic treatment had no effect on exchangeable Cu in the nonrhizosphere soil of the spruce-fir forest soils in the laboratory equilibration, greenhouse, and field studies. In the greenhouse study, however, there was a plant-acidic treatment interaction on the concentration of exchangeable Cu in the spruce-fir forest soil, as acidic treatment decreased the concentration of exchangeable Cu in the rhizosphere soil. No such effect occurred in the field study.

b. Foliar Cu. The effect of acidic treatment on Cu bioavailability differed among soils and between greenhouse and field studies. In the greenhouse study, acidic treatment deceased the foliar concentration of Cu in red spruce. Conversely, in the field study, it increased Cu concentrations in red spruce and fern. In the greenhouse study, acidic treatment decreased foliar content of Cu in loblolly pine that were potted in soil from the MBW field site and increased foliar content of Cu in those that were potted in the soil from the WBW site. There was no effect of acidic treatment on foliar concentrations of Cu in any of the examined plant species that were treated at either of the oak-hickory forest field sites.

The cause of the difference in treatment effects on foliar Cu in red spruce between the field and the greenhouse studies cannot be determined. However, treatment effects on exchangeable Cu may be important in this regard. As previously mentioned, the concentration of exchangeable Cu was decreased in the rhizosphere soil of red spruce that were treated in the greenhouse, but was not affected in the field study. If the concentration of exchangeable Cu is correlative with Cu bioavailability, foliar

concentrations of Cu should reflect effects of treatment on the exchangeable Cu pool in the rhizosphere soil.

The depletion of exchangeable Cu in the rhizosphere under acidic treatment could be caused by several different mechanisms. Exchangeable Cu is presumably in equilibrium with soil solution Cu. Plant uptake of soil solution Cu could deplete exchangeable Cu if the exchange complex is not correspondingly replenished. Enhanced uptake of Cu by red spruce is not indicated, however, by either foliar content or concentration of Cu. Enhanced leaching of Cu from the soil under acidic treatment could deplete exchangeable Cu in the rhizosphere soil. The lack of a corresponding depletion of exchangeable Cu in the nonrhizosphere soil, however, does not indicate enhanced leaching of rhizosphere Cu under acidic treatment.

Another mechanism that could decrease the rhizosphere concentration of exchangeable Cu is the immobilization of Cu in a form that is not extractable with 1N KCl. The presence of elevated concentrations of DOM in the rhizosphere solutions of the pH 3.5-treated plants supports the hypothesis that a greater proportion of the soil Cu pool may be complexed by organic matter in the rhizosphere than in the nonrhizosphere soil.

Dissolved Cu could either be adsorbed by the exchange complex or be complexed by fulvic/humic acids. Since these reactions are presumably controlled by thermodynamics, increases in concentrations of dissolved organic ligands will increase Cu-organic complexation reactions relative to Cu-exchange reactions and, as a consequence, decrease exchangeable Cu. Bioavailable Cu should correspondingly decrease if the organic-Cu complexes are more stable than exchangeable Cu bonds.

Conversely, acidic treatment increased the foliar concentration of Cu in red spruce in the field study, appeared to decrease DOM in lab-equilibrated rhizosphere samples, and did not affect exchangeable Cu in the rhizosphere of red spruce. If soil

solution concentrations of Cu were similar under the different treatments, the lower concentration of organic ligands in solution under the acidic treatment would probably complex less solution Cu and, as a result, would cause a relative increase the solution concentration of bioavailable Cu (ionic Cu).

In the greenhouse study, the difference in effect of acidic treatment on foliar Cu between loblolly pine that were grown in the soil from the WBW field site and those that were grown in the soil from the MBW field sites may have been related to differences between the two soils in the relative mobilization of Ca (and possibly other base cations) compared with Cu. This proposed mechanism is similar to that discussed previously for differences in treatment effects on Ca and Al between the two soils. There would presumably be greater H^+-exchangeable Ca interactions in the MBW site soil than in the WBW site soil due to the greater concentration of exchangeable Ca in the former soil. However, since exchangeable Cu was not detected in the two oak-hickory forest soils, it cannot be determined if exchangeable Cu differed between the two soils. This, in turn, limits the evaluation of the influence of the status of exchangeable Ca/Cu of the soil on the mobilization of soil Cu by acidic treatment.

Since the concentrations of exchangeable metals tend to increase with decreasing soil pH, it is reasonable to assume that based upon the lower soil pH in the WBW soil, the concentration of exchangeable Cu was probably greater in that soil than in the MBW soil. If this is the case, it is very likely that H^+-exchangeable Cu reactions would be proportionately greater in the WBW soil. This would increase solution Cu relative to Ca in the WBW soil and, as a consequence, increase the bioavailability and plant uptake of Cu.

3. Acidic Precipitation , Soil Manganese and Copper, and Forest Decline.

In the spruce-fir field plots, enhanced foliar concentrations of Cu in red spruce

and fern under artificial acidic precipitation support the hypothesis that acidic precipitation has the potential to increase the bioavailability of certain heavy metals. Baes and McLaughlin (1986) reported the presence of increases in xylem tissue concentrations of Cu, Al, Fe, Cd, and Ni in tissues that have been produced since 1950 in several coniferous tree species in the Great Smoky Mountains of Tennessee. They attributed this to either enhanced air pollution or mobilization of soil Cu by anthropogenic causes. The findings of this study support the conclusion that the increases in Cu concentrations in xylem tissue that were found by Baes and McLaughlin were due to the solubilization of soil Cu by acidic precipitation.

In this study, the decrease in Mn bioavailability (as indicated by foliar Mn concentrations) under acidic treatment corresponds to a pattern in the concentration of xylem tissue Mn in red spruce and eastern hemlock in the Great Smoky Mountains of Tennessee. As previously mentioned, the data of Baes and McLaughlin (1986) show that Mn concentrations are lower in xylem tissues that were produced over the last 30-50 years compared with those concentrations in tissues that were produced previous to that period. These results indicate a decrease in the bioavailability of Mn. One of the sampling sites at which such a pattern in xylem tissue Mn was found by Baes and McLaughlin was within 1/2 km of the spruce-fir field site of this study. Taken together, the pattern in xylem tissue Mn and results of this study support the conclusion that acidic precipitation can reduce, and has reduced, Mn bioavailability in certain of the spruce-fir forest soils of the Great Smoky Mountains.

Results of this study suggest that acidic precipitation can affect the bioavailability of different heavy metals in forest soils. Elevated foliar concentrations of Cu in red spruce and fern in the field study support the conclusion that bioavailability of certain heavy metals can be enhanced by acidic precipitation. This, in turn, indicates the potential for acidic precipitation to correspondingly increase metal toxicity to forest

plants. The decrease in foliar concentrations of Mn in the loblolly pine, red spruce, and fern indicate an opposite effect of acidic precipitation on certain other soil heavy metals--that of reducing metal bioavailability. For those metals that are required plant nutrients (e.g., Mn), this points to the possibility that acidic precipitation may cause certain nutrient deficiencies in impacted soils. In the case of Mn, which is important in soil redox reactions (R. J. Bartlett, University of Vermont, pers. comm., 1984), there also exists the potential for acidic precipitation to alter the redox status of forest soils.

V. CONCLUSIONS

The goal of this study was to examine several hypotheses concerning the effects of acidic precipitation on the soil chemistry and bioavailability of Al, Cu, and Mn. Experimental manipulations, such as this, cannot duplicate the exact nature of anthropogenic acidic precipitation inputs (e.g., variability of precipitation chemical and physical parameters) to forests. Since the chemistry and solution volumes of the simulated acidic precipitation treatments in this study appoximate that of natural rain (but not cloud water inputs) in the studied forests, the results of this study should be reasonably representative of such effects of natural precipitation in the forests. With this consideration in mind, the following conclusions are presented:

1. Acidic precipitation can affect the soil solution chemistry of Al through decreases in the solubility of nonlabile monomeric Al (NLMAl; i.e., organic monomeric Al complexes) and increases in the solubility of labile monomeric Al (LMAl; i.e., inorganic monomeric Al).

a. The results of this study confirm the hypothesis that acidic precipitation will significantly alter the speciation of dissolved Al in the soil zone that contains fine roots, and that this alteration occurs as an increase in free ionic Al plus inorganic Al complexes (LMAl) relative to organic Al complexes (NLMAl).

The occurrence of altered speciation of Al under acidic treatment was common to all examined levels of system complexity--soil, soil-plant, and intact system. Acidic treatment decreased NLMAl concentrations in the spruce-fir and oak-hickory forest soils and enhanced LMAl concentrations in all soils, but only in the laboratory equilibration and greenhouse studies.

b. Although speciation of Al was affected by acidic treatment, the hypothesis that

acidic precipitation will not significantly mobilize Al in the soil zone that contains fine roots was confirmed by results of the field studies in both spruce-fir and oak-hickory forest types. At the spruce-fir field plots, however, high variability in LMAl concentrations may have obscured such an effect of acidic treatment. There is evidence that acidic precipitation can mobilize soil Al (as LMAl); although this evidence comes from only the laboratory equilibration and greenhouse studies.

Conversely, in the spruce-fir forest field plot study, the dampening of an increase in LMAl concentration at three and six days following acidic treatment during October is contrary to the prediction of the general metal toxicity hypothesis of forest decline. This effect of the acidic treatment may have been related to either the inhibition of soil nitrification, or the formation of an insoluble alumino-sulfate mineral phase.

c. Significant changes in soil solution chemistry of Al--which are likely of biological significance--can be present during soil drying following precipitation events and among different portions of the growing season. These temporal dynamics emphasize the importance of examining the soil system over a time interval which is biologically relevant--over time following wetting of soil--when one is interested in the bioavailability and toxicity of Al or any other element.

2. The plant is not a passive receptor of the soil solution, but actively influences soil Al chemistry through rhizosphere acidification and effects on soil organic matter. This influence needs to be included in any consideration of forest decline that incorporates metal toxicity as a significant plant stress.

a. The results of this study confirm the hypothesis that Al chemistry of the rhizosphere differs from that of the nonrhizosphere soil. Contrary to the hypothesis, however, the rhizosphere did not have relatively greater concentrations of organically-

complexed Al. Although the rhizosphere concentration of NLMAl was increased, it was not increased relative to that of LMAl which also increased.

b. The plant can moderate the effects of acidic precipitation on the soil solution chemistry of Al. The hypothesis that acidic precipitation will affect the Al chemistry of the rhizosphere less than that of the nonrhizosphere soil was confirmed in one of three cases. This effect varied between tree species and among soil types. Mobilization of rhizosphere LMAl by acidic treatment was decreased by loblolly pine potted in mineral soil having comparatively high exchangeable Ca/Al, not affected by red spruce, and enhanced by loblolly pine potted in mineral soil having comparatively low exchangeable Ca/Al.

c. Results of the greenhouse studies of the loblolly pine potted in mineral soil having comparatively low exchangeable Ca/Al also support the hypothesis that precipitation acidity can be transferred from the foliage to the rhizosphere as has been predicted elsewhere.

3. Acidic precipitation can affect the bioavailability of certain soil metals in manners which may result in metal toxicity or deficiency to trees and, as a consequence, could serve as stresses important in forest decline.

a. The results of this study, for the most part, did not confirm the hypothesis that acidic precipitation increases the bioavailability of soil Al. Enhanced Al bioavailability (as indicated by elevated foliar content of Al) was only present in the greenhouse study of loblolly pine that were potted in a mineral soil having comparatively low exchangeable Ca/Al. There was no supporting evidence of enhanced Al bioavailability at any of the three field sites.

b. Acidic precipitation has the potential to alter the bioavailabilities of certain heavy metals. Acidic treatment increased Cu bioavailability (as indicated by foliar Cu

concentrations) to red spruce and fern at the spruce-fir forest field site and has potential toxicity implications. Conversely, acidic treatment decreased Mn bioavailability (as indicated by foliar Mn concentrations) to fern and red spruce at the spruce-fir and loblolly pine at the oak-hickory forest field sites and has potential nutrient deficiency implications.

c. If Al is mobilized by acidic preciptation, the potential for enhanced bioavailability will increase with decreased exhangeable Ca/Al status of the soil. This conclusion is supported by results of the greenhouse study where acidic treatment increased foliar Ca/Al values in loblolly pine that were potted in mineral soil having comparatively high exchangeable Ca/Al) and may have decreased foliar Ca/Al values in loblolly pine potted in mineral soil having comparatively low exchangeable Ca/Al.

4. Simple H^{+}-Al^{+3} exchange reactions (as cation exchange or chemical weathering) represented by H^{+}-additions to soils in the laboratory do not completely describe the effects of acidic deposition on soil Al in the intact ecosystem. Interactions of ecosystem components must also be considered, as well as effects of experimental conditions.

a. The complexity of effects of acidic treatment on soil Al chemistry increased within a given soil as the complexity of the examined system increased--the soil alone, plant-soil, and intact system. This underscores the complexity of evaluating a given hypothesis of forest decline. In particular, given the apparent active role of the plant in influencing soil chemistry, the rhizosphere--the plant-soil interface--is a location within forest ecosystems where component interactions of significant importance to elemental cycling very likely occur and should receive further attention.

b. Caution should be used in the extrapolation of results of any laboratory and greenhouse study to the field situation. In this study, differences in effects of acidic

treatment on soil Al chemistry and the plant occurred among the laboratory, greenhouse, and field manipulations. Certain of these differences were very likely related to soil disturbance during collection for the greenhouse and laboratory equilibration studies. Solution pH and limited nitrate values (relative measurements) suggest that nitrification--due to soil disturbance--was significant in the spruce-fir forest soils in the laboratory equilibration study. Enhanced nitrification also very likely occurred in the greenhouse soils given the similar extent of soil disturbance during collection and high greenhouse temperatures during the experiments. In addition, because the total volume of treatment dosage differed between the field and greenhouse studies, greater treatment additions of Ca and Mg were added to the greenhouse soils. This may have decreased Al bioavailability relative to that in the spruce-fir field study.

5. Effects of acidic precipitation on soil Al chemistry can differ among forest types (e.g. spruce-fir and oak-hickory) and different geograhic locations having a given forest type. Given this variability, caution must also be used in the extrapolation of results of such acid precipitation studies from one geographic area to another or from one type of forest ecosystem to another.

6. Taken together, the results of this study do not strongly support the prediction of the metal toxicity hypothesis of forest decline that acidic precipitation will mobilize soil Al in a bioavailable form at concentrations which are sufficient to singly cause forest decline. The multiple effects of acidic treatment on the soil chemistry and bioavailability of Al, Mn, and Cu, coupled with results of other forest decline-related studies, support the likelihood that forest decline is a system-level response to multiple stresses (including stresses caused by effects of acidic precipitation on soil metals) rather than a plant-single stressor or a soil-single pollutant interaction.

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APPENDIX A.

METHODS SECTION

Appendix A 1. Characterization of Soils at the Three Forest Field Sites of this Study.

Great Smoky Mountains field site

Typic Haplumbrept: sandy loam, mixed, frigid

O	6 to 0 cm	Spruce, fir, birch, and fern litter Oi: 6 to 4 cm; Oe 4 to 1.5 cm; Oa 1.5 to 0 cm
A1	0 to 4 cm	Black (10YR 2/1), sandy loam
A2	4 to 10 cm	Dark grayish brown (10 YR 4/2), sandy loam
B	10 to 40 cm	Yellowish brown (10 YR 5/6), sandy loam
C	40 to 60 cm	Light brown (10 YR 5/3), sandy loam with sandstone fragments

Melton Branch Watershed field site

Typic Hapludult: fine loamy, mixed, thermic and within the "Shelocta Series" (Lietzke, 1982).

O	3 to 0 cm	Hardwood litter; lower part partially decomposed
A	0 to 8 cm	Dark brown (10YR3/3), loam
Bt1	8 to 20 cm	Brown (75.YR4/4), loam
Bt2	20 to 105 cm	Strong brown (7.5YR5/6), light clay loam with many fine fragments

Walker Branch Watershed field site

Typic Paleudult: clayey, kaolinitic, thermic and within the "Fullerton Series" (Peters *et al.*, 1970)

O	2 to 0 cm	Hardwood litter; lower part partially decomposed
A1	0 to 6 cm	Grayish brown (10YR 5/2), cherty silt loam
A2	6 to 26 cm	Pale brown (10YR 6/3), cherty silt loam
A3	26 to 34 cm	Light yellowish brown (10YR 6/4), cherty silt loam
B1t	34 to 40 cm	Strong brown (7.5YR 5/6), cherty silt loam
B21t	40 to 56 cm	Yellowish red (5YR 5/6), cherty silt loam
B22t	56 to 72+ cm	Red (2.5YR 5/8), cherty clay

Appendix A. 1, cont. Characterization of Soils at the Three Forest Field Sites of this Study.

Table A.1. Characteristics of the Field Site Soils Used in this Study.

Soil	Horizon	pH	CEC (meq/100 g)	% loss on ignition
Spruce-fir forest	Oe-Oa	3.6	14	40
Oak-hickory forest Melton Branch Watershed	A	5.6	6	15
Oak-hickory forest Walker Branch Watershed	A1	5.0	3.5	12

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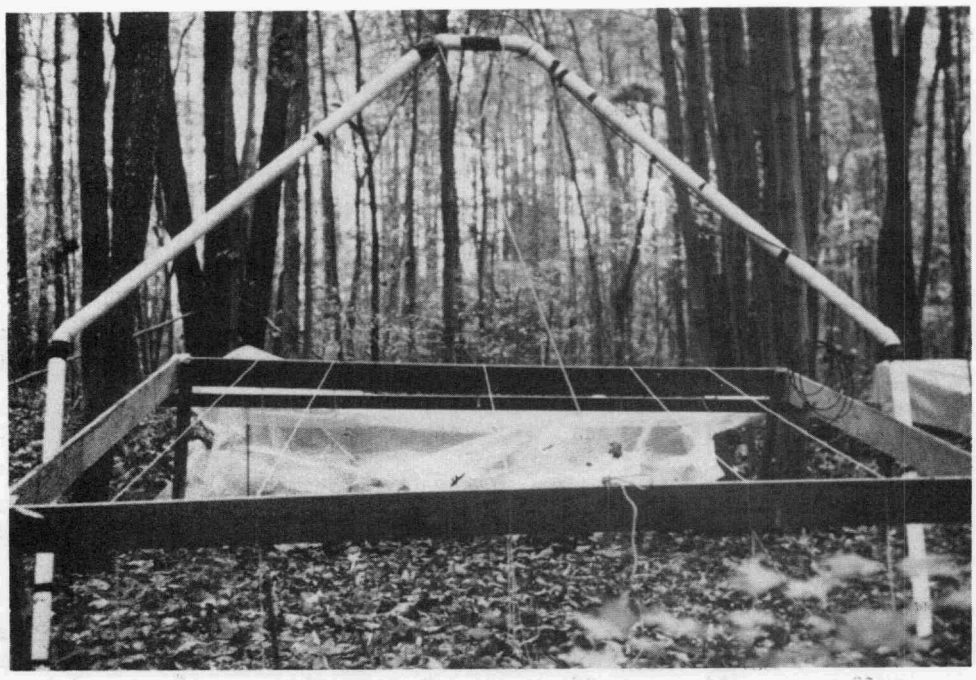

(a)

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(b)

Appendix A 2. View of (a) Walker Branch Watershed and (b) Great Smoky Mountains Field Plots.

Appendix A 3 Characterization of tree vegetation at the three forest field sites of this study.

Spruce-Fir Forest

Stems	Picea rubens	Abies fraseri	Betula alleghaniensis	Sorbus americana	Acer spicatum
#/300 m	16	2 (6 dead)	4	2	5
#/hectare	533	67	135	67	167
Basal Area					
m /300 m	0.771	0.0006	0.438	0.0018	0.0039
m /hectare	25.7	0.021	14.6	0.6	0.13

Oak-Hickory Forest: Melton Branch

Stems	Acer rubrum	Liquidamber stryaciflua	Amelanchier sp	Quercus alba	Carya ovalis	Cornus florida	Quercus falcata
#/300 m	22	8	3	3	4	9	1
#/hectare	733	266	100	100	133	300	33
Basal Area							
m /300m	0.0576	0.177	0.0037	0.46	0.163	0.0142	0.0177
m /hectare	1.92	5.9	0.12	15.35	5.44	0.47	0.59

Oak-Hickory Forest: Walker Branch

Stems	Acer rubrum	Quercus prinus	Quercus alba	Quercus falcata	Oxydendrum arboreum	Carya tomentos	Pinus echinata
#/300 m	36	36	2	2	5	2	1
#/hectare	1200	167	67	67	167	67	33
Basal Area							
m /300m	0.342	0.923	0.503	0.196	0.049	0.265	0.088
m /hectare	11.41	30.78	16.78	6.456	1.632	8.817	5.876

Vegetation survey at each site was done on 3 plots 10m x 10m. Survey plots were located on three sides adjacent to the field treatment plots, with a survey plot located directly upgrade of the treatment plots. an the other two plots were located 120° with respect to the first.

Appendix A. 3, cont. Diameter at breast height measurements of tree vegetation at three field sites of this study.

Spruce-fir forest

Picea rubens		*Abies fraseri*	*Birch alleghaniensis*	*Sorbus americana*	*Acer spicatum*
3	2	9.1 d	62	3.5	2.4
29.7	72.5	7.3 d	11	3.3	3
2	5.5	2	27.3		1.9
3	5.2	7 d	29.5		5.2
3.3	5.5	9.5 d			3.2
33	5.8	2 d			
9.3	6	4.2 d			
2.2	48	2			

d=dead

Oak-hickory forest
Melton Branch

Acer rubrum		*Liquidamber stryacillua*	*Amelanchier sp*	*Quercus alba*	*Carya ovalis*	*Cornus florida*	*Quercus falcata*
5.5	18	10	1.5	26.5	43	2	15
2.5	3.5	2	5	39.5	10.5	3	
3.5	4	3.5	4.5	60	6	1.5	
5.5	4.5	12			9	6	
2	3.5	4				2	
1.5	3	33.5				2	
5	2.5	27.5				9	
3	6	10				4	
11	3.5					5	
4	4						
2.5	2.5						

Oak-hickory forest
Walker Branch

Acer rubrum			*Quercus prinus*	*Quercus alba*	*Quercus falcata*	*Oxydendrum arboreum*	*Carya tomentosa*	*Pinus echinata*
4	8	3	22	48	17	8	28	33.5
5	20.5	2	33.5	30	31	9	30	
8	7	2.5	34.5			4.5		
8.8	9	4.5	39			7.5		
9	4		39.5			9.5		
15.5	3.5	4						
9.5	7	3						
8.5	10.5	4						
9.5	9.5	29						
2.5	2	30						
8.5	3.5	3						
	8	3.5						
	2.5	27						

Appendix A. 4

Chemistry of the Artificial Precipitation.

The chemistry of the artificial precipitation that was used in this study was based upon the major ion chemistry of precipitation that was collected at the Walker Branch Watershed, Oak Ridge National Laboratory, Oak Ridge, Tennessee, during 1983 (G. M. Lovett, Oak Ridge National Laboratory, 1984, pers. comm.). The pertinent chemistry of the natural precipitation on which the artificial precipitation in this study was based and the reagents used to make the concentrated stock solutions of the artificial precipitation are presented on the following two pages. The low and high range in pH and the mean of the pH of the natural precipitation were used to make three different artificial precipitation solutions. These pH parameters are pH 3.5--low range, pH 4.1--mean, and pH 5.0--high range. The mean ratio of SO_4^{-2} to NO_3^- in natural precipitation was 3.2 and this was supplied to the artificial precipitaiton solutions by additions of HNO_3 and H_2SO_4. The mean concentrations of the neutral salts in the natural precipitation were also added to the artificial precipitation.

Table A.2. Mean Annual Concentrations of Major Dissolved Constituents in Precipitation Collected at Walker Branch Watershed, Oak Ridge National Laboratory, Tennessee, during 1983.

Ion	Mean Concentration (ueq/L)
SO_4^{-2}	68.1
NO_3^-	22.5
Cl^-	7.4
Ca^{+2}	14.8
NH_4^+	13.3
K^+	0.92
Na^+	4.7
H^+	68.2
Range H^+	13-282
$SO_4^{-2} : NO_3^-$	3.2

Table A.3. Chemistry of Artificial Precipitation in this Study.

Salt	mg/L
$CaSO_4$	2.05
$MgSO_4$	0.028
$(NH_4)_2SO_4$	0.032
NH_4NO_3	1.09
NaCl	0.56
KCl	0.14
NH_4Cl	0.36

Treatment pH	H_2SO_4 (17.8M)	HNO_3 (15.4M)
	mL/24.6 L	
3.5	8.195	6.315
4.1	2.06	1.59
5.0	0.257	0.20

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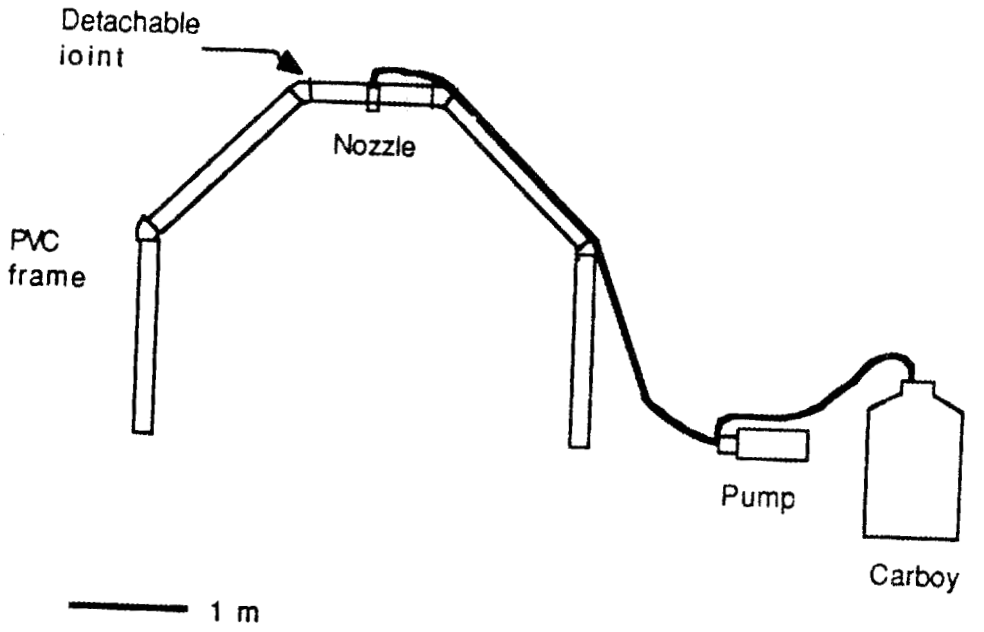

Appendix A. 5. Portable rain system. Scale is for PVC frame only.

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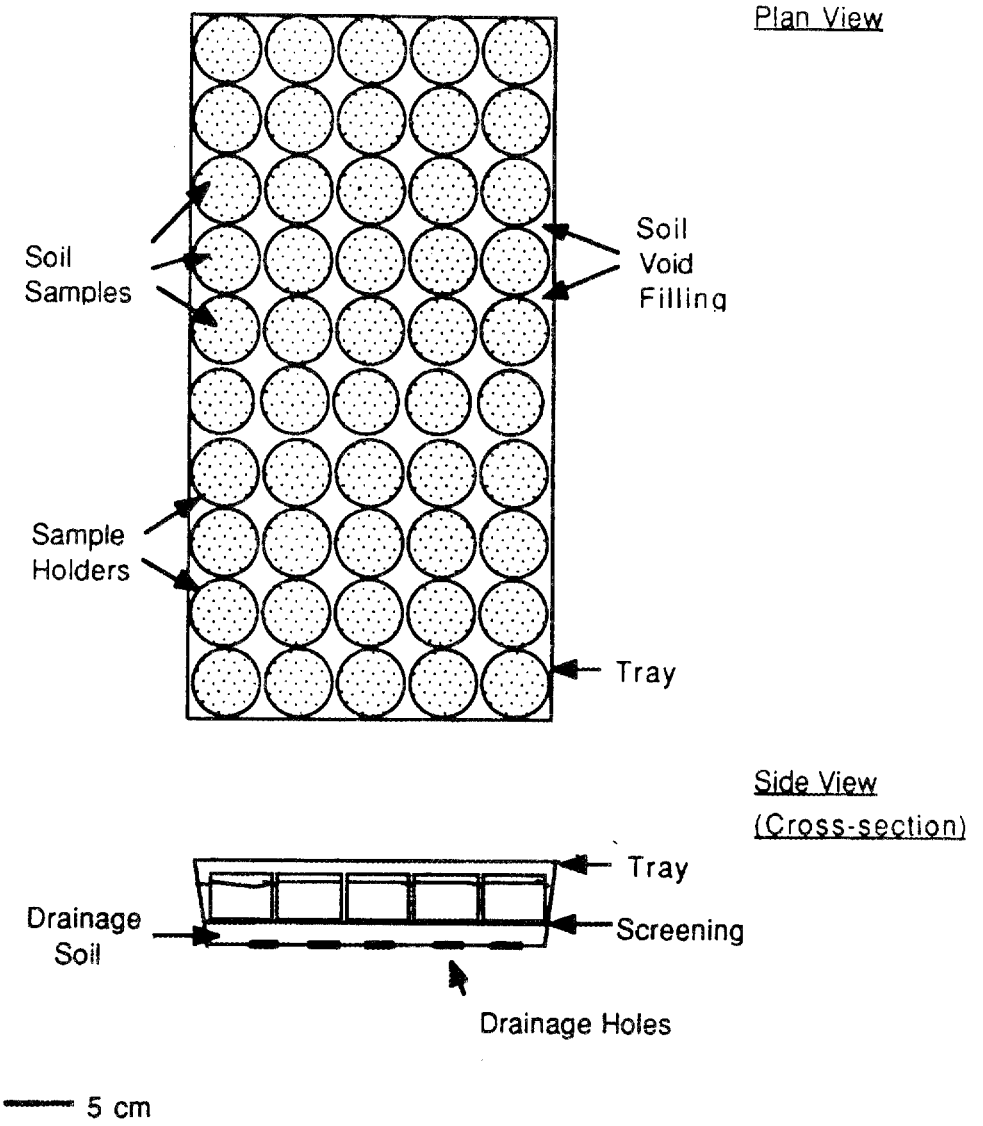

Appendix A. 6. Soil sample holder for laboratory equilibration study.

Design of Centrifugation Tube.

The choice of the design of the centrifuge tube that was used in this study was based on the requirements of proper shape and size, minimal expense, and ease of production. The tube needed to hold a soil sample of up to 4 cm depth (the approximate thickness of the soil zone of fine roots), and it also needed to be able to contain a volume of soil that would yield a volume of soil solution that was sufficient for use in the metal speciation scheme of this study. The soil samples could not be too large in diameter, however, as there was minimal collection area in the field plots. This necessitated the the soil samples to be of greater width than could be used in the tube of Davies and Davies (1963), but less than that which could be acccomodated by the tube of Adams *et al.* (1980). These size constraints and the requirements of minimal expense and ease of production eliminated the other centrifuge tubes that have been described in the literature (e.g., Edmunds and Bath, 1976; Kinniburgh and Miles, 1983) from use.

A centrifuge tube of this writer's design was used to hold the soil samples during centrifugation. This two-piece tube consisted of a upper cup which held the soil sample and a lower collection cup into which the soil water drained and was collected. The soil cup was the cup with perforated plate of a two-piece 4.1 cm-diameter polyethylene Buchner funnel. A piece of 4.0 cm filter paper (Whatman 40) was placed in the bottom of this cup to prevent large soil particles from passing with the water to the water collection cup during centrifugation. The soil sample was placed in the cup on top of the filter paper. Up to 50 g (dry weight) of soil could be used without failure of the centrifuge tube during centrifugation.

The water collection cup was the bottle cap of a 250 mL wide-mouth polyethylene bottle (Nalgene). This cap was modified by grinding through the removal of the outer 5 to 7 cm of the screw-closure ridge. This modification was necessary to allow the two

pieces of the centrifuge tube to fit together for use. The funnel cup fit snugly into the bottle cap once this modification was made. It was found that the heating of the bottle cap to 80-100° C for 15 minutes caused the expansion of the cap which facilitated the putting of the cap and the funnel cup together. No additional modification of the original parts was necessary. A snap-on lid can be easily made for the centrifuge tube if desired. The lid off a 50 ml hinged-lid polyethylene container (Poly-cons, Cole-Parmer, Chicago, IL, 60648) fits snugly onto the funnel cup.

In this study, the centrifuge tubes were used in 6 cm inner-diameter centrifuge buckets. Since the bucket was reasonably wider than the centrifuge tube, the tubes were placed in the bottom halves of the 250 mL polyethylene Nalgene bottles from which the bottle caps that were used as the water collection cups were taken. The bottles were cut off approximately 2.5 cm from the top. The arrangement of placing the centrifuge tube inside of the bottle prevented the centrifuge tube from wandering about the centrifuge bucket. The centrifuge tube is presented in on the following page.

This composite centrifuge tube proved to be very inexpensive, of the proper shape for the requirements of this study, required minimal alteration of the parts, and was very durable. The water collection cup was susceptible to failure at forces greater than 2500 times gravity when the weight of the soil sample was greater than 50 g. Minor distortion of both the soil cup and the water collection cup may occur during centrifugation, but both return to approximately their original shape. A large number of the components were used from sixty to seventy times without failure.

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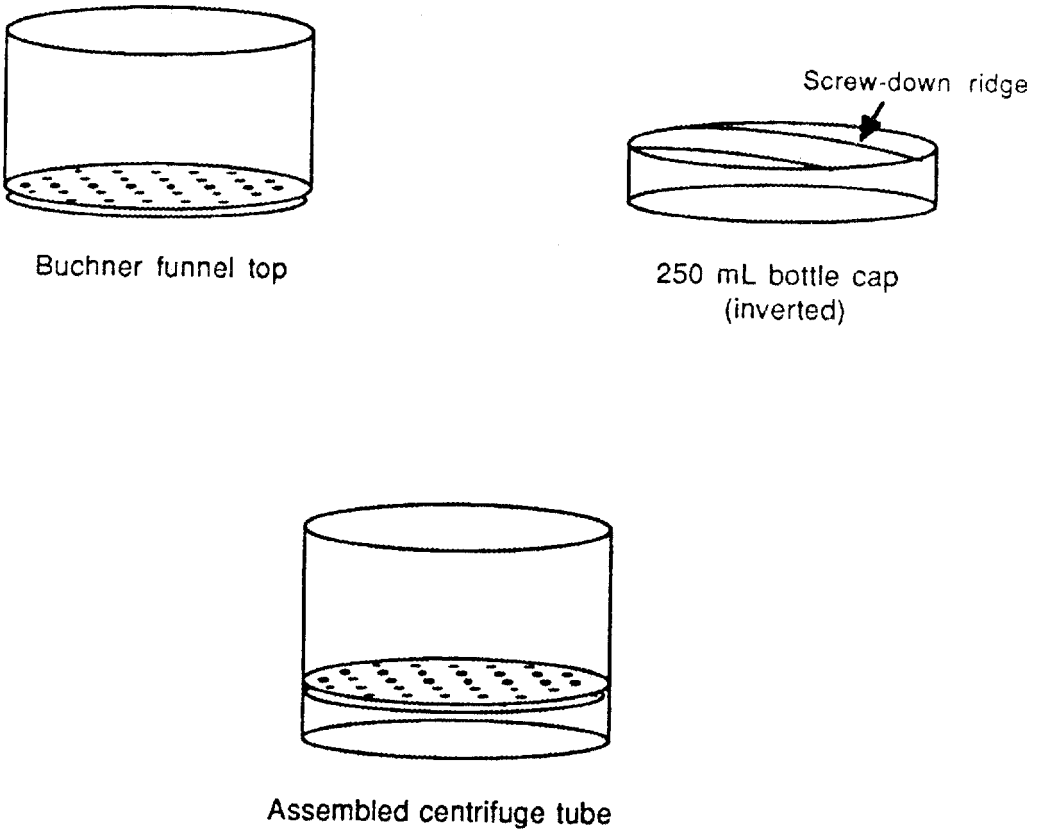

Fig. A.7. Diagram of Centrifuge Tube.

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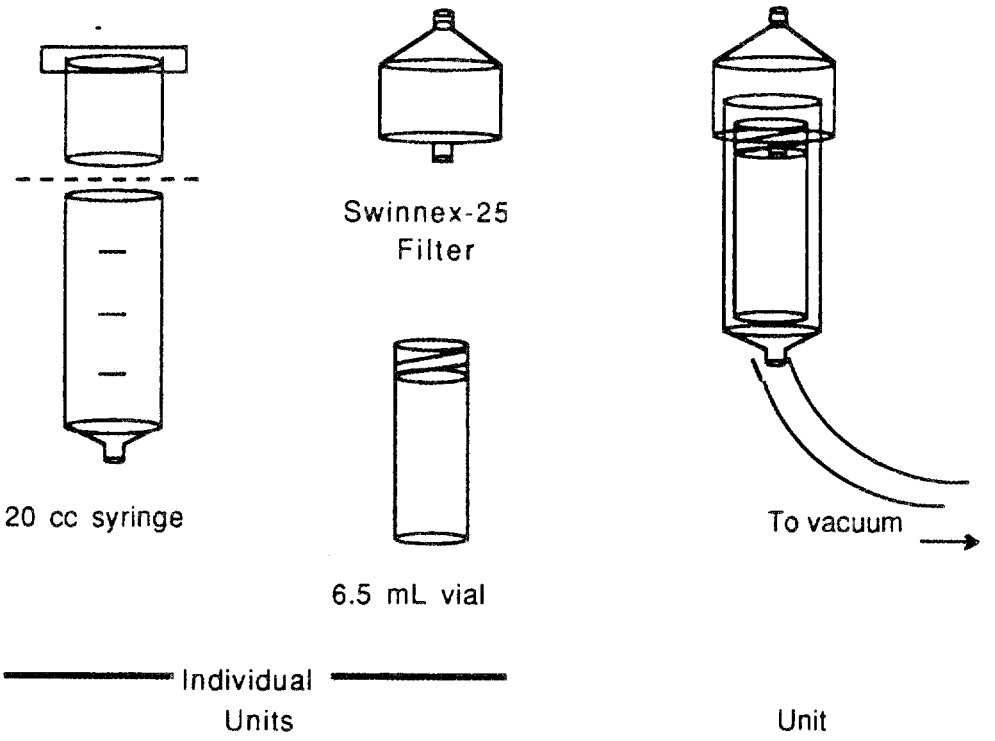
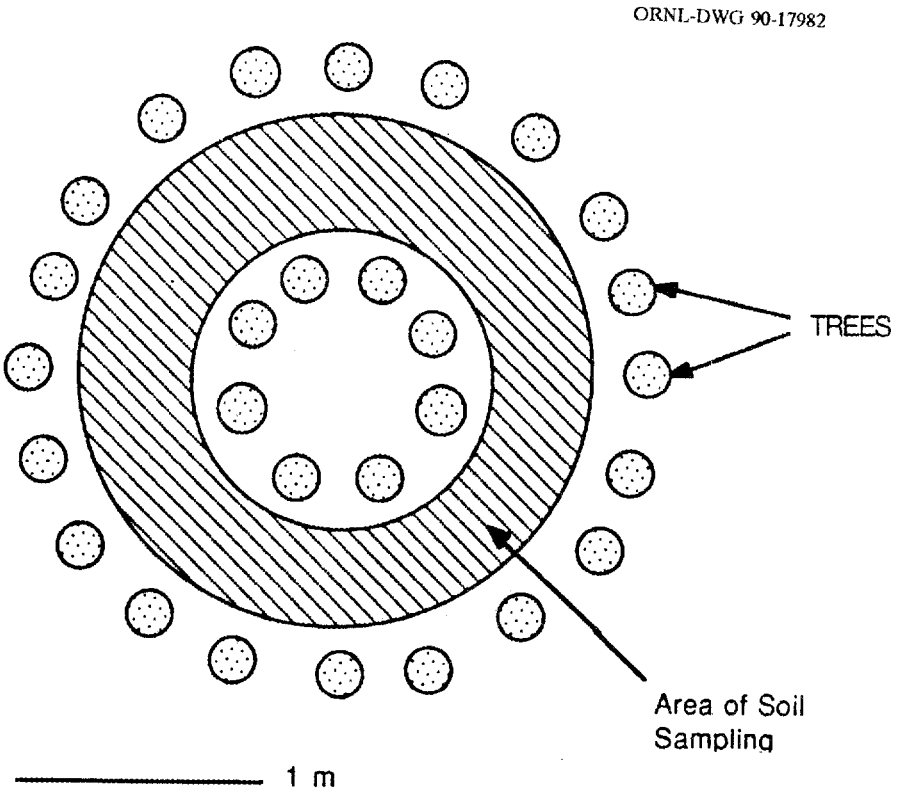


Appendix A. 8. Vacuum filtration unit and component parts.



Appendix A. 9. Plan view of locations of seedlings and area of soil sampling on field plots.

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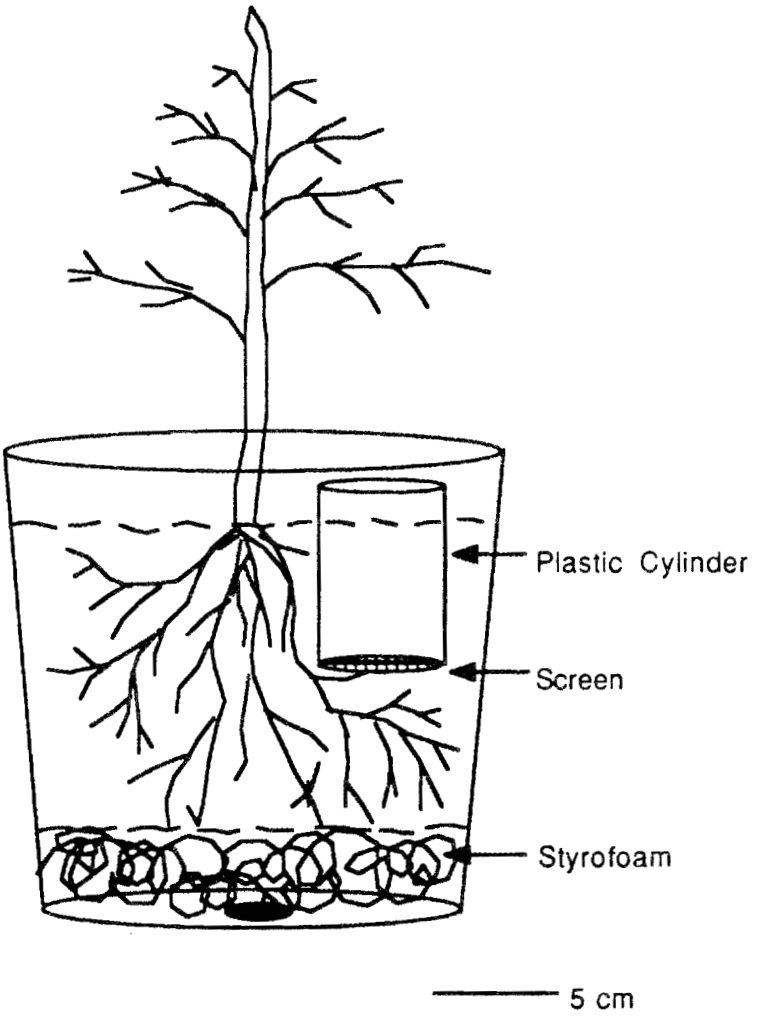

Appendix A. 10. Pot showing arrangement of root exclusion cylinder used in greenhouse experiment on the chemistry of the red spruce rhizosphere (follow-up experiment).

APPENDIX B.

RESULTS SECTION

Appendix B 1. Solution Parameters: Smoky Mountains Soils, Week 0, Laboratory Study.

Indian Gap Site		TMAI	NLMAI	LMAI	pH	DOM	Collins Gap Site		TMAI	NLMAI	LMAI	pH	DOM
Hour 1													
pH 3.5	1	0.085	0.055	0.03	3.45	0.17	pH 3.5	1	0.255	0.175	0.08	3.57	0.14
	2	0.085	0.055	0.03	3.51	0.159		2	0.3	0.195	0.105	3.52	0.17
	3	0.105	0.07	0.035	3.41	0.215		3	0.255	0.185	0.07	3.56	0.18
	4	0.09	0.05	0.04	3.49	0.183		4	0.24	0.155	0.085	3.53	0.13
mean		0.091	0.058			0.182			0.263	0.177			0.15
s.e.		0.005	0.004			0.012			0.013	0.009			0.01
pH 5.0	1	0.08	0.065	0.015	3.63	0.22	pH 5.0	1	0.275	0.2	0.075	3.67	0.21
	2	0.065	0.055	0.01	3.76	0.187		2	0.22	0.175	0.055	3.77	0.18
	3	0.08	0.06	0.02	3.7	0.223		3	0.27	0.185	0.085	3.65	0.21
	4	0.095	0.085	0.01	3.55	0.28		4	0.3	0.2	0.1	3.63	0.22
mean		0.08	0.066			0.227			0.266	0.19			0.21
s.e.		0.006	0.007			0.019			0.017	0.006			0.01
Day 1													
pH 3.5	1	0.15	0.07	0.08	3.37	0.214	pH 3.5	1	0.51	0.17	0.34	3.33	0.15
	2	0.13	0.075	0.055	3.36	0.25		2	0.52	0.19	0.33	3.37	
	3	0.16	0.08	0.08	3.31	0.248		3	0.47	0.145	0.325	3.35	0.14
	4	0.19	0.08	0.11	3.32	0.232		4	0.535	0.2	0.335	3.35	0.15
mean		0.157	0.076			0.236			0.509	0.176			0.14
s.e.		0.013	0.002			0.009			0.014	0.012			.005?
pH 5.0	1	0.145	0.07	0.075	3.5	0.327	pH 5.0	1	0.515	0.2	0.312	3.42	0.19
	2	0.155	0.08	0.075	3.44	0.307		2	0.5	0.23	0.265	3.44	0.21
	3	0.165	0.09	0.075	3.38	0.278		3	0.495	0.2	0.295	3.42	0.18
	4	0.155	0.09	0.065	3.38	0.279		4	0.45	0.19	0.26	3.38	0.18
mean		0.155	0.083			0.298			0.49	0.206			0.19
s.e.		0.004	0.005			0.012			0.014	0.01			.013?
Day 3													
pH 3.5	1	0.155	0.075	0.08	3.25	0.174	pH 3.5	1	.45?	0.175	0.275	3.29	0.1
	2	0.155	0.07	0.085	3.22	0.17		2	0.535	0.165	0.37	3.22	0.11
	3	0.165	0.07	0.095	3.23	0.193		3	0.575	0.17	0.405	3.16	0.11
	4	0.18	0.065	0.115	3.18	0.169		4	0.445	0.19	0.255	3.25	0.09
mean		0.164	0.07			0.177			0.501	0.175			0.1
s.e.		0.006	0.002			0.005			0.032	0.005			0.01
pH 5.0	1	0.14	0.085	0.055	3.28	0.181	pH 5.0	1	0.565	0.155	0.41	3.2	0.09
	2	0.145	0.09	0.055	3.24	0.191		2	0.51	0.2	0.31	3.25	0.12
	3	0.165	0.085	0.08	3.29	0.197		3	0.56	0.155	0.405	3.2	0.1
	4	0.14	0.075	0.065	3.25	0.189		4	0.47	0.165	0.3	3.22	0.1
mean		0.147	0.084			0.189			0.526	0.173			0.1
s.e.		0.006	0.03			0.003			0.022	0.014			0.01
Day 7													
pH 3.5	1	0.225	0.09	0.135	3.07	0.152	pH 3.5	1	1.02	0.165	0.855	3.06	0.11
	2	0.245	0.085	0.16	3.06	0.172		2	0.77	0.16	0.61	3.08	0.11
	3	0.215	0.07	0.145	3.04	0.139		3	0.865	0.21	0.655	3.04	0.11
	4	0.215	0.105	0.11	3.06	0.197		4	0.93	0.185	0.745	3.05	0.12
mean		0.225	0.087			0.165			0.896	0.18			0.11
s.e.		0.007	0.007			0.012			0.053	0.011			0
pH 5.0	1	0.215	0.065	0.15	3.06	0.139	pH 5.0	1	0.83	0.155	0.675	3.05	0.11
	2	0.18	0.065	0.115	3.06	0.125		2	0.865	0.15	0.715	3.03	0.11
	3	0.21	0.06	0.15	3.06	0.139		3	0.81	0.205	0.605	3.05	0.11
	4	0.205	0.07	0.135	3.06	0.152		4	1	0.155	0.845	3.04	0.12
mean		0.202	0.065			0.138			0.876	0.166			0.11
s.e.		0.008	0.002			0.005			0.043	0.013			0

Appendix B 1. con't. Solution Parameters: Smoky Mountains Soils, Week 0, Laboratory Study.

		TMAI	NLMAI	LMAI	pH	DOM			TMAI	NLMAI	LMAI	pH	DOM
Day 14													
pH 3.5	1	0.275	0.09	0.185	3.01	0.125	pH 3.5	1	0.76	0.235	0.525	3.03	0.11
	2	0.305	0.11	0.185	3	0.137		2	0.67	0.3	0.37	3.06	0.1
	3	0.305	0.12	0.175	2.98	0.152		3	0.875	0.285	0.59	2.98	0.11
	4	0.305	0.115	0.19	3	0.15		4	0.82	0.26	0.56	2.98	0.11
mean		0.297	0.109			0.141			0.781	0.27			0.11
s.e.		0.008	0.007			0.007			0.044	0.014			0
pH 5.0	1	0.315	0.12	0.195	2.96	0.098	pH 5.0	1	0.665			2.98	0.1
	2	0.315	0.12	0.195	2.99	0.119		2	0.72	0.22	0.5	3.01	0.09
	3	0.35	0.115	0.235	2.94	0.112		3	0.785	0.28	0.5	2.97	0.11
	4	0.32	0.135	0.185	2.94	0.127		4	0.885	0.285	0.5	2.95	0.13
mean		0.325	0.123			0.114			0.764	0.262			0.11
s.e.		0.008	0.004			0.006			0.047	0.021			0.01

Appendix B 2. Solution Parameters: Adirondack Mountains Soils, Week 0, Laboratory Study.

Healthy site		TMAI	NLMAI	LMAI	pH	DOM
pH 3.5 1 Hr						
	1	0.1	0.085	0.02	4.07	0.157
	2	0.095	0.085	0.01	4.09	0.132
	3	0.095	0.095	0	4.14	0.166
mean		0.097	0.088			0.152
s.e.		0.002	0.003			0.01
ph 5.0 1 Hr						
	1	0.1	0.09	0.01	4.16	0.183
	2	0.115	0.095	0.02	4.1	0.201
	3	0.095	0.09	0.05	4.1	0.205
mean		0.103	0.092	0.01	4	0.196
s.e.		0.006	0.002	0		0.007
Day 3						
pH 3.5						
	1	0.19	0.165	0.03	3.84	0.325
	2	0.215	0.185	0.03	3.76	0.357
	3	0.215	0.165	0.05	3.85	0.302
mean		0.207	0.172	0.04		0.328
s.e.		0.008	0.007	0.01		0.016
pH 5.0						
	1	0.19	0.165	0.03	3.92	0.351
	2	0.205	0.19	0.03	3.87	0.382
	3	0.195	0.185	0.01	3.92	0.369
mean		0.2	0.18	0.02		0.367
s.e.		0.008	0.008	0		0.009
7 Day						
pH 3.5						
	1	0.23	0.165	0.07		
	2	0.23	0.16	0.07		
	3	0.24	0.205	0.04		
mean		0.233	0.177	0.06		
s.e.		0.003	0.014	0.01		
pH 5.0						
	1	0.27	0.215	0.06		
	2	0.215	0.21	0.01		
	3	0.235	0.18	0.06		
mean		0.24	0.202	0.04		
s.e.		0.016	0.011	0.01		

Unhealty Site		TMAI	NLMAI	LMAI	pH	DOM
pH 3.5 1 Hr						
	1	0.195	0.14	0.055	4.16	0.111
	2	0.22	0.16	0.06	4.1	0.132
	3	0.215	0.175	0.04	4.1	0.129
mean		0.21	0.158	0.052		0.124
s.e.		0.008	0.01	0.006		0.007
pH 5.0 1 Hr						
	1	0.155	0.14	0.015	4.48	0.14
	2	0.22	0.195	0.025	4.29	0.166
	3	0.205	0.175	0.03	4.31	0.177
mean		0.193	0.17	0.023		0.161
s.e.		0.02	0.016	0.004		0.011
pH 3.5						
	1	0.34	0.32	0.02	3.76	0.22
	2	0.335	0.315	0.02	3.87	0.251
	3	0.365	0.33	0.035	3.82	0.281
mean		0.347	0.332	0.025		0.251
s.e.		0.009	0.004	0.005		0.018
pH 5.0						
	1	0.41	0.345	0.065	3.94	0.298
	2	0.435	0.36	0.075	3.94	0.349
	3	0.395	0.34	0.055	3.89	0.313
mean		0.413	0.348	0.065	4	0.322
s.e.		0.012	0.006	0.006		0.015
pH 3.5						
	1	0.41	0.37	0.04		
	2	0.46	0.385	0.075		
	3	0.5	0.335	0.165		
mean		0.457	0.363	0.093		
s.e.		0.026	0.013	0.037		
pH 5.0						
	1	0.5	0.4	0.1		
	2	0.44	0.43	0.01		
	3	0.415*	0.365	0.055		
mean		0.452	0.321	0.053		
s.e.		0.025	0.031	0.026		

*2.5ml in resin extraction
1.3ml in TMAI

Appendix B 3. Solution Parameters: Smoky Mountains Soils, Week 10, Laboratory Study.

Indian Gap Site		TMAI	NLMAI	LMAI	pH	DOM	Collins Gap Site		TMAI	NLMAI	LMAI	pH	DOM
Hour 1													
pH 3.5	1	0.1	0.07	0.03	3.47	0.089	pH 3.5	1	0.255	0.15	0.11	3.54	0.066
	2	0.08	0.065	0.02	3.54	0.049		2	0.32	0.165	0.16	3.54	0.069
	3	0.08	0.065	0.02	3.5	0.068		3	0.28	0.15	0.13	3.55	0.053
	4	0.08	0.055	0.03	3.54	0.062		4	0.27	0.155	0.12	3.57	0.075
mean		0.085	0.064	0.02		0.067	mean		0.281	0.155			0.066
s.e.		0.005	0.003	0.01		0.008	s.e.		0.014	0.004			0.005
pH 5.0	1	0.125	0.1	0.03	3.71	0.139	pH 5.0	1	0.465	0.325	0.14	3.72	0.148
	2	0.095	0.075	0.02	3.77	0.12		2	0.45	0.31	0.14	3.73	0.127
	3	0.095	0.08	0.02	3.73	0.134		3	0.45	0.325	0.13	3.72	0.133
	4	0.1	0.08	0.02	3.79	0.132		4	0.385	0.305	0.8	3.77	0.119
mean		0.104	0.084			0.131	mean		0.438	0.316			0.132
s.e.		0.007	0.006			.008?	s.e.		0.019	0.005			0.006
Day 1													
pH 3.5	1	0.175	0.095	0.08	3.29	0.118	pH 3.5	1	0.425	0.295		3.38	0.088
	2	0.125	0.085	0.04	3.39	0.096		2	0.405	0.27		3.42	0.106
	3	0.145	0.08	0.07	3.36	0.1		3	0.475	0.22		3.43	0.086
	4	0.17	0.105	0.07	3.4			4	0.42	0.27		3.43	0.106
mean		0.154	0.091			0.105	mean		0.431	0.264			0.098
s.e.		0.012	0.006			0.007	s.e.		0.015	0.016			0.007
pH 5.0	1	0.155	0.12	0.04	3.54	0.17	pH 5.0	1	0.43	0.365		3.58	0.143
	2	0.18	0.125	0.06	3.5	0.143		2	0.44	0.355		3.54	0.15
	3	0.155	0.115	0.04	3.54	0.166		3	0.42	0.355		3.55	0.13
	4	0.155	0.125	0.03	3.51	0.165		4	0.42	0.355		3.59	0.143
mean		0.161	0.121			0.161	mean		0.427	0.357			0.142
s.e.		0.007	0.002			0.006	s.e.		0.005	0.003			0.004
Day 3													
pH 3.5	1	0.185	0.125		3.25	0.088	pH 3.5	1	0.7	0.285		3.31	0.077
	2	0.17	0.115		3.3	0.1		2	0.725	0.255		3.32	0.085
	3	0.16	0.1		3.28	0.103		3	0.645	0.27		3.31	0.099
	4	0.16	0.115		3.26	0.081		4	0.62	0.29		3.31	0.087
mean		0.169	0.114			0.093	mean		0.672	0.275			0.087
s.e.		0.06	0.005			0.005	s.e.		0.024	0.008			0.005
pH 5.0	1	0.16	0.125		3.41	0.135	pH 5.0	1	0.49	0.33		3.4	0.105
	2	0.19	0.13		3.36	0.124		2	0.51	0.345		3.41	0.119
	3	0.185	0.13		3.37	0.142		3	0.555	0.395		3.42	0.134
	4	0.2	0.14		3.4	0.146		4	0.575	0.37		3.39	0.111
mean		0.184	0.131			0.137	mean		0.533	0.36			0.117
s.e.		0.009	0.003			0.005	s.e.		0.02	0.014			0.006
Day 7													
pH 3.5	1	0.195	0.125		3.09	0.071	pH 3.5	1	0.605	0.325		3.22	0.064
	2	0.175	0.125		3.11	0.061		2	0.67	0.315		3.2	0.058
	3	0.2	0.115		3.11	0.064		3	0.685	0.28		3.19	0.06
	4	0.195	0.105		3.17	0.074		4	0.62	0.335		3.15	0.065
mean		0.191	0.117			0.067	mean		0.645	0.314			0.062
s.e.		0.006	0.005			0.003	s.e.		0.019	0.012			0.002
pH 5.0	1	0.18	0.11		3.21	0.094	pH 5.0	1	0.565	0.34		3.25	0.081
	2	0.175	0.13		3.19	0.08		2	0.59	0.37		3.27	0.082
	3	0.2	0.125		3.21	0.113		3	0.59	0.32		3.25	0.078
	4	0.185	0.14		3.22	0.098		4	0.605	0.325		3.25	0.078
mean		0.185	0.126			0.096	mean		0.587	0.339			0.08
s.e.		0.005	0.006			0.007	s.e.		0.008	0.001			0.001

Appendix B 3, con't. Solution Parameters: Smoky Mountains Soils, Week 10, Laboratory Study.

		TMAI	NLMAI	LMAI	pH	DOM			TMAI	NLMAI	LMAI	pH	DOM
Day 14													
pH 3.5	1	0.34	0.145	0.2	2.96	.065/.082		pH 3.5	1	1.02	0.335	2.98	0.079
	2	0.37	0.145	0.23	2.95	0.07			2	0.965	0.405	3.02	0.076
	3	0.34	0.155	0.19	2.95	0.079			3	0.87	0.335	2.98	0.07
	4	0.31	0.135	0.18	2.96	0.063			4	0.945	0.335	3.04	0.068
		0.34	0.145							0.95	0.353		
		0.012	0.004							0.031	0.018		
pH 5.0	1	0.215	0.12	0.1	3.09			pH 5.0	1	0.855	0.38	3.09	0.067
	2	0.31	0.13	0.18	2.98	0.063			2	0.945	0.28	3.09	0.069
	3	0.25	0.105	0.15	2.97	0.069			3	0.855	0.27	3.04	0.076
	4	0.335	0.12	0.22	2.97	0.77			4	0.875	0.345	3.08	0.069
		0.278	0.119							0.882	0.319		
		0.027	0.005							0.021	0.027		

Appendix B 4. Solution Parameters: Adirondack Mountains Soils, Week 10, Laboratory Study

		TMAl	NLMAl	LMAl	pH	DOM
Unhealthy Site						
Hour 1						
pH 3.5	1	0.08	0.075	0.005	3.59	no
	2	0.09	0.082	0.008	3.7	data
	3	0.085	0.06	0.025	3.63	
	4	0.092	0.062	0.03	3.63	
mean		0.087	0.07			
s.e.		0.003	0.005			
pH 5.0	1	0.125	0.092	0.003	3.74	
	2	0.11	0.08	0.03	3.69	
	3	0.1	0.08	0.02	3.63	
	4	0.12	0.095	0.025	3.85	
mean		0.114	0.087			
s.e.		0.006	0.008			
Day 3						
pH 3.5	1	0.19	0.142	0.048	3.55	
	2	0.195	0.185	0.01	3.56	
	3	0.16	0.15	0.01	3.33	
	4	0.2	0.165	0.035	3.4	
mean		0.186	0.161			
s.e.		0.009	0.009			
pH 5.0	1	0.245	0.205	0.04	3.51	
	2	0.25	0.205	0.045	3.44	
	3	0.295	0.265	0.03	3.56	
	4	0.28	0.23	0.05	3.54	
mean		0.267	0.226			
s.e.		0.012	0.014			
Day 7						
pH 3.5	1	0.155	0.11	0.045	3.39	
	2	0.19	0.135	0.055	3.43	
	3	0.17	0.12	0.05	3.3	
	4	0.175	0.13	0.045	3.28	
mean		0.172	0.124			
s.e.		0.007	0.006			
pH 5.0	1	0.21	0.145	0.065	3.34	
	2	0.17	0.105	0.065	3.29	
	3	0.17	0.135	0.035	3.37	
	4	0.175	0.145	0.03	3.45	
mean		0.181	0.132			
s.e.		0.01	0.01			

		TMAl	NLMAl	LMAl	pH	DOM
Healthy Site						
pH 3.5	1	0.055	0.044	0.011	3.8	
	2	0.06	0.05	0.01	3.83	
	3	0.06	0.044	0.016	3.58	
	4	0.04	0.038	0.02	3.67	
mean		0.054	0.004			
s.e.		0.005	0.002			
pH 5.0	1	0.06	0.05	0.01	3.9	
	2	0.055	0.05	0.005	4.06	
	3	0.055	0.044	0.011	3.08	
	4	0.055	0.05	0.005	4	
mean		0.056	0.048			
s.e.		0.001	0.002			
pH 3.5	1	0.11	0.11	0	3.47	
	2	0.105	0.105	0	3.61	
	3	0.14	0.115	0.025	3.49	
	4	0.115	0.1	0.015	3.5	
mean		0.118	0.108			
s.e.		0.008	0.006			
pH 5.0	1	0.122	0.108	0.018	3.68	
	2	0.135	0.1	0.025	3.62	
	3	0.13	0.108	0.022	3.73	
	4	0.135	0.113	0.022	3.68	
mean		0.131	0.107			
s.e.		0.006	0.003			
pH 3.5	1	0.105	0.085	0.02	3.37	
	2	0.105	0.08	0.025	3.42	
	3	0.1	0.07	0.03	3.37	
	4	0.12	0.08	0.04	3.33	
mean		0.105	0.079			
s.e.		0.006	0.006			
pH 5.0	1	0.1	0.085	0.015	3.55	
	2	0.125	0.1	0.015	3.55	
	3	0.095	0.07	0.025	3.55	
	4	0.12	0.1	0.02	3.6	
mean		0.111	0.089			
s.e.		0.007	0.007			

Appendix B 5. Solution Parameters: Smoky Mountains Soils, Week 15, Laboratory Study.

Indian Gap Site		TMAl	NLMAl	pH	DOM	H2O
Hour 1						
pH 3.5	1	0.1	0.065	3.31	0.122	8.3
	2	0.105	0.065	3.28	0.106	11
	3	0.11	0.085	3.29	0.13	5.8
	4	0.12	0.07	3.29	0.123	7.3
mean		0.109	0.071		0.12	
s.e.		0.004	0.005		0.005	
pH 5.0	1	0.105	0.1	3.61	0.18	5.5
	2	0.14	0.12	3.45	0.207	7.7
	3	0.105	0.1	3.43	0.153	7.2
	4	0.1	0.1	3.62	0.164	4.8
mean		0.112	0.105		0.176	
s.e.		0.009	0.005		0.012	
Day 1						
pH 3.5	1					
	2	0.125	0.095	3.17	0.121	7.2
	3	0.14	0.115	3.19	0.125	6.2
	4	0.165	0.095	3.17	0.138	8.3
mean		0.143	0.102		0.128	
s.e.		0.012	0.007		0.005	
pH 5.0	1					
	2	0.155	0.125	3.33	0.222	7.3
	3	0.155	0.115	3.15	0.148	5.5
	4	0.145	0.105	3.26	0.193	7.2
mean		0.152	0.115		0.188	
s.e.		0.003	0.006		0.022	
Day 3						
pH 3.5	1	0.165	0.08	3.14	0.116	8.5
	2	0.15	0.1	3.14	0.136	8.6
	3	0.155	0.09	3.14	0.137	6.4
	4	0.17	0.11	3.07	0.148	8.2
mean		0.16	0.095		0.134	
s.e.		0.005	0.006		0.007	
pH 5.0	1	0.155	0.1	3.17	0.124	6.5
	2	0.17	0.13	3.27	0.218	7.9
	3	0.145	0.125	3.24	0.199	5.8
	4	0.185	0.13	3.19	0.21	7.6
mean		0.164	0.121		0.188	
s.e.		0.009	0.007		0.022	
Day 7						
pH 3.5	1	0.22	0.9	3	0.09	7.4
	2	0.215	0.9	3	0.086	8.4
	3	0.31	0.17	2.97	0.104	3.7
	4	0.235	0.125	3.01	0.084	7.4
mean		0.245	0.119		0.091	
s.e.		0.022	0.019		0.005	
pH 5.0	1	0.18	0.095	3.1	0.12	6.2
	2	0.205	0.095	3.09	0.102	4.8
	3	0.215	0.13	3.04	0.098	7.6
	4	0.285	0.145	3	0.091	7
mean		0.221	0.116		0.103	
s.e.		0.022	0.013		0.006	

Collins Gap Site		TMAl	NLMAl	pH	DOM	H2O
Hour 1						
pH 3.5	1	0.31	0.172	3.22	0.105	7.7
	2	0.31	0.187	3.26	0.092	9
	3	0.445	0.172	3.22	0.111	8.2
	4	0.272	0.159	3.3	0.105	5.2
mean		0.334	0.172		0.103	
s.e.		0.038	0.006		0.005	
pH 5.0	1	0.295	0.242	3.31	0.143	6.8
	2	0.352	0.25	3.33	0.13	6.5
	3	0.242	0.258	3.3	0.118	7.2
	4	0.295	0.214	3.39	0.129	6.7
mean		0.296	0.241		0.13	
s.e.		0.022	0.01		0.005	
Day 1						
pH 3.5	1					
	2	0.465	0.165	3.16	0.122	7.1
	3	0.515	0.235	3.06	0.099	6.4
	4	0.465	0.2	3.2	0.183	3.5
mean		0.482	0.2		0.135	
s.e.		0.017	0.02		0.025	
pH 5.0	1					
	2	0.41	0.194	3.22	0.141	6.4
	3	0.465	0.194	3.1	0.123	6.3
	4	0.435	0.221	3.15	0.132	9.2
mean		0.437	0.203		0.132	
s.e.		0.016	0.009		0.005	
Day 3						
pH 3.5	1	0.45	0.159	3.12	0.1	8.2
	2	0.61	0.207	3.09	0.11	7.4
	3	.57/.43	.272/.13	.21/..	.193/.1	5.5
	4	0.595	0.214	3.1	0.145	7.1
mean		0.552	0.21		0.117	
s.e.		0.051	0.031		0.012	
pH 5.0	1	0.505	0.194	3.19	0.125	7.2
	2	0.317	0.214	3.23	0.139	5.3
	3	.435/.5	.18/.27	3.11/	.114/.1	6
	4	0.53	0.265	3.15	0.146	7.5
mean		0.451	0.224		0.135	
s.e.		0.067	0.021		0.005	
Day 7						
pH 3.5	1	0.95	0.265	3.05	0.098	7.9
	2	0.805	0.339	3.06	0.086	6.6
	3	0.91	0.374	3.03	0.104	6.2
	4	1.2	0.265	3.01	0.086	6.8
mean		0.966	0.311		0.094	
s.e.		0.084	0.055		0.004	
pH 5.0	1	0.93	0.317	3.04	0.118	6.2
	2	0.805	0.31	3.07	0.089	4.1
	3	0.95	0.288	3.04	0.094	3.6
	4	0.805	0.228	3.06	0.106	5.3
mean		0.873	0.286		0.097	
s.e.		0.039	0.02		0.007	

Appendix B 5. con't. Solution Parameters: Smoky Mountains Soils, Week 15, Laboratory Study.

Indian Gap Site		TMAl	NLMAl	pH	DOM	H2O
Day 14						
pH 3.5	1	0.425	0.175		0.086	2.2
	2	0.425	0.17	2.89	0.075	3.5
	3	0.395	0.185	2.9	0.082	3.4
	4	0.37	0.215	2.88	0.111	3.2
mean		0.404	0.186		0.088	
s.e.		0.013	0.01		0.008	
pH 5.0	1	0.32	0.16			1.5
	2	0.385	0.17		0.071	2.2
	3	0.37	0.17			1.9
	4	0.345	0.155			1.8
mean		0.355	0.164			
		0.014	0.004			

Collins Gap Site		TMAl	NLMAl	pH	DOM	H2O
Day 14						
pH 3.5	1	1.85	0.25			1.8
	2	2.48	0.287	2.93	0.086	2.6
	3	1.65		2.99	0.072	1.1
	4	2.85	0.381	2.88	0.1	1.1
mean		2.207	0.306		0.086	
s.e.		0.278	0.039		0.008	
pH 5.0	1	0.95			0.079	2.3
	2		0.31		0.114	2.1
	3	1.61	0.395		0.108	2.2
	4	1.445	0.31			1.2
mean		1.337	0.338		0.1	
		0.199	0.028		0.011	

Appendix B 6. Solution Parameters: Adirondack Mountains Soils, Week 15, Laboratory Study.

Unhealthy Forest Site		TMAl	NLMAl	pH	DOM
Hour 1					
pH 3.5	1	0.062	0.048	3.54	0.073
	2	0.059	0.038	3.57	0.072
	3	0.084	0.073	3.56	0.133
	4	0.087	0.059	3.53	0.116
pH 5.0	1	0.107	0.073	3.86	0.148
	2	0.084	0.073	3.87	0.165
	3	0.087	0.073	3.82	0.156
	4	0.099	0.078	3.82	0.175
Day 1					
pH 3.5	1	0.107	0.096		
	2	0.12	0.084	3.47	0.168
	3	0.127	0.11	3.48	0.253
	4	0.11	0.078	3.49	0.148
pH 5.0	1	0.151	0.127	3.55	0.236
	2	0.136	0.11	3.64	0.218
	3	0.139	0.139	3.59	0.23
	4	0.118	0.128	3.66	0.218
Day 3					
pH 3.5	1			3.4	
	2			3.3	0.12
	3			3.31	0.123
	4			3.3	
pH 5.0	1			3.39	0.159
	2			3.47	0.184
	3			3.46	0.175
	4			3.45	0.254
Day 7					
pH 3.5	1	0.242	0.148		0.133
	2	0.192	0.1		0.112
	3	0.168	0.078		0.103
	4	0.27	0.128		
pH 5.0	1	0.258	0.13		
	2	0.142	0.095		0.124
	3	0.155	0.078		
	4	0.125	0.08		0.154

Healthy Forest Site		TMAl	NLMAl	pH	DOM
Hour 1					
pH 3.5		0.035	0.025	3.22	0.075
	2	0.067	0.035	3.26	0.099
	3	0.058	0.058	3.22	0.121
	4	0.042	0.036	3.3	0.074
pH 5.0		0.042	0.03	3.9	0.129
	2	0.049	0.036	3.97	0.133
	3	0.055	0.033	3.97	0.139
	4	0.058	0.044		0.139
Day 1					
pH 3.5		0.048	0.04	3.57	0.233
	2	0.076	0.064	3.62	0.181
	3	0.075	0.067	3.67	0.199
	4		0.067	3.7	0.252
pH 5.0		0.074	0.071	3.77	0.218
	2	0.074	0.076	3.76	0.217
	3	0.077	0.076	3.81	0.268
	4	0.076	0.076	3.74	0.225
Day 3					
pH 3.5			0.064	3.5	0.177
	2	0.097	0.075	3.63	0.259
	3	0.083	0.065	3.34	0.142
	4	0.083	0.076	3.53	0.178
pH 5.0		0.075	0.068	3.49	0.178
	2	0.084	0.086	3.58	0.199
	3	0.092	0.07	3.46	0.181
	4	0.094	0.078	3.64	0.241
Day 7					
pH 3.5		0.095	0.078		0.151
	2	0.118	0.072		0.142
	3	0.125	0.052		0.164
	4	0.072	0.058		
pH 5.0		0.107	0.072		0.136
	2	0.082	0.065		0.178
	3	0.075	0.045		0.123
	4	0.082	0.052		

Appendix B 7 Total Solution Concentrations of Selected Elements in Smoky Mountains Soils, Laboratory Study

Collins Gap Site		Ca	Mg	Fe	Mn	Cu	Al
		mg/L					
Week O, Hour 1							
pH 3.5							
	1	15.6	3.58	1.24	0.54	0.117	26.1
	2	17.8	4.35	1.83	0.74	0.084	18.15
	3	14.9	3.48	1.25	0.56	0.113	17.29
	4						
pH 5.0							
	1	13.7	3.15	1.68	0.45	0.197	26.48
	2	10.6	2.27	1.54	0.29	0.085	25.13
	3						
	4	13.7	3.12	1.67	0.51	0.121	25.27
Day 7							
pH 3.5							
	1	126	32.1	0.93	6.45	0.671	34.05
	2						
	3	129	32.3	0.86	6.65	0.197	27.4
	4	131	33.3	1	7.53	0.289	28.95
pH 5							
	1	116	29.8	0.79	6.26	0.113	30.28
	2						
	3	124	31.2	1.05	6.37	0.129	31.98
	4	122	31.3	0.92	6.31	0.191	34.29
Week 15, Hour 1							
pH 3.5							
	1	19.4	3.31	0.87	0.63	0.078	10.77
	2	17.5	3.04	0.87	0.58	0.145	14.15
	3	0.49	2.3	1.07	0.42	0.078	14.39
	4						
pH 5.0							
	1	15.1	2.69	1.27	0.51	0.163	12.61
	2	15.2	2.67	1.24	0.5	0.101	14.18
	3	30.5	6.01	0.99	1.14	0.095	13.76
	4						
Day 7							
pH 3.5							
	1	49.9	8.75	1.19	1.86	0.149	15.79
	2	49.3	8.32	0.76	1.92	0.083	15.29
	3	55.6	8.96	0.87	2.01	0.116	19.82
	4						
pH 5							
	1	62.6	11.6	0.96	2.49	0.095	21.14
	2	36.7	6.95	0.75	1.46	0.249	14.56
	3						
	4	65.6	12.7	1.03	2.57	0.173	27.97

Unhealthy Site		Ca	Mg	Fe	Mn	Cu	Al
		mg/L					
Week O, Hour 1							
pH 3.5							
	1	14.47	2.95	0.97	0.47	0.198	21.08
	2	11.64	2.27	1.68	0.31	0.3	22.76
	3	16.91	3.35	1.68	0.51	0.399	25.99
	4						
pH 5.0							
	1	9.265	1.74	1.48	0.22	0.189	19.7
	2	8.609	1.54	1.15	0.17	0.153	21.43
	3	8.606	1.6	1.27	0.17	0.181	25.27
	4						
Day 7							
pH 3.5							
	1	65.15	14.3	0.88	3.03	0.177	25.41
	2						
	3	65.21	14.2	0.85	2.94	0.362	24.01
	4	66.95	14.7	1.02	3.02	0.178	24.64
pH 5.0							
	1	56.92	12.8	0.87	2.63	0.116	22.17
	2						
	3	63.88	14.4	0.78	2.8	0.161	24.72
	4	56.72	12.2	0.67	2.72	0.067	8.556
Week 15, Hour 1							
pH 3.5							
	1	10.29	1.85	1.08	0.32	0.091	9.808
	2	11.15	1.96	0.62	0.37	0.178	10.45
	3	12.03	2.17	0.72	0.4	0.099	11.66
	4						
pH 5.0							
	1	5.738	1.07	0.97	0.14	0.091	10.77
	2	7.716	1.37	1.2	0.22	0.078	12.57
	3	9.925	1.75	1.03	0.22	0.144	17.51
	4						
Day 7							
pH 3.5							
	1	47.74	8.26	0.72	1.88	0.103	11.79
	2	49.36	8.8	0.61	1.92	0.103	9.964
	3						
	4	46.34	8.25	0.57	1.85	0.116	12.64
pH 5.0							
	1	33.14	6.29	0.78	1.3	0.149	13.06
	2						
	3	44.55	8.09	0.94	1.81	0.132	16.19
	4	56.64	10.7	0.67	2.41	0.152	13.24

Appendix B 8. Total Solution Concentrations of Selected Elements in Adirondack Mountains Soils, Laboratory Study.

Healthy Site		Al	Ca	Cu	Fe	Mg	Mn
				mg/L			
Week 0, Hour 1							
pH 3.5							
	1	33.82	6.16	1.34	1.36	0.26	21.84
	2	26.63	4.79	1.24	1.13	0.15	25.05
	3						
	4						
pH 5.0							
	1	22.71	3.66	1.35	0.89	0.61	21.6
	2	33.27	5.47	1.36	1.43	0.12	23
	3	26.77	4.43	1.14	1.1	0.18	22.07
	4						
Day 7							
pH 3.5							
	1	109.1	18.1	3.26	6.03	0.32	24.53
	2	89.51	15.6	2.93	4.36	0.12	24.53
	3	100.1	16.9	2.92	5.01	0.15	20.23
	4						
pH 5							
	1	72.44	12.2	2.35	3.41	0	37.39
	2	108.6	17.7	4.4	5.45	1.18	41.71
	3						
	4						
Week 15							
One Hour							
pH 3.5							
	1	15.71	2.47	0.48	0.69	0.07	8.312
	2	18.51	2.79	0.2	0.73	0.05	9.291
	3						
	4	17.31	2.77	0.15	0.8	0.07	8.825
pH 5.0							
	1	8.723	1.46	0.29	0.31	0.07	12.55
	2	7.278	1.19	0.43	0.25	0.05	9.612
	3	8.458	1.37	0.47	0.29	0.07	13.54
	4						
Day 7							
pH 3.5							
	1	71.53	11.9	0.62	3.51	0.17	19.18
	2	77.73	14.5	0.67	4.06	0.17	16.71
	3	65.9	10.2	0.94	3.06	0.33	18.67
	4						
pH 5							
	1						
	2	37.6	6.21	0.56	1.86	0.11	12.34
	3	43.23	7.54	0.96	1.98	0.07	13.61
	4	49.75	8.6	0.58	2.55	0.1	10.42

Unhealthy Site		Al	Ca	Cu	Fe	Mg	Mn
				mg/L			
Week 0, Hour 1							
pH 3.5							
	1	19.41	2.49	1.13	0.84	0.2	21.17
	2	23.53	2.87	1.52	1.09	0.14	23.43
	3	19.67	2.29	1.3	1.13	3.44	47.75
	4						
pH 5.0							
	1	11.36	1.45	1.38	0.34	0.13	22.25
	2	16.65	2.02	1.53	0.63	0.18	19.89
	3	16.9	2.07	1.69	0.62	0.22	24.98
	4						
Day 7							
pH 3.5							
	1						
	2	82.64	9.53	4.56	4.4	0.13	36.32
	3	77.19	8.83	3.44	4.34	0.13	27.83
	4						
pH 5							
	1	82.51	9.74	5.3	4.1	0.27	51.89
	2	84.85	9.77	4.54	4.58	0.2	34.79
	3	78.72	9.98	5.03	4.12	0.35	55.46
	4						
Week 15							
One Hour							
pH 3.5							
	1						
	2	14.01	1.89	0.56	0.56	0.18	11.64
	3	19.75	2.79	0.8	0.74	0.17	21.73
	4	15.61	2.18	0.43	0.63	0.08	10.42
pH 5.0							
	1	9.368	1.5	0.87	0.32	0.17	12.58
	2	8.942	1.53	0.56	0.47	0.09	9.53
	3	7.629	1.2	0.81	0.25	0.09	10.89
	4						
pH 3.5							
	1	60.93	7.44	1.29	3.19	0.14	23.24
	2	68.57	8.75	1.28	3.68	0.67	18.24
	3	53.34	7.06	0.59	2.35	0.18	16.31
	4						
pH 5							
	1	44.08	7.06	2.12	1.79	0.15	22.09
	2	50.22	7.4	1.41	2.5	0.22	22.94
	3						
	4	48.02	7.96	2.37	1.86	0.26	35.55

Appendix B 9. Concentrations of Selected 1N KCl-Exchangeable Elements: Great Smoky Mountains Soils, Laboratory Study.

Collins Gap Site — mg/100 g soil

	AL	Ca	Cu	Fe	Mg	Mn
Week 0, Hour 1						
pH 3.5						
1	55	66	0.092	2.217	8.89	2.09
2	57	68	0.288	2.266	9.39	2.27
3	57	65	0.054	2.204	8.85	2.12
4	57	70	0.092	2.194	9.16	2.3
pH 5.0						
1						
2	47	21	0.067	3.5	5.47	1.43
3	53	69	0.029	0.051	8.94	2.3
4	55	65	0.064	2.088	9.28	2.32
Day 1						
pH 5						
1	46	11	0.058	4.231	3.57	0.46
3	75	38	0.062	3.97	13.5	1.56
5	40	9	0.034	3.134	2.62	0.47
Week 15, Day 7						
pH 3.5						
1	59	40	0.063	2.886	4.4	0.86
2	66	50	0.078	3.286	5.22	1.1
3						
4	65	43	0.097	3.409	4.75	0.94
pH 5						
1	38	29	0.07	2.008	3.19	0.67
2	68	57	0.06	3.208	6.22	1.42
3	34	27	0.053	1.905	3.23	0.65
4	30	67	0.068	2.024	6.04	1.8

Indian Gap Site — mg/100 g soil

	AL	Ca	Cu	Fe	Mg	Mn
Week 0, Hour 1						
pH 3.5						
1	25	89	0.08	1.45	9.81	2.92
2	26	89	0.116	1.64	9.41	2.52
3	27	90	0.09	1.75	9.99	2.66
4	26	88	0.116	1.62	9.36	2.52
pH 5.0						
1	26	90	0.068	1.52	9.6	2.65
2	27	93	0.082	1.61	9.86	2.96
3	29	93	0.139	1.68	9.91	2.74
4	28	93	0.084	1.71	10.3	2.84
Week 15, Day 7						
pH 3.5						
1	31	73	0.084	2.15	6.58	1.77
2	31	73	0.074	2.12	7.16	1.81
3						
4	31	76	0.08	2.17	6.98	1.85
pH 5.0						
1	31	79	0.078	2.15	7.62	2.02
2	30	83	0.115	2	8.12	2.45
3	31	78	0.112	2	7.61	2.08
4	29	77	0.092	2.02	7.64	2.08

Appendix B 10. Concentrations of Selected 1N KCl-Exchangeable Elements: Adirondack Mountains Soils, Laboratory Study.

Healthy Site	Al	Ca	Cu	Fe	Mg	Mn
	mg/100 g soil					
Week 0, Hour 1						
pH 3.5						
1	40.4	30.3	0.073	5.63	6.77	1.63
2	1.38	200	0.081	0.12	18.1	6.29
3	1.42	189	0.078	0.12	17.6	6.34
pH 5.0						
1	1.37	190	0.137	0.15	17	7.13
2	1.68	195	0.077	0.16	17.8	8.68
3	1.47	200	0.079	0.17	18.3	8.8
Week 15, Day 7						
pH 3.5						
1	5.74	177	0.217	0.33	12.3	5.84
2	5.08	167	0.063	0.36	12.3	5.8
3	5.83	168	0.246	0.38	12.1	5.68
4	3.91	210	0.057	0.28	16.1	7.83
pH 5.0						
1	5	193	0.08	0.3	14.5	6.91
2	4.09	187	0.068	0.31	14.9	6.91
3	4	200	0.147	0.25	15.8	7.45
4	5.42	181	0.073	0.32	14	6.29

Unhealthy Site	Al	Ca	Cu	Fe	Mg	Mn
	mg/100 g soil					
Week 0, Hour 1						
pH 3.5						
1	6.33	185	0.125	0.29	11.6	8.36
2	2.85	90.4	0.104	0.18	5.62	4.32
3	4.77	195	0.096	0.28	12.5	9.63
pH 5.0						
1	4.74	203	0.083	0.27	12.8	9.78
2	40.4	22.4	0.06	3.3	4.35	1.09
3	4.52	194	0.108	0.28	12.4	9.23
Week 15, Day 7						
pH 3.5						
1	16.1	135	0.077	0.85	8.59	4.13
2	13.7	148	0.084	0.62	8.73	4.95
3	13.7	146	0.07	0.9	8.13	5.07
4	15.9	140	0.072	0.71	8.75	4.45
pH 5.0						
1	16.3	138	0.068	0.62	9.53	4.33
2	12	181	0.189	0.54	11.3	6.97
3	13	154	0.063	0.83	10.5	5.1
4	13.1	169	0.122	0.61	10.9	6.24

Appendix B 11. Effects of Treatment pH on Selected Parameters of Soil Solution Chemistry of Red Spruce Seedlings in Follow-up Greenhouse Study.

	Nonrhizosphere Soil				Rhizosphere Soil			
	TMAl	NLMAl	pH	H2O DOM	TMAl	NLMAl	pH	H2O DOM
	mg/L				mg/L			
pH 3.5 Treatment								
1	0.58	0.27	3.34	0.194	1.5	1.08	3.27	1.138
2	0.74	0.3	3.41	0.183	2.13	0.95	3.15	0.684
3	0.42	0.31	3.41	0.308	1.08	0.87		
4	0.64	0.27	3.35	0.221	0.64	0.31	3.34	0.335
5	0.69	0.52	3.38	0.223	1.26	0.67	3.26	0.43
6	0.29	0.26	3.47	0.23	0.41	0.3	3.29	0.268
7	0.72	0.27	3.28	0.166	2.5	0.96	3.02	0.43
8	0.8	0.26	3.36	0.196				
9					0.69	0.43		
pH 4.1 Treatment								
	0.45	0.27			1.12	0.89	3.44	0.507
2	0.43	0.27	3.63	0.201	1.16	1.06		
3	0.26	0.3	3.53	0.238	0.69	0.6	3.51	0.474
4	0.45	0.32	3.5	0.294	0.72	0.67	3.44	0.473
5	0.92	0.34	3.52	0.221	0.96	1.12	3.36	
6	0.25	0.22	3.73	0.305	1.28	0.49	3.33	0.55
7	0.37	0.24	3.49	0.2	0.84	0.52	3.65	0.413
8							3.46	0.471
pH 5.0 Treatment								
2	0.58	0.3	3.66	0.286	1.28	0.67	3.36	0.649
3	0.84	0.67	3.43	0.472	1.13		3.28	
4	0.52	0.43	3.63	0.255	1.01	0.64	3.38	0.452
5	0.35	0.35			0.49	0.46	3.58	0.401
6	0.87	0.35	3.07	0.199	1.22	0.64	3.14	0.335
7	0.87	0.38	3.31	0.256	1.06	0.62	3.31	0.388

Appendix B 12. Effects of Treatment pH on Concentrations of Total Dissolved Elements in Red Spruce Soil in Follow-up Greenhouse Study.

	Al	K	Ca	Cu	Fe	Mg	Mn	P	Al	K	Ca	Cu	Fe	Mg	Mn	P
	Rhizosphere Soil								Nonrhizosphere Soil							
pH 3.5 Treatment																
	28.72	241.8	40.13	0	0.17	8.76	0.41	0	28.82	167.4	23.9	0	0	4.87	0.55	0
	35.98	171.3	47.84	0	0.51	12.65	0.41	15.16	34.26	226.2	21.36	0.01	0.85	5.35	0.41	0
	34.15	204.7	65.77	0.15	0.18	15.09	0.41	5.08	21.12	216.4	125.5	0.01	1.68	5.84	0.55	8.44
	33.72	299.3	116.2	0.01	2.19	25.79	0.55	23.55	32.11	238	35.03	0.44	0	7.3	0.68	22.71
pH 4.1 Treatment																
	29.79	228.3	26.47	0.43	1.51	5.84	0.14	1.68	25.97	259.9	13.68	0.01	0.34	3.89	0.41	0
	31.89	263.3	29.05	0.01	1.52	7.79	0.41	12.64	20.93	255.2	20.51	0	0.18	5.84	0.55	18.51
	28.5	249.2	30.73	0	2.01	7.78	0.27	16.79	26.19	316.1	53.82	2.16	2.69	8.76	0.48	16.84
	22.75	170.3	27.34	0	0.85	4.87	0	11.8	26.46	274.4	35.86	0	0	7.3	0.55	1.68
pH 5.0 Treatment																
	44.4	238.9	53.72	0.56	13.88	13.61	0.41	9.14	25.01	308.8	33.32	0.58	1.52	5.84	0.41	6.76
	37.59	189.5	47.84	0.44	2.69	12.17	0.27	21.87	18.61	221.9	23.9	0	1.68	5.84	0.41	0
	35.44	272	40.15	0.01	1.52	13.14	0.34	16	33.65	242.3	75.91	0.27	1.32	19	1.5	5.79

Appendix B 13. Effects of Treatment pH on Concentrations of 1N KCl-Extractable Elements in Red Spruce Soil in Follow-up Greenhouse Study.

Rhizosphere Soil	Al	Ca	Cu	Fe	Mg	Mn	P	Bulk Soil	Al	Ca	Cu	Fe	Mg	Mn	P
	(mg/67 g Soil)								(mg/67 g Soil)						
pH 3.5 Treatment															
	49.94	99.09	0.079	6.73	13.84	0.81	1.76		48.8	83.44	0.124	6.11	8.44	2	1.21
	50.06	99.74	0.08	5.47	10.91	0.85	1.68		60.14	94.3	0.102	6.29	9.85	1.63	1.31
	46.2	115	0.11	5.08	11.8	0.93	1.17		50.07	108.1	0.085	5.63	9.3	1.68	1.12
	40.91	116.3	0.072	2.12	11.13	0.92	1.45		56.06	94.54	0.105	5.35	7.49	1.18	1.17
	62.23	77.75	0.085	6.47	7.56	1.03	0.95								
	39.5	125.8	0.109	4.83	12.46	0.58	1.11		39.16	142.6	0.086	4.78	11.2	1.83	1.14
	54.39	63.47	0.104	7.16	5.75	0.69	1.17								
	39.82	191.7	0.057	4.453	10.24	1.82	1.51								
pH 4.1 Treatment									20.33	87.56	0.119	1.61	6.68	1.24	0.71
	44.89	99.64	0.075	4.72	9.87	0.68	1.05		51.16	112.3	0.122	5.62	11.7	2.01	1.04
	52.91	83.34	0.104	7.33	12.73	0.53	1.01		48.54	94.04	0.091	7.4	11.3	1.59	1.05
									43.38	116	0.099	4.14	12.5	2.27	1.01
	40.22	117	0.077	5.2	14.25	0.99	1.42		38.78	152.1	0.113	5.36	13.4	2.77	1.13
	39.49	177.3	0.061	5.06	12.06	0.92	1.24		32.75	146.9	0.111	4.2	14.9	2.26	1.06
	40.35	173.7	0.072	5.5	14.15	0.39	1.12		39.14	155	0.089	5.02	12.3	1.65	1.02
	40.09	130.2	0.073	4.77	12.76	0.51	0.75								
pH 5.0 Treatment															
	35.13	151.5	0.096	4.27	17.42	0.65	0.98		39.45	147.4	0.079	5.42	14.6	1.94	0.94
	43.21	142.2	0.073	5.21	21.01	0.79	1.68		39.26	117.4	0.113	5.74	16.5	1.72	0.87
	52.05	106.1	0.129	7.21	13.51	0.4	1.09		50.89	106	0.071	7.48	11.6	1.47	1.3
	38.5	146.9	0.134	4.81	17.19	0.99	0.86		37.77	145.4	0.096	5.1	15.3	3.21	0.9
	46.25	131.4	0.105	5.39	14.49	0.85	1.24		44.27	126.4	0.079	5.38	12.4	1.59	1.35
	52.69	104.8	0.087	5.77	14.47	0.6	1.17		40.74	125.5	0.08	5.37	12.9	1.75	1.07

Appendix B 14. Effects of Treatment pH on Transpiration Rates of Red Spruce Seedlings in Initial Greenhouse Study.

Treatment					
pH 3.5		pH 4.1		pH 5.0	
		(mg H_2O gdw^{-1} needle tissue)			
1[1]	0.45	x1	0.51	33	0.33
	0.41		0.47		0.39
2	0.33	2	0.42	34	0.37
	0.31		0.39		0.45
4	0.89	4	0.40	35	0.96
	0.95		0.36		1.17
6	1.10	5	0.36	36	0.37
	0.96		0.36		0.40
8	0.34	6	1.05	37	0.46
	0.32		1.06		0.47
9	0.47	7	2.03	39	0.19
	0.34		1.55		0.24
10	0.27	8	0.59	40	0.39
	0.28		0.17		0.49
12	0.28	9	0.35	41	0.34
	0.36		0.35		0.33
13	0.50	10	0.35	42	0.84
	0.50		0.27		0.66
14	0.33	11	0.37	45	0.30
	0.27		0.19		0.32
15	0.36	13	0.26	46	0.28
	0.42		0.19		0..32
16	0.40				
	0.49				
Mean	0.47		0.53		0.48
Std.Dev.	0.24		0.45		0.36

[1]Measurements made on two branches per plant.

Appendix B 15. Effects of Treatment pH on Photosynthetic Rates of Red Spruce Seedlings in Initial Greenhouse Study.

pH 3.5		Treatment pH 4.1		pH 5.0	
		(nmol CO_2 gdw^{-1} needle tissue s^{-1})			
1[1]	144	x1	119	33	61
	101		31		56
2	88	2	108	34	129
	82		104		131
4	102	4	77	35	114
	111		77		110
6	92	5	156	36	89
	83		75		121
8	104	6	101	37	135
	71		113		135
9	87	7	147	39	61
	81		103		96
10	92	8	221	40	81
	110		62		102
12	90	9	117	41	102
	113		112		102
13	118	10	97	42	106
	77		82		73
14	124	11	110	45	132
	121		97		125
15	84	13	56	46	83
	139		71		123
16	117				
	150				
Mean	104		107		102
Std.Dev.	22		38		33

[1]Measurements made on two branches per plant.

Appendix B 16. Effects of Treatment pH on Concentrations of Selected Elements in Foliage of Red Spruce (Physiological Parameter Needles): Initial Greenhouse Experiment.

	Chlorosis*	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 3.5 Treatment									mg/Kg												(mol)
1	7	7631	7340	21402	5631	159	6579	282	15.4	4.45	1170	164	379	2	9.6	12.8	4.8	1.7	78	307	88.3
2	3	8669	13686	26345	5713	146	6701	325	18	5.25	1359	134	401	2.14	10	16	8.8	1.5	78	365	132
4	5	4862	5069	16890	4937	134	4412	228	15.4	3.94	1050	123	741	1.76	7.5	9.8	5.6	1.2	58	260	93
6	4	6169	6040	16142	4623	141	5126	287	15	3.7	1744	142	263	1.79	7.8	13.1	6	1.3	63	288	76.9
8	7	8764	8126	27561	5516	158	8684	389	17.1	3.79	1454	181	173	2.91	11	15.6	9.2	1.8	80	499	103
9	1	6218	6855	15186	4893	128	4427	241	13.8	1.81	920	119	234	1.47	7.2	11.4	4.7	1.4	57	295	86.1
10	7	5900	7859	20229	5239	122	6018	259	14.9	4.22	1004	189	657	2.46	8.7	13.6	6	1.3	88	333	72.2
12	6	5657	7174	17983	5419	126	3563	200	12.9	3.88	1325	144	518	2.69	7.4	12.7	5.4	1.2	68	267	84.5
13	1	6419	6521	20958	4650	151	5788	260	16.4	2.52	1501	147	346	1.67	8	10.4	7.7	1.3	64	309	96.3
14	3	9267	8096	18030	4530	165	6107	259	16.4	2.07	760	90	268	1.63	8.3	7.75	7.7	1.4	59	281	135
15	3	7026	5649	21502	4836	131	4801	258	15.1	3.77	1056	153	414	1.47	7.7	8.98	7.5	1.2	44	220	95
Mean		6962	7492	20203	5090	142	5655	272	15.5	3.58	1213	144	399	2	8.5	12	6.7	1.4	67	311	96.6
Std. Dev.		1437	2283	3973	429	15	1411	51	1.45	1.04	291	28	177	0.49	1.2	2.63	1.6	0.2	13	73	20.4
Std. Error		431.1	684.9	1192	129	4.4	423	15	0.44	0.31	87.2	8.5	53	0.15	0.4	0.79	0.5	0.1	4	22	6.12
pH 4.1 Treatment																					
16	4	6222	6460	23000	7934	145	6147	329	17.3	2.93	1367	262	733	2.83	11	15.4	9.7	1.5	84	377	59.3
22	13	5498	8220	21940	6378	178	5307	219	17.3	1.73	628	204	640	1.74	9.5	23.2	6.6	1.9	99	440	72.7
28	11	7206	8102	25945	6016	168	6123	392	18.5	2.69	1750	215	779	1.83	9.6	17.6	8.5	0.9	87	331	81.4
29	12	8086	8137	14584	7791	162	5505	331	18.9	5.62	990	227	517	2.13	11	24.7	8.5	1.7	61	236	43.4
23	12	6818	5458	30328	7489	175	9314	404	19.3	4.74	469	216	477	2.61	13	19.9	11	2	##	713	94.8
21	4	6483	7438	18624	6242	185	5085	256	17.4	4.72	840	244	566	1.8	9.1	28.6	12	1.4	63	237	51.6
x13	7	6160	7913	20820	4484	140	7422	263	16.5	3.22	1739	177	353	2.3	8.7	13.1	7.8	1.5	94	415	79.5
26	13	7682	7600	21008	5532	192	6855	325	19.2	2.62	1230	162	432	2.02	9.3	15.6	6.9	1.8	78	351	87.5
24	13	6187	6780	24675	7189	180	8243	315	23.2	3.75	1612	187	487	2.32	12	19.2	8.5	2.1	93	449	89.2
25	12	6998	8312	15532	6661	189	7750	329	17.9	2.62	1929	198	407	2.6	11	30.3	7.6	1.5	71	216	53
27	9	4960	6862	13540	5119	158	4935	230	17.2	1.62	1670	144	709	1.43	7.7	21	6.3	0.9	40	123	63.5
x2	10	6250	7326	23991	5913	172	7508	328	20.3	5.24	1676	203	523	1.97	10	16.1	7.6	1.6	62	285	79.7
Mean		6546	7384	21166	6396	170	6683	310	18.6	3.46	1325	203	552	2.13	10	20.4	8.4	1.6	80	348	71.3
Std. Dev.		877.2	862	4962	1072	17	1390	58	1.83	1.34	488	33	136	0.41	1.4	5.42	1.7	0.4	23	152	16.8
Std. Error		254.4	250	1439	311	4.8	403	17	0.53	0.39	141	9.6	39	0.12	0.4	1.57	0.5	0.1	7	44	4.87

*Degree of chlorosis of terminal shoot needles increases with increasing number.

Appendix B 16, con't. Effects of Treatment pH on Concentrations of Selected Elements in Foliage of Red Spruce (Physiological Parameter Needles): Initial Greenhouse Experiment.

Chlorosis*	P	k	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 5.0 Treatment								mg/Kg												(mol)
33	9	5726	7812	20786	5863	131	4099	200	18.9	4.21	1022	138	961	1.92	9	11.3	3.9	1.4	98	380	102
34	6	6901	6489	22950	6965	162	6945	283	17.8	3.7	856	227	##	2.4	11	15.2	8.8	1.5	89	405	68.3
35	3	5422	7641	17905	6624	134	5214	215	16.9	4.42	1310	214	993	2.2	10	18.3	6.5	1.1	66	268	56.5
36	2	8295	8079	15193	4746	169	5817	211	15.9	2.2	1164	144	662	1.5	9.1	17.2	6.7	1	66	154	71
37	2	7836	9053	22064	4637	177	7630	371	17	4.55	1416	172	684	2	10	13.5	7.4	1.4	99	419	86.6
39	2	9548	9692	23054	6522	173	8151	278	25.9	3.84	417	157	282	2.22	12	15.4	10	2.1	##	444	98.9
40	8	5443	6429	20023	5126	166	4969	270	17.7	2.39	1154	145	935	1.97	11	29.6	15	1.1	84	387	93.1
41	4	7003	8086	21197	5184	146	7238	272	18.2	2.48	1267	149	661	1.64	11	14.6	8.5	1.4	45	248	96
45	7	13017	12313	24009	6698	191	9243	381	24.7	3.79	1183	195	254	2.17	13	14	7.8	1.9	85	393	83
46	10	7771	6554	31000	6404	156	6325	282	22.5	3.55	672	192	464	2.57	11	15.8	9.1	1.5	##	527	109
48	2	5148	7393	11585	4215	117	3298	184	15	3.14	1098	183	594	1.35	6.7	15.5	6.7	0.9	32	130	42.6
Mean		7465	8140	20888	5726	157	6266	268	19.1	3.48	1051	174	683	1.99	10	16.4	8.2	1.4	82	341	82.4
Std. Dev.		2308	1725	5011	974	22	1794	65	3.6	0.82	296	30	274	0.38	1.6	4.74	2.7	0.4	29	125	20.6
Std. Error		669.3	500.3	1453	282	6.4	520	19	1.04	0.24	85.7	8.8	79	0.11	0.5	1.38	0.8	0.1	8	36	5.97

*Degree of chlorosis of terminal shoot needles increases with increasing number.

Appendix B 17. Effect of Treatment pH on Growth and Biomass of Greenhouse Red Spruce Seedlings: (A) Growth Parameters.

pH 3.5 Treatment			pH 4.1 Treatment			pH 5.0 Treatment		
Sample	ΔH^1	$\Delta H/H_{in}^2$	Sample	ΔH^1	$\Delta H/H_{in}^2$	Sample	ΔH^1	$\Delta H/H_{in}^2$
1	4.5	16	17	5.4	47	34	8.7	29
2	4.1	11	18	4.3	13	36	8.2	33
3	6.7	23	19	6.0	19	37	7.3	26
4	4.4	12	21	8.7	29	38	5.0	15
5	5.6	23	22	4.4	17	39	5.0	22
6	3.8	12	23	5.2	16	40	2.8	9
7	2.3	6	24	8.1	25	41	6.7	20
8	4.2	14	25	5.7	16	42	4.6	14
11	7.4	22	26	6.3	21	43	5.0	13
12	6.3	14	27	6.0	16	44	4.6	15
13	1.0	3	28	4.9	15	45	9.1	25
14	3.9	14	29	5.2	17	46	9.8	36
15	4.2	16	30	5.2	17	48	3.8	11
16	5.2	17	31	7.4	19			
Mean	4.5	15		5.9	18		6.2	21
Std. Dev.	1.7	5		1.3	4		2.2	9

[1]growth increment in height during treatment period
[2]in=initial

Appendix B 17, Con't. Effect of Treatment pH on Growth and Biomass of Greenhouse Red Spruce Seedlings: (B) Root Tissue Biomass.

Sample	Fine Roots	Large Roots	Σ Roots	Fine Roots/Total Roots
		(g of tissue)		
Treatment: pH 3.5				
2	1.37	4.14	5.51	0.25
3	1.40	2.75	4.14	0.34
4	2.57	6.29	8.87	0.29
5	0.79	2.09	2.88	0.27
6	1.39	5.03	6.42	0.22
7	1.36	2.55	3.81	0.33
8	1.19	2.14	3.33	0.36
10	2.50	7.37	9.87	0.25
11	1.69	3.37	5.05	0.33
14	0.58	2.30	2.88	0.20
Mean	1.47	3.80	5.28	0.28
Std. Dev.	0.64	1.87	2.45	0.06
Treatment: pH 4.1				
19	1.62	4.15	5.77	0.28
20	1.28	3.09	4.37	0.29
22	2.24	5.01	7.25	0.21
24	1.27	3.69	4.96	0.26
25	1.18	2.84	4.02	0.29
26	0.74	3.88	4.62	0.16
28	3.12	5.11	8.25	0.38
30	2.05	3.88	5.93	0.35
31	3.39	4.66	8.06	0.42
Mean	1.88	4.03	5.91	0.30
Std. Dev.	0.90	0.79	1.60	0.08
Treatment: pH 5.0				
34	2.58	4.41	7.00	0.37
36	0.80	2.99	3.79	0.21
37	1.38	3.26	4.64	0.30
38	2.66	5.16	7.81	0.34
39	2.33	2.68	5.01	0.46
40	2.25	4.26	6.51	0.35
41	1.48	4.53	6.01	0.25
43	2.05	3.45	5.50	0.37
45	0.68	2.58	3.26	0.21
46	2.57	3.27	5.83	0.44
48	3.03	5.77	8.80	0.34
Mean	1.98	3.85	5.83	0.33
Std.Dev.	0.79	1.04	1.66	0.08

Appendix B 17, Con't. Effect of Treatment pH on Growth and Biomass of Greenhouse Red Spruce Seedlings: (C) Wood Tissue Biomass.

Sample	New Wood	Second Flush	Σ New Wood	Old Wood	Σ Wood
			(g. tissue)		
Treatment: pH 3.5					
2	1.60	0.75	2.34	10.69	13.04
3	1.17	2.26	3.43	9.69	13.12
4	1.92	0.81	2.72	13.68	16.41
5	1.01	1.01	2.02	3.66	5.69
6	1.75	1.99	3.74	10.92	14.65
7	1.02	1.20	2.39	7.93	10.32
8	0.90	0.44	1.33	5.51	6.85
10	1.47	0.07	1.53	8.66	10.19
11	1.59	1.82	3.51	8.44	11.94
14	1.11	1.19	2.30	5.49	7.79
Mean	1.38	1.15	2.53	8.47	11.00
Std. Dev.	0.35	0.70	0.82	2.99	3.48
pH 4.1 Treatment					
19	1.13	0.16	1.29	6.32	7.6
20	1.54	0.28	1.32	7.67	8.99
22	1.30	0.48	1.77	8.59	10.36
24	1.65	0.14	1.80	7.61	9.41
25	0.97	0.29	1.26	7.50	8.76
26	0.82	0.33	1.15	6.14	7.28
28	1.14	0.00	1.14	9.35	10.49
30	1.20	0.20	1.40	5.43	6.82
31	1.60	0.05	1.65	13.49	15.14
Mean	1.26	0.26	1.36	6.66	9.42
Std. Dev.	0.29	0.17	0.21	2.34	2.51
pH 5.0 Treatment					
34	1.48	0.25	1.73	7.95	9.77
36	0.78	0.56	1.34	6.42	7.76
37	0.80	0.04	0.84	8.46	9.30
38	1.18	0.00	1.18	10.86	12.04
39	0.52	0.00	0.52	4.01	4.54
40	1.45	0.09	1.53	9.69	11.22
41	1.37	0.27	1.64	8.91	10.55
43	1.36	0.00	1.36	9.90	11.27
45	0.89	0.06	0.95	5.95	6.89
46	1.59	0.00	1.59	10.05	11.64
48	1.33	0.00	1.33	10.36	11.69
Mean	1.16	0.12	1.27	8.41	9.70
Std. Dev.	0.36	0.18	0.37	2.10	5.39

Appendix B 17, Con't. Effect of Treatment pH on Growth and Biomass of Greenhouse Red Spruce Seedlings: (D) Needle Tissue Biomass.

Sample	New	New: 2nd Flush	Σ New	Old	Σ Needles
			(g. tissue)		
pH 3.5 Treatment					
2	3.01	1.11	4.12	1.78	5.90
3	1.60	4.63	6.23	2.27	8.50
5	1.11	1.92	3.03	0.51	3.54
6	2.95	2.83	5.78	1.93	6.71
7	2.41	4.00	6.40	1.91	8.31
8	2.30	1.00	3.30	1.02	4.32
10	3.91	0.32	4.23	3.02	7.25
11	2.49	4.84	7.32	2.11	9.44
14	1.96	2.82	4.78	1.23	6.01
Mean	2.42	2.45	5.02	1.92	6.66
Std. Dev.	0.83	1.62	1.49	0.87	1.95
pH 4.1 Treatment					
19	2.74	0.79	3.53	1.76	5.30
20	2.74	0.69	3.80	1.30	5.11
22	3.08	1.16	4.24	2.00	6.24
24	2.94	0.66	3.59	1.28	4.87
25	1.65	0.84	2.49	1.34	3.83
26	2.01	1.39	3.40	1.17	4.57
28	3.43		3.43	2.70	6.21
30	2.65	0.94	3.59	1.76	5.34
31	3.47	0.08	3.55	3.20	6.75
Mean	2.74	0.74	3.51	1.84	5.35
Std. Dev.	0.60	0.47	0.46	0.71	0.92
pH 5.0 Treatment					
34	2.92	0.66	3.59	1.75	5.33
36	1.75	1.94	3.69	1.30	4.99
37	2.20	0.00	2.20	1.45	3.65
38	3.89	0.21	4.00	2.70	6.70
39	2.22	0.39	2.61	1.75	4.36
40	3.44	0.00	3.44	2.27	5.71
41	3.03	1.33	4.36	2.15	6.40
43	2.71	0.00	2.71	1.79	4.50
45	1.48	0.36	1.84	1.55	3.39
46	3.38	0.00	3.38	2.23	5.62
48	4.82	0.00	4.82	3.39	8.21
Mean	2.89	0.45	3.33	2.03	5.35
Std. Dev.	0.97	0.64	0.91	0.61	1.41

Appendix B 17, Con't. Effect of Treatment pH on Growth and Biomass of Greenhouse Red Spruce Seedlings: (E) Biomass Summary.

Sample	Σ Wood	Σ Needles	Σ Roots	ΣWood +ΣNeedles/ΣRoots
		(g. tissue)		
Treatment: pH 3.5				
2	13.00	5.90	5.51	3.44
3	13.10	8.50	4.14	5.22
4	16.40	6.28	8.87	2.56
5	5.69	3.54	2.88	3.20
6	14.65	7.71	6.42	3.48
7	10.32	8.31	3.81	4.89
8	6.85	4.32	3.33	3.35
10	10.19	7.25	9.87	1.77
11	11.94	9.44	5.05	4.23
14	7.79	6.01	2.88	4.79
Mean	11.00	6.78	5.28	3.69
Std. Dev.	3.48	1.98	2.45	1.09
Treatment: pH 4.1				
19	7.60	5.30	5.77	2.24
20	8.99	5.11	4.37	3.23
22	10.36	6.24	7.25	2.29
24	9.41	4.87	4.96	2.88
25	8.70	3.83	4.02	3.13
26	7.28	4.57	4.62	2.57
28	10.49	6.21	8.24	2.03
30	6.82	5.34	5.93	2.05
31	15.14	6.75	8.06	2.72
Mean	9.42	5.36	5.90	2.57
Std. Dev.	2.50	0.91	1.60	0.45
Treatment: pH 5.0				
34	9.77	5.33	7.00	2.16
36	7.76	5.00	3.79	3.36
37	9.30	3.65	4.64	2.79
38	12.04	6.70	7.81	2.40
39	4.54	4.36	5.01	1.78
40	11.22	5.71	6.51	2.60
41	10.55	6.50	6.01	2.84
43	11.27	4.50	5.50	2.87
45	6.89	3.39	3.26	3.15
46	1.64	5.62	5.83	2.96
48	11.69	8.21	8.80	2.26
Mean	9.70	5.36	5.83	2.65
Std. Dev.	2.39	1.42	0.66	0.47

Appendix B 18. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Red Spruce: Greenhouse Follow-up Study.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 3.5 Treatment							mg/Kg													(mol)
	11321	9360	42788	6906	190	9209	136	14.3	5.6	297	130	572	3.2	18.9	7.61	14.2	2.48	157	829	222
2	6718	5406	21287	4818	148	5895	135	13.1	4.3	98	99	568	1.8	11.9	6.08	7.24	1.51	103	405	145
3	4296	3263	19574	6114	110	5210	104	16.47	5	115	122	677	2.1	12.8	9.68	7.86	1.1	212	595	108
4	7993	6356	23979	5677	151	7557	149	16.19	5.3	173	141	436	2.3	14.1	9.02	10.2	1.26	161	474	115
5	7890	8376	23324	4925	160	8613	120	13.4	5.1	83	147	316	2.3	13.5	7.76	8.91	1.28	136	455	107
6	6732	7284	35582	5174	149	9487	178	15.63	5.5	450	143	441	3	15.5	9.43	10.5	1.71	252	947	168
7	5464	7504	33255	5257	126	5411	105	11.95	3.9	494	113	529	2	12.2	11.9	7.28	1.06	178	885	199
8	7188	8606	27788	4966	126	5811	127	12.52	4.3	316	146	398	2	12.6	10.2	7.4	1.39	188	567	128
Mean	7200	7019	28447	5480	145	7149	132	14.2	4.9	253	130	492	2.3	13.9	8.96	9.2	1.47	173	644	149
Std. Dev.	2070	1975	8074	720	25	1779	24	1.728	0.6	161	17.5	115	0.5	2.32	1.8	2.4	0.46	46	212	43.4
Std. Erro	732.7	699	2858	255	8.7	629.9	8.6	0.612	0.2	57	6.2	41	0.2	0.82	0.64	0.85	0.16	16	75	15.4
pH 4.1 Treatment																				
	6278	11016	27874	5524	121	7295	157	14.05	4.9	458	128	427	2.4	14.4	12.5	9.29	1.39	236	1020	147
2	6444	5677	23012	5389	142	5211	110	10.93	4.1	101	96	436	1.6	11.5	8.33	6.98	1.52	77	311	162
3	5604	8078	31994	3826	118	5441	120	14.99	3.6	504	131	269	2	10.8	9.83	8.02	1.34	134	694	165
4	5080	7458	19781	5055	127	7214	147	15.13	4.6	147	131	392	1.5	12.6	8.76	8.12	1.08	140	396	102
5	4779	6680	22571	4250	136	5846	82	15.61	5	310	121	380	1.1	11.8	5.8	5.78	0.89	128	275	126
6	4608	5096	29733	4835	115	6503	92	16.56	4.7	151	85	584	1.7	12.4	7.07	10.7	1.16	152	504	236
7	8221	11124	29231	5385	140	6585	167	19.04	4.8	342	184	237	2.7	12.9	8.17	11	1.48	307	1246	107
8	8006	10475	42958	4904	168	8585	174	18.91	5	441	186	281	2.6	15	12.5	12.5	1.73	234	1049	156
Mean	6128	8201	28394	4896	133	6585	131	15.65	4.6	307	133	376	1.9	12.7	9.12	9.05	1.32	176	687	150
Std. Dev.	1390	2406	7220	594	17	1112	35	2.632	0.5	157	36.4	113	0.6	1.41	2.4	2.25	0.27	75	375	42.3
Std. Erro	492.2	851.8	2556	210	6.1	393.5	12	0.932	0.2	56	12.9	40	0.2	0.5	0.85	0.8	0.1	27	133	15

Appendix B 18 con't. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Red Spruce: Greenhouse Follow-up Study.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 5.0 treatment							mg/Kg													(mol)
	5263	5125	32078	5164	132	4772	124	21.41	4.3		107	578	1.5	11.5	8.37	9.18	1.19	148	556	202
2	6229	9300	37093	4501	129	5832	144	21.76	4	617	146	577	2.3	12.4	11.8	9.59	1.21	251	845	171
3	5646	6702	16096	4507	187	7949	74	20.24	4.3	183	126	409	1.6	13.9	7.88	11.5	1.18	90	309	86.2
4	7125	9344	41759	4868	181	7817	152	25.96	4.6	429	138	364	2.5	14.9	8.14	12.2	1.51	221	913	204
5	6244	10988	30561	5260	142	11061	176	20.45	5.9	252	175	300	2.5	15	11	13.9	1.78	203	638	118
6	7922	7458	25196	7271	141	9179	98	22	6.6	436	113	529	2.3	17.8	12.6	10.8	1.59	252	668	151
7	7110	9916	27797	4433	128	5797	131	21.7	4.1	394	134	417	2.4	11.9	11.6	9.49	1.19	185	829	140
Mean	6506	8405	30083	5143	149	7487	128	21.93	4.8	385	134	453	2.2	13.9	10.2	11	1.38	193	680	153
Std. Dev.	929.4	2049	8311	995	25	2196	34	1.899	1	153	22.6	109	0.4	2.21	1.99	1.72	0.25	58	207	43.3
Std. Erro	329	725.4	2942	352	8.8	777.3	12	0.672	0.4	54	8.01	39	0.2	0.78	0.71	0.61	0.09	21	73.4	15.3
NBS Pine	4289	7913	13731	3586	543	2410	48	8.904	3.4	794		329	0.8	15.4	8.67	46.1	0.98	15	25.3	

Appendix B 19. Selected Parameters of Equilibrium Soil Solution of Rhizosphere of Spruce Grown on Field Plots in Great Smoky Mountains as Affected by Treatment pH.

	pH	DOM[1]	TMAl	NLMAl	LMAl	NLMAL/TMAl
				mg/L		
pH 3.5 Treatment						
	3.47	0.15	0.78	0.24	0.54	0.31
	3.53	0.12	0.96	0.27	0.69	0.28
	3.61	0.59	0.58			
	3.41	0.12	1.18	0.33	0.85	0.28
	3.58	0.34	0.68	0.41	0.27	0.60
	3.60	0.20	0.88	0.52	0.35	0.59
	3.43	0.09	0.73	0.45	0.28	0.62
	3.61	0.58	0.48			
	3.47	0.14	0.97	0.48	0.49	0.49
	3.55	0.22	1.52	0.83	0.69	0.55
Mean	3.53	0.26	0.88	0.44	0.52	0.47
s.e.[2]		0.06	0.10	0.07	0.08	0.05
pH 5.0 Treatment						
	3.34			0.85		
	3.43	0.37	1.23			
	3.55	0.33	0.93	0.45	0.48	0.48
	3.56		0.82	0.50	0.32	0.61
	3.44	0.11	1.57	0.33	1.24	0.21
	3.33	0.41	0.83	0.22	0.61	0.27
	3.62	0.18	0.79	0.33	0.46	0.42
	3.58	0.43	0.78	0.57	0.21	0.73
	3.52	0.58	0.43			
	3.48	0.36	0.70	0.07	0.63	0.10
Mean	3.49	0.35	0.90	0.42	0.56	0.40
s.e.		0.05	0.11	0.08	0.13	0.09

[1]Absorbance at 250 nm.
[2]standard error

Appendix B 20. Effects of Treatment pH on Concentrations of 1N KCl-Extractable Elements in Rhizosphere Soils of Red Spruce: Great Smoky Mountains Field Plots.

	Al	Ca	Cu	Fe	Mg	Mn
			(mg/67 g Soil)			
pH 3.5 Treatment						
	23.89	111	0.12	1.81	16.5	6.45
	46.3	19.3	0.06	3.51	4.51	0.73
	56.77	30.5	0.06	2.59	7.11	2.01
	62.26	16.3	0.06	3.5	5.17	0.73
	39.53	46.1	0.07	2.47	6.14	3.71
	44.83	57.2	0.15	2.24	8.59	3.25
	38.75	45.3	0.07	3.15	8.41	2.64
	46.28	26.4	0.07	2.49	5.26	1.97
	61.51	30.7	0.06	3.04	5.37	0.93
	34.08	58.3	0.06	3.03	9.17	1.66
	52.61	33	0.09	3.03	5.72	1.26
mean	46.05	44.7	0.08	2.84	7.67	2.34
std. error	3.93	8.61	0.01	0.17	1.1	0.56
pH 5.0 Treatment						
	61.2	11.1	0.08	2.65	3.42	0.68
	48.26	37.1	0.1	2.57	5.72	1.56
	70.47	18.8	0.06	3.01	4.93	1.06
	31.58	74.8	0.1	1.33	8.4	3.19
	31.23	112	0.11	1.83	10.1	4.77
	56.44	36.3	0.11	2.1	6.05	2.12
	40.36	78.2	0.06	2.82	9.39	2.54
	49.81	41.2	0.07	2.59	6.82	2.26
mean	46.64	55.5	0.09	2.44	7.28	2.63
std. error	4.79	11.5	0.01	0.19	0.83	0.59

Appendix B 21. Growth Parameters of Red Spruce Seedlings from Smoky Mountains Field Plots as Affected by Treatment pH 5.0

Sample	Δ Ht	Δ Diam	Δ Ht %	Δ Diam %
1	1.3	0.70	0.04	0.20
2	1.2	0.35	0.04	0.11
3	1.0	0.10	0.07	0.04
4	1.5	0.40	0.07	0.09
5	1.8	0.75	0.06	0.25
6	1.8	0.00	0.07	0.00
7	1.4	0.75	0.05	0.19
8	1.6	0.00	0.05	0.00
9	3.8	0.60	0.13	0.13
10	1.9	0.60	0.10	0.20
11	1.7	0.20	0.07	0.05
12	1.3	0.40	0.05	0.10
13	1.9	0.45	0.07	0.10
14	1.5	0.75	0.07	0.25
15	2.1	0.60	0.09	0.17
16				
17	1.9	0.00	0.07	0.00
18	1.6	0.00	0.06	0.00
19	2.0	0.00	0.11	0.00
20	2.1	0.40	0.07	0.10
21	2.0	0.50	0.07	0.09
A	2.8	0.65	0.10	0.17
B	2.3	0.20	0.10	0.04
C	1.5	0.55	0.05	0.13
D	2.4	0.50	0.10	0.17
E	2.5	0.20	0.09	0.05
F	2.0	0.25	0.07	0.07
G	2.2	0.00	0.10	0.00
H	2.2	0.10	0.06	0.02
Mean	1.90	0.43	0.08	0.13
Std.Dev.	0.56	0.23	0.01	0.01

Appendix B 22. Growth Parameters of Red Spruce Seedlings from Smoky Mountains Field Plots as Affected by Treatment pH 3.5

Sample	Δ Ht	Δ Diam	Δ Ht %	Δ Diam %
1	1.7		0.06	0.00
2	1.2	0.35	0.04	0.11
3	1.6	0.50	0.06	0.11
4	0.5	0.25	0.02	0.07
5	4.4	0.50	0.18	0.01
6	1.6	0.25	0.07	0.08
7	1.5	0.25	0.08	0.08
8	1.5	0.75	0.07	0.21
9	2.5	0.25	0.08	0.06
10	2.0	0.30	0.07	0.09
11	1.8	0.50	0.06	0.17
12	1.8	0.60	0.08	0.30
13	1.2	0.60	0.05	0.17
14	1.2	0.50	0.04	0.17
15	1.3	0.20	0.05	0.07
16	1.6	0.50	0.05	0.13
17	1.5	0.70	0.07	0.28
18	2.0	0.50	0.07	0.13
19	1.8	0.25	0.06	0.07
20	2.1	0.25	0.07	0.05
A				
B	1.1	0.25	0.04	0.08
C	1.0		0.03	
D	1.2	0.80	0.04	0.27
E	1.7	0.10	0.07	0.03
F	1.9	0.50	0.10	0.17
G	3.0	0.25	0.01	0.08
H	4.2	0.25	0.25	0.08
Mean	1.77	0.41	0.07	0.12
Std.Dev.	0.45	0.10	0.01	0.02

Table B 23. Biomass Parameters of Red Spruce Seedlings from Smoky Mountains Field Plots.

	Needles		Wood		Roots		Sum		
Sample	New	Old	New	Old	< 1mm	> 1mm	Needles	Wood	Roots
				(g of tissue)					
pH 3.5 Treatment									
1	1.40	2.23	0.25	3.28	0.39	1.51	3.63	3.53	2.00
3	1.29	1.64	0.31	3.22	0.35	1.25	2.93	3.23	1.60
5	1.39	1.49	0.28	2.76	0.36	1.06	2.88	3.04	1.43
9	0.94	1.01	0.18	2.11	0.40	1.02	1.95	2.29	1.42
10	0.43	0.66	0.10	2.16	0.19	0.76	1.09	2.26	0.96
11	0.35	0.60	0.07	1.10	0.15	0.40	0.95	1.17	0.55
14	0.50	0.78	0.10	1.81	0.14	0.53	1.38	1.91	0.67
16	0.76	0.95	0.14	2.71	0.19	0.96	1.71	2.85	1.15
17	0.32	0.49	0.07	1.09	0.10	0.32	0.81	1.16	0.42
19	0.43	0.73	0.01	2.05	0.19	0.57	1.16	2.15	0.76
20	1.75	1.55	0.42	4.34	0.42	1.57	3.30	4.76	1.99
A	0.81	0.74	0.19	2.16	0.21	1.24	1.55	2.35	1.45
B	0.35	0.40	0.05	1.09	0.08	0.27	0.75	1.14	0.35
C	0.23	0.40	0.04	0.97	0.03	0.23	0.63	1.01	0.26
F	0.19	0.40	0.03	0.75	0.11	0.24	0.57	0.57	0.35
H	0.66	0.46	1.53	0.84	0.19	0.45	1.12	1.12	0.64
Mean	0.74	0.86	0.16	1.87	0.22	0.77	1.65	2.16	1.00
Std.Dev.	0.49	0.54	0.11	0.87	0.13	0.46	1.00	1.12	0.59
pH 5.0 Treatment									
1	0.27	0.56	0.06	2.56	0.17	0.55	0.83	2.62	0.72
2	0.57	0.69	0.11	1.64	0.14	0.39	1.27	1.75	0.54
4	0.99	1.07	0.21	2.33	0.34	1.18	2.06	2.54	1.52
6	0.60	1.17	0.13	2.96	0.22	0.97	1.77	3.09	1.19
8	0.91	1.20	0.20	3.00	0.20	1.00	2.11	3.21	1.31
10	0.50	0.78	0.11	1.47	0.23	0.60	1.28	1.58	0.86
13	0.78	1.00	0.14	2.50	0.24	0.80	1.78	2.64	1.04
15	0.45	1.16	0.10	1.90	0.24	0.83	1.61	2.00	1.05
19	0.61	0.79	0.14	2.36	0.11	0.61	1.40	2.50	0.72
20	0.90	1.55	0.18	3.83	0.43	1.53	2.54	4.03	1.96
A	0.80	0.83	0.17	2.32	0.33	0.71	1.63	2.49	1.04
C	0.54	0.91	0.12	2.21	0.24	0.67	1.45	2.33	0.91
D	0.66	0.73	0.14	1.32	0.23	0.59	1.39	1.46	0.72
F	0.36	0.92	0.07	1.99	0.14	0.95	1.28	2.06	1.09
H	0.71	0.89	0.14	3.09	0.16	0.93	1.60	3.23	1.09
Mean	0.64	0.95	0.14	2.37	0.23	0.82	1.60	2.50	1.05
Std.Dev.	0.21	0.24	0.04	0.67	0.09	0.29	0.42	0.69	0.36

Appendix B 24. Effects of Treatment pH of Foliar Concentrations of Selected Elements in Tissues of Red Spruce: Spruce-Fir Field Plots.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 3.5 treatment											mg/Kg									
	8303	17299	880	3495	128	1282	65	19	2.19	2335	221	277	0.81	4.21	12	1.8	0.29	3.5	7.5	2.688
	10881	19475	5575	4108	127	3152	76	21	2.91	3189	185	274	10.9	5.89	14.5	2.66	0.87	4.75	8.8	20.34
	7778	17171	3673	3653	142	1979	52	21	2.38	2531	212	321	1	4.96	17.4	0.7	0.69	2.64	6.6	11.69
	7768	15569	3765	3342	116	1970	58	19	2.42	2910	238	142	0.99	4.57	11.1	0.94	0.4	3.12	7.7	10.68
	8002	18600	3245	3124	141	1233	47	16	2.04	1753	216	164	2.24	3.87	13.9	0.65	0.38	3.09	8.1	10.14
	7426	14528	6201	3096	125	2575	52	38	2.9	1786	192	305	1.88	5.22	10.4	1.17	0.85	9.38	27	21.8
		15320	4567	3267	174	1675	79	26	2.35	1405	228	335	7.59	4.41	12.9	2.07	0.6	4.89	13	13.52
	8792	15240	4806	3857	142	2383	75	22	2.98	1878	194	481	2.73	5.33	13.6	2.8	0.68	2.4	5.4	16.72
	11281	18857	3558	5689	184	1237	71	15	3.18	1542	175	818	1.66	6.52	19.7	1.88	0.84	2.7	6.4	13.72
	7903	14807	2934	2876	162	1110	56	16	3.25	1943	230	265	2.72	3.54	16.2	1.07	0.36	2.77	7.7	8.611
	8157	15950	6459	4085	146	2247	102	28	2.73	2177	286	197	1.31	5.11	13.8	1.58	0.59	4.36	8.9	15.24
	7183	13854	3668	3153	141	2402	63	17	2.24	2011	217	359	2.91	4.86	11.2	7.82	0.69	1.77	5.1	11.41
Mean	8498	16389	4111	3645	144	1937	66	22	2.63	2122	216	328	3.06	4.87	13.9	2.09	0.6	3.78	9.4	13.05
Std. Dev.	1349	1850	1541	756	20	644	15	6	0.41	538	29.4	179	3.05	0.83	2.75	1.94	0.2	2	6	5.173
Std. Error	404.7	536.6	446.9	219	5.9	187	4.4	2	0.12	156	8.53	51.9	0.88	0.24	0.8	0.56	0.06	0.58	1.7	1.5
pH 5.0 treatment																				
	9299	17305	6054	3036	135	3061	71	13	2.43	1553	168	467	1.35	5.14	10.6	7.62	0.68	6.04	18	24.32
	7376	17116	1500	2959	147	672	71	16	1.74	2593	254	171	0.67	3.07	10.8	0.47	0.36	0.88	3.2	3.986
	8912	14131	5145	3847	137	2840	82	14	2.79	1909	183	614	2.02	5.89	16.8	2.38	0.79	3.9	17	18.98
	10856	26000	4314	3826	156	2619	47	17	2.28	1126	236	179	2.09	4.72	11.3	0.23	0.6	1.88	4.5	12.34
	7479	12877	5994	2599	132	2791	70	15	2.42	1761	260	279	1.43	4.49	11.1	2.25	0.66	3.4	11	15.56
	9137	15222	9085	3832	192	5893	96	14	3.85	2462	206	435	1.61	7.85	14.5	2.79	0.97	11.5	44	29.77
	9442	17702	4979	4310	175	2704	85	12	3.29	3563	213	330	1.69	6.29	16.1	0.98	1.06	1.4	3	15.78
	9287	17448	4070	3648	125	1915	51	14	2.28	1773	191	404	1.1	4.43	13.2	0.98	0.57	2.81	4.7	14.38
	8166	12893	5885	3608	142	3307	78	16	3.1	5507	208	51.5	0.76	5.07	7.86	0.29	0.34	7.55	16	19.1
	8520	16941	3524	3179	160	1586	68	12	2.02	3240	259	127	1.13	4.06	10.1	0.55	0.46	1.69	5.2	9.184
	7943	15036	3100	3855	155	1505	73	15	2.36	1739	244	372	0.89	5.11	15.3	1.09	0.7	1.05	3.1	8.576
	8848	16284	2014	3024	151	1000	51	11	1.65	1890	244	313	1.84	4.66	25.7	3.93	0.44	1.24	3.1	5.572
Mean	8772	16580	4639	3477	151	2491	70	14	2.52	2426	222	312	1.38	5.07	13.6	1.96	0.64	3.61	11	15.63
Std. Dev.	964.5	3429	2052	504	19	1365	15	2	0.64	1199	31.5	161	0.48	1.21	4.67	2.12	0.23	3.24	12	7.57
Std. Error	279.7	994.3	595.1	146	5.5	396	4.4	1	0.19	348	9.14	46.7	0.14	0.35	1.35	0.61	0.07	0.94	3.5	2.195
NBS pine	4197	8934	14782	3579	414	2423	62	10	3.54	808	1510	1019	0.68	9.98	9.41	13.1	1.1	18.5	22	6.608

Appendix B 25. Effects of Treatment pH on Foliar Tissue Concentrations of Selected Elements in Fern: Spruce-Fir Forest Field Site.

	P	K	Fe	Mn	B	Cu	Mo	Na	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca	Mg	Al	Ca/Al
								mg/Kg												(mol)
pH 3.5 Treatment																				
	5039	12253	411	1940	199	35.19	4.23	1012	3167	1.48	7.93	8.96	15.9	1.5	114	463	23566	7071	877	18.1
	5815	13476	366	1940	230	42.06	4.75	880	4031	1.87	8.67	11.1	14.1	1.6	168	535	39964	7185	888	30.4
	3912	7575	442	3680	177	19.59	5.61	2660	596	1.84	7.97	10.7	16	4.4	50	292	12897	5991	3437	2.53
	4347	14122	799	5840	277	25.39	6.98	4466	1453	2.89	11.1	12	20.6	7.5	49	463	16585	7447	2608	4.29
	3650	11702	416	2000	265	32.2	4.51	698	3582	1.48	7.99	11.4	12.5	1.2	147	510	28298	7311	1518	12.6
	3693	7432	669	6060	172	18.29	6.85	1655	945	2.69	11	11.3	25.6	4.9	64	438	14470	6897	2138	4.57
	4699	13805	436	2260	227	38.12	4.94	666	3866	1.44	8.89	9.28	15.9				29592	8011	1102	18.1
	4772	12507	504	1860	225	35.95	4.67	1117	4119	1.72	8.43	9.71	16.4	1.5	173	588	33792	7169	1133	20.1
	5111	21844	487	5700	282	26.33	7.22	4430	1168	2.88	11.3	13	22.5	6.5	97	600	25053	7406	2603	6.5
Mean	4560	12746	503	3476	228	30.35	5.53	1954	2547	2.03	9.25	10.8	17.7	3.6	108	486	24913	7165	1811	13
Std. Dev.	726	4223	141	1879	41	8.347	1.18	1541	1472	0.61	1.45	1.32	4.26	2.5	51	98	9106	540	921	9.38
Std. Error	229	1334	45	594	13	2.638	0.37	487	465	0.19	0.46	0.42	1.35	0.8	16	31	2877	171	291	2.97
pH 5.0 Treatment																				
	3403	12313	377	7180	251	23.47	7.2	4895	1004	2.68	13	13.1	15.5	6	76	483	19453	9271	1346	9.76
	5372	10152	343	5180	170	23.73	6.23	3226	440	2.53	10.4	11.4	14.8	4.1	70	383	21268	8023	2251	6.38
	4293	17704	441	8240	317	25.26	7	5599	865	2.57	13	13.5	18.5	6.2	64	459	19905	8181	1142	11.8
	3208	12065	354	5960	218	24.61	6.12	4843	717	2.04	10.9	10.8	17.6	5.5	77	401	18271	7829	1400	8.81
	3508	7823	407	7560	236	20.19	7.78	3507	640	3.29	13.6	12.2	19.4	5.5	74	533	19123	9265	1727	7.47
	3822	8458	461	8340	278	21.17	6.62	4135	707	2.75	11.8	12.9	19.8	5.2	56	522	15508	6959	1809	5.79
	3195	6538	335	8180	214	19.34	6.78	2738	556	2.68	12.2	13.5	19	5.9	56	445	15586	7355	1163	9.05
	4378	12938	622	4860	308	24.84	6.56	5165	1371	2.79	9.75	11.7	23.4	5.1	70	390	16748	6640	3301	3.42
	5277	15036	649	5700	325	27.11	6.22	5618	1100	2.17	11.4	10.5	22.2	5.3	50	385	13718	7700	1605	5.77
Mean	4051	11448	443	6800	257	23.3	6.72	4414	822	2.61	11.8	12.2	18.9	5.4	66	445	17731	7914	1749	7.58
Std. Dev.	839	3592	117	1386	53	2.565	0.54	1058	293	0.36	1.29	1.14	2.78	0.6	9.9	59	2476	912	678	2.53
Std. Error	265	1135	37	438	17	0.811	0.17	334	92.6	0.11	0.41	0.36	0.88	0.2	3.1	19	782.4	288	214	0.8

Appendix B 26. Effects of Treatment pH on pH of Bulk and Rhizosphere Soil of Greenhouse Loblolly Pine Seedlings: Melton Branch Soil.

	Bulk Soil pH		Rhizosphere Soil pH	
Sample	H_2O	KCl	H_2O	KCl
pH 3.5 Treatment				
2	6.00	5.28	6.10	5.36
3	5.78	5.08	6.25	5.45
4	6.09	5.50	5.92	5.15
6	5.49	4.90	5.91	5.19
7	6.03	5.30	5.83	5.13
8	5.89	5.10	5.79	5.00
10	5.96	5.28	5.90	5.19
11	6.05	5.42	5.76	5.12
13	5.85	5.07	5.83	5.06
14	6.00	5.30	5.72	5.07
pH 4.1 Treatment				
16	6.10	5.38	6.02	5.28
17	6.10	5.34	5.96	5.17
18	5.96	5.23	5.77	5.05
19	•	•	5.90	5.20
20	6.32	5.63	5.94	5.23
22	5.90	5.18	5.98	5.22
24	5.97	5.23	5.98	5.30
25	6.18	5.47	•	•
26	•	•	•	•
28	5.97	5.26	5.81	5.22
pH 5.0 Treatment				
32	6.21	5.43	5.93	5.23
33	6.22	5.55	5.99	5.15
35	6.02	5.23	•	•
36	6.17	5.45	5.79	5.16
37	6.29	5.63	5.86	5.19
38	6.07	5.19	5.96	5.26
39	6.18	5.46	6.07	5.32
40	6.03	5.24	5.85	5.14
41	5.97	5.24	•	•
43	5.76	5.14	5.90	5.19
44	6.24	5.15	5.91	5.18

Appendix B 27. Effects of Treatment pH on pH of Bulk and Rhizosphere Soil of Greenhouse Loblolly Pine Seedlings: Walker Branch Soil.

	Bulk Soil pH		Rhizosphere Soil pH	
Sample	H_2O	KCl	H_2O	KCl
pH 3.5 Treatment				
1	5.53	4.89	5.64	4.80
3	5.53	4.77	5.56	4.73
4	5.89	5.18	5.39	4.92
7	5.06	4.30	5.37	4.64
8	5.68	5.01	5.70	4.93
9	•	•	5.44	4.94
10	5.78	5.17	•	•
12	5.66	5.32	5.54	4.90
13			5.54	4.87
14	5.73	4.86	5.57	4.74
pH 4.1 Treatment				
17	5.65	4.96	5.56	4.82
20	5.67	4.98	5.64	4.91
22	5.74	4.84	5.68	4.88
23	5.52	4.86	•	•
24	5.79	5.00	5.52	4.90
25	5.74	5.10	5.65	4.89
28	5.80	5.04	5.84	5.17
29	5.90	5.17	5.75	5.00
27	5.70	4.97	5.48	4.81
30	5.73	4.94	5.66	4.93
pH 5.0 Treatment				
31	5.93	5.07	5.76	5.10
32	6.10	5.44	5.71	4.91
35	5.87	4.96	5.72	4.97
36	5.83	5.08	5.69	4.96
38	5.54	4.90	5.68	4.85
40	6.11	5.29	5.63	4.92
41	5.89	5.12	5.64	4.99
43	5.61	5.05	5.42	4.87
44	5.57	4.88	5.97	5.12
45	5.96	5.29	•	•

Appendix B 28. Effects of Treatment pH on Concentrations (mg/67g Soil) of 1 N KCl-Extractable Elements: Pine Rhizosphere--Melton Branch Soil, Greenhouse Study.

	Bulk Soil						Rhizosphere Soil					
	Al	Ca	Cu	Fe	Mg	Mn	Al	Ca	Cu	Fe	Mg	Mn
pH 3.5 Treatment												
2	0.1	186	0.035	0.033	16.28	0.5	0.1	187	0.056	0.03	18.55	0.83
3	0.11	246	0.031	0.033	24.27	0.2	0.3	157	0.045	0.03	18.2	1.17
4							0.17	177	0.029	0.03	18.21	1.01
6	0.23	168	0.036	0.04	14.15	1.1	0.13	185	0.024	0.03	18.58	1.18
7	0.21	202	0.037	0.038	20.03	0.5	0.25	192	0.037	0.04	18.85	0.75
8							0.19	170	0.03	0.03	17.61	1.36
9	0.12	194	0.034	0.037	18.96	0.4						
10	0.13	202	0.029	0.037	22.66	0.4	0.12	191	0.034	0.03	21.21	0.58
11	0.23	237	0.048	0.039	21.56	0.3	0.12	187	0.046	0.03	19.79	1.02
13							0.22	181	0.035	0.04	17.69	0.79
14	0.22	205	0.039	0.04	21.35	0.4	0.24	93	0.055	0.04	10.27	0.24
10							0.2	187	0.026	0.03	20.27	1.12
9x	0.11	193	0.034	0.031	20.18	0.3						
13							0.21	182	0.039		19.14	0.84
2	0.27	232	0.039	0.042	22.92	0.2						
pH 4.1 Treatment												
16	0.1	203	0.025	0.029	19.7	0.3	0.04	3.64	0.036	0.01	0.43	0.01
17	0.11	199	0.028	0.032	18.56	0.4	0.18	177	0.041		17.57	1.17
18	0.21	171	0.03	0.035	17.91	0.8						
19	0.21	206	0.038	0.038	18.4	0.3						
20	0.12	225	0.032	0.037	22.38	0.4	0.25	186	0.042	0.06	20.84	0.61
22	0.21	206	0.039	0.034	19.67	0.3	0.11	182	0.028	0.03	17.9	0.74
24	0.22	188	0.055	0.037	18.74	0.3	0.12	197	0.024	0.03	20.76	0.61
25	0.27	207	0.063	0.042	20.36	0.3						
26	0.39	177	0.038	0.038	17.53	0.8	0.25	183	0.045	0.04	17.91	1.39
28	0.22	186	0.047	0.035	19.84	0.8	0.24	189	0.034	0.06	20.86	0.87
24	0.25	177	0.028	0.034	16.56	0.8						
pH 5.0 Treatment												
33							0.17	182	0.076	0.04	19.35	1.12
36	0.12	209	0.026	0.033	21.25	0.6	0.14	199	0.034	0.04	21.14	0.7
37	0.1	190	0.026	0.03	20.47	0.3	0.14	177	0.03	0.03	20.73	0.92
38	0.1	187	0.028	0.03	21.58	0.3	0.16	183	0.037	0.06	19.93	0.72
39	0.12	201	0.03	0.037	20.39	0.3	0.24	175	0.053	0.05	16.74	0.37
40	0.22	173	0.04	0.038	19.44	0.7	0.12	186	0.053	0.03	20.57	0.7
41	0.29	173	0.058	0.046	18.79	0.9	0.15	208	0.028	0.04	22.09	0.83
43	0.12	169	0.077	0.029	17.96	0.6						
44	0.12	207	0.064	0.031	23.34	0.4	0.14	164	0.026	0.03	19.18	0.97
45												

Appendix B 29. Effects of Treatment pH on Concentrations (mg/67g Soil) of 1 N KCl-Extractable Elements: Pine Rhizosphere--Walker Branch Soil, Greenhouse Study.

	Al	Ca	Cu	Mn		Al	Ca	Cu	Mn
Bulk Soil					Rhizosphere Soil				
pH 3.5 Treatment									
1	0.59	114	0.036	1.156		0.69	103	0.05	1.296
3	0.65	97	0.05	1.199	1	0.99	93	0.04	1.237
4	0.23	123	0.037	0.739	3	0.29	122	0.05	1.127
7	0.53	80	0.05	0.941	4	1	95	0.04	1.432
8	0.19	123	0.04	0.961	7	0.68	94	0.04	0.892
					8	0.49	122	0.04	1.153
10	0.1	133	0.057	0.408	9	0.67	97	0.04	0.937
12	0.41	108	0.046	0.565	12	0.49	108	0.05	1.289
13	0.19	111	0.047	0.701	13	1.32	90	0.05	1.666
14	0.28	126	0.041	0.857					
pH 4.1 Treatment									
17	0.3	107	0.035	0.802	17	0.58	91	0.04	0.893
20	0.2	144	0.035	0.947	20	0.41	106	0.04	1.336
22	0.25	90	0.042	0.934	22	0.5	102	0.05	0.953
24	0.38	102	0.036	0.825	24	0.6	103	0.04	1.039
25	0.3	121	0.062	1.028	25	0.57	102	0.04	1.119
27	0.39	99	0.034	0.753	27	0.54	104	0.05	0.954
					28	0.24	124	0.04	1.057
29	0.13	99	0.035	0.654	29	0.41	108	0.05	1.289
					29	0.26	107	0.05	0.841
30	0.34	94	0.037	0.688	30	0.29	114	0.05	1.04
pH 5.0 Treatment									
31	0.16	119	0.036	0.518	31	0.54	101	0.04	0.801
32	0.13	117	0.046	0.716	32	0.49	101	0.04	0.95
35	0.13	117	0.033	0.651	35	0.38	98	0.04	0.807
36	0.35	111	0.044	0.639	36	0.5	106	0.05	1.125
38	0.46	105	0.041	1.11	38	0.39	90	0.06	1.151
40	0.2	85	0.047	0.429	40	0.57	88	0.04	1.014
41	0.29	109	0.039	0.812	41	0.37	113	0.05	1.016
41	0.28	94	0.033	0.632					
43	0.16	101	0.066	1.199	43	0.56	113	0.04	0.95
44	0.48	93	0.039	0.79	44	0.35	107	0.05	0.786
45	0.16	124	0.037	0.692					
40	0.22	100	0.036	0.784	17	0.18	177	0.04	1.165
28	0.34	105	0.039	1.082	13	0.21	182	0.04	0.834
23	0.31	117	0.041	1.112					
10	0.22	145	0.043	0.822					

Appendix B 30. Soil Solution Parameters of Greenhouse Grown Loblolly Pine Seedlings as Affected by Treatment pH: Melton Branch Soil--Bulk Soil.

	TMAl	NLMAl	DOM	pH
	-------mg/L------			
pH 3.5 Treatment	0.043	0.033	0.022	5.77
	0.053	0.045	0.038	6.02
	0.113	0.065	0.027	5.30
	0.042	0.035	0.017	5.03
	0.050	0.047	0.024	5.37
	0.046	0.050	0.020	5.71
	0.053	0.038	0.020	5.39
	0.063	0.046	0.041	5.56
	0.133	0.075	0.057	4.86
	0.063	0.042	0.032	5.48
Mean	0.066	0.048	0.030	
s.e.[1]	0.010	0.004	0.004	
pH 4.1 Treatment	0.070	0.073	0.083	6.12
	0.068	0.067	0.049	6.23
	0.060	0.053	0.036	5.51
	0.047	0.039	0.034	6.61
	0.048	0.050	0.062	6.41
	0.044	0.043	0.029	5.92
	0.068	0.055	0.028	•
	0.040	0.043	0.049	6.70
	0.053	0.043	0.021	5.12
	0.053	0.055	0.036	6.01
Mean	0.055	0.052	0.043	
s.e.	0.003	0.003	0.006	
pH 5.0 Treatment	0.058	0.059	0.040	6.31
	0.050	0.060	0.117	6.75
	0.058	0.053	0.052	5.81
	0.040	0.045	0.037	5.82
	0.073	0.075	0.047	6.45
	0.035	0.043	0.050	6.74
	0.055	0.068	0.052	6.00
	0.036	0.039	0.032	6.48
	0.098	0.038	0.022	5.06
	0.133	0.125	0.106	5.60
Mean	0.064	0.061	0.055	
s.e.	0.031	0.008	0.010	

[1]standard error

Appendix B 31. Soil Solution Parameters of Greenhouse Grown Loblolly Pine Seedlings as Affected by Treatment pH: Melton Branch Soil--Rhizosphere Soil.

	TMAl	NLMAl	DOM	pH
	-------mg/L------			
pH 3.5 Treatment	0.090	0.003		6.36
	0.121	0.100	0.038	6.00
	0.098	0.110	0.029	5.75
	0.185	0.113	0.037	5.44
	0.150	0.123	0.033	5.53
	0.098	0.089	0.049	6.05
	•	0.093	0.042	4.50
	0.061	0.050	•	5.02
	0.113	0.080	0.045	5.79
	0.1 00	0.093	0.042	5.18
Mean	0.114	0.092	0.049	
s.e.[1]	0.012	0.007	0.002	
pH 4.1 Treatment	0.075	0.080	0.035	6.16
	0.330	0.113	0.061	6.25
	0.085	0.070	0.028	6.43
	0.075	0.058	0.070	6.00
	0.060	0.053	0.031	6.53
	0.126	0.114	0.085	5.95
	0.228	0.210	0.046	5.75
	•	•	•	6.37
	0.127	0.100	0.082	6.26
	0.168	0.053	0.113	5.89
Mean	0.142	0.092	0.061	
s.e.	0.030	0.017	0.010	
pH 5.0Treatment	0.188	0.123	0.060	6.16
	0.125	0.105	0.086	6.25
	0.053	0.043	0.025	6.43
	0.150	0.108	0.041	6.00
	0.118	0.088	0.045	6.53
	0.188	0.148	0.058	5.95
	0.133	0.078	0.042	5.75
	0.083	0.060	0.033	6.37
	0.070	0.065	0.064	6.26
	0.198	0.113	0.033	5.89
Mean	0.131	0.093	0.049	
s.e.	0.016	0.010	0.006	

[1]standard error

Appendix B 32. Soil Solution Parameters of Greenhouse Grown Loblolly Pine Seedlings as Affected by Treatment pH: Walker Branch Soil--Rhizosphere Soil.

	TMAI	NLMAI
	-------mg/L------	
pH 3.5 Treatment		
	0.75	0.40
	0.75	0.42
	0.49	
	0.49	0.26
	0.44	0.15
	0.72	0.40
	0.58	0.41
	0.49	0.31
pH 4.1 Treatment		
	0.36	0.22
	0.45	0.38
	0.39	0.28
	0.61	0.30
	0.43	0.30
	0.48	0.44
	0.71	0.57
	0.24	0.18
	0.49	0.40
pH 5.0 Treatment		
	0.49	0.38
	0.43	0.67
	0.30	0.16
	0.29	0.19
	0.39	0.31
	0.43	0.35

Appendix B 33. Soil Solution Parameters of Greenhouse Grown Loblolly Pine Seedlings as Affected by Treatment pH: Walker Branch Soil--Bulk Soil.

	TMAI	NLMAI
	-------mg/L------	
pH 3.5 Treatment		
	0.52	0.37
		0.46
	0.46	0.32
	0.21	0.17
	0.20	0.12
	0.15	0.13
	0.40	0.36
	0.39	0.36
	0.39	
	0.31	0.15
pH 4.1 Treatment		
	0.23	0.14
	0.41	0.30
	0.38	0.24
	0.34	0.20
	0.28	0.22
	0.28	0.21
	0.30	0.18
	0.24	0.25
	0.18	0.16
	0.17	0.14
pH 5.0 Treatment		
	0.49	0.20
	0.38	0.29
	0.20	0.22
	0.15	0.20
	0.27	0.21
	0.22	0.17
	0.20	0.16
	0.41	0.29

Appendix B 34. Effects of Treatment pH on Growth and Biomass Parameters of Loblolly Pine: Greenhouse--Melton Branch Soil.

	ΔHt	ΔHt/Htin	ΔD	ΔD/Din	Old Wood	Old Needles	New Wood	New Needles	Large Roots	Fine Roots
	cm		cm		g	g	g	g	g	g
pH 3.5	34.6	0.53	0.4	0.5	22.59	1.9	5.07	19	9.83	6.33
Treatment	32.5	0.56	0.6	0.75	24.61		7.76	25.07		
	22.5	0.45	0.3	0.34	16.24	1.17	2.99	13.57	14.46*	
	28.7	0.53	0.5	0.88	18.25	0.61	5.2	26.52	16.60*	
	28.3	0.51	0.4	0.44						
	30.6	0.57	0.5	0.81	18.55	0.38	6.05	23.12	16.37*	
	24.3	0.46	0.4	0.63	17.9	0.36	5.46	24.61		
	36.7	0.66	0.5	0.82	19.78	0.05	4.56	24.96	15.63*	
	37.5	0.8	0.4	0.58						
	31.1	0.5	0.5	0.63	20.52	0.33	7.37	24.22		
	38.3	0.77	0.6	1	16.4	0.28	7.36	20.15	10.96	4.11
	42.9	0.74	0.5	0.63	23.05	0.11	7.23	17.39		
	21.5	0.51	0.3	0.6	7.91		2.28	8.73	4.94	0.9
	28.3	0.76	0.4	0.58	9.47		5.48	17.81	11.9	1.48
	32	0.5	0.5	0.68	22.95		5.76	24.45		
pH 4.1	34.8	0.72	0.5	0.79	19.47	0.8	7.68	24.77		
Treatment	43.1	1.09	0.6	0.62	9.59	1.7	1.59	13.9	9.8	2.02
	42.9	0.79	0.6	0.71	23.36		9.11	18.85		
	46.2	0.5	0.6	0.79	16.5	0.36	6.71	24.84	20.97*	
	31.6	0.54	0.4	0.44	21.3	0.03	7.02	17.5	11.49	2.95
	49.3	0.95	0.4	0.44						
	17	0.37	0.3	0.64	9.11		2.04	14.77		
	33.5	0.6	0.4	0.48	18.21	1.88	7	21.34	15.86*	
	38.2	0.72	0.4	0.37	21.51	1.25	11.76	25.17		
	28.4	0.51	0.4	0.54	16	0.69	6.29	19.41	14.06*	
	26.4	0.67	0.3	0.48	11.57	0.67	4.41	17.52	15.63*	
	23.5	0.47	0.5	0.63	19.58		5.6	22.84	19.42*	
	33.4	0.56	0.6	0.72	26.16	0.34	7.3	24.39	25.76*	
	29.8	0.56	0.6	0.77	23.77	1.5			25.49*	
	32.1	0.5	0.6	0.69	23.67	0.91	4.85	19.28	19.67*	

in=initial

*Large + Fine Roots

Appendix B 34, Con't. Effects of Treatment pH on Growth and Biomass Parameters of Loblolly Pine: Greenhouse--Melton Branch Soil.

	ΔHt cm	ΔHt/Ht in	ΔD cm	ΔD/D in	Old Wood g	Old Needles g	New Wood g	New Needle: g	Large Roots g	Fine Roots g
pH 5.0	31	0.61	0.4	0.54	18.04	0.08	6.28	19.76	19.40*	
Treatment	37	0.7	0.5	0.61	17.69	0.26	5.87	19.47	21.43*	
	15.5	0.25	0.7	0.96	23.76	0.15	4.27	15.78	22.32*	
	19.3	41	0.5	0.66	18.25	1.01	4.9	20.63	17.24	3.6
	23	0.43	0.6	1.09	16.79	0.5	4.39	12.2	16.88*	
	15.1	0.33	0.5	0.6	14.46	0.16	6.11	17.93		
	28.2	0.49	0.5	0.64	21.89	0.18	5.83	15.6	14.93*	
	9.2	0.2	0.4	0.57	12.39	0.23	2.27	12.26	13.14*	
	28.4	0.58	0.5	0.71	18.81	0.21	5.57	16.45	17.13*	
	19.5	0.34	0.5	0.63	21.14	0.48	5.31	21.02		
	19.1	0.34	0.5	0.7	20.76	1.25	6.12	12.1	10.82	3.37
	21.7	0.48	0.4	0.68						
	21.7	0.39	0.4	0.61	16.49	0.01	3.91	15.67	16.93*	
	25	0.5	0.5	0.67	17.7		4.6	17.58		

*Large + Fine Roots

Appendix B 35. Effects of Treatment pH on Growth and Biomass Parameters of Loblolly Pine: Greenhouse--Walker Branch Soil.

	ΔHt cm	ΔHt/Ht in	ΔD cm	ΔD/D in	Old Wood g	Old Needles g	New Wood g	New Needle g	Large Roots g	Fine Roots g
pH 3.5	41.2	0.79	0.55	0.76	21.34	0.03	7	23.08	26.83*	
Treatment	23	0.49	0.48	0.73	14.07	0.1	3.65	16.35		
	31.4	0.74	0.45	0.86	13.98	1.21	4.54	18.55	13.90*	
	33.8	0.68	0.5	0.71	20.82	1.76	6.11	22.49	17.40*	
	34	0.65	0.46	0.66						
	34.7	0.72	0.44	0.56	22.49	0.22	8.13	22.94	22.57*	
	32.6	0.75	0.48	0.86	13.9		4.97	16.63	17.70*	
	35.7	0.69	0.4	0.57	16.81	0.55	5.74	20.42	14.68	3.57
	30.5	0.57	0.46	0.66						
	19.8	0.4	0.35	0.4	16.39	0.67	5.25	16.52		
	29.2	0.51	0.5	0.63	24.44	0.24	8.31	17.39	11.95	3.46
	43.4	0.75	0.38	0.43	24.73	0.14	7.59	23.23	11.2	5.52
	42	1.1	0.56	0.93	16.27	0.1	9.42	26.98	11.61	4.37
pH 4.1	22.3	0.59	0.45	0.64	12.13		5.2	13.18	10.61	2.77
Treatment	18.6	0.36	0.48	0.58	20.74	0.19	6.56	27.38	26.93*	
	33.6	0.89	0.4	0.64	11.31	0.25	5.25	17.01	17.61*	
	41	0.5	0.45	0.69	15.65		6.91	21.71	14.70*	
	32.2	0.62	0.53	0.75	19.58	0.13	12.42	28.61	12.9	4.21
	229.5	0.73	0.55	0.69						
	20.1	0.44	0.45	0.69	16.98	1.25	5.92	23.89	10.95	4.26
	33.5	0.8	0.65	1.08						
	42.4	0.95	0.48	0.79	19.06	0.43	7.65	28.8	11.11	5.77
	33	0.73	0.5	0.83	20.11	0.11	7.9	24.94	12.82	6.2
	44.9	1.01	0.51	0.68	16.21	0.14	9.97	19.93		
	41.7	0.93	0.56	0.86	18.64		8.47	22.06	14.52	4.04
	34.5	0.63	0.48	0.66	20.4	2.65	5.38	19.8	17.36*	
	27.8	0.46	0.54	0.74	25.13	3.25	5.28	27.08	15.57	4.97
	38.5	0.66	0.52	0.66	23.1	0.29	7.14	23.35	12.46	3.62

in=initial

*Large + Fine Roots

Appendix B 35, Con't. Effects of Treatment pH on Growth and Biomass Parameters of Loblolly Pine: Greenhouse--Walker Branch Soil.

	ΔHt cm	ΔHt/Ht in	ΔD cm	ΔD/D in	Old Wood g	Old Needles g	New Wood g	New Needle g	Large Roots g	Fine Roots g
pH 5.0	26	0.55	0.39	0.56	16.98	0.1	5.61	17.81	18.56	4.79
Treatment	35.7	0.7	0.7	1	24.77		9.78	23.12	14.76	4.6
	17.5	0.69	0.43	0.62						
	11	0.24	0.33	0.54	11.43		3.18	9.21		
	17.6	0.31	0.43	0.5	21.23	0.41	3.82	14.07	22.90*	
	22.3	0.5	0.55	0.92	17.3	0.04	4.96	17.73	11.75	3.87
	32	0.68	0.52	0.71	16.39	0.22	6.03	16	14.28*	
	29.9	0.67	0.49	0.75	17.35	0.17	5.41	15.9	13.62	4.19
	7.7	0.14	0.55	0.79	21.06	0.12	3.06	13		
	13.8	0.23	0.43	0.59	14.44	0.75	3.58	16.33	16.5	3.85
	12	0.31	0.5	0.83						
	26.4	0.47	0.48	0.68	19		5.86	17.39		
	19.3	0.38	0.46	0.66	15.7	0.1	3.3	11.01	26.70*	
	22.7	0.5	0.63	1.04	20.09	0.02	6.35	16.62	15.35	3.85
	23.4	0.42	0.45	0.6	18.83	0.23	5.5	15.51	27.43*	

in=initial

*Large + Fine Roots

Appendix B 36. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Greenhouse Loblolly Pine Seedlings: Hapludult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Cd	Sr	Ba	Ca/Al
										mg/Kg									(mol)
Treatment pH 3.5																			
	3414	6323	10141	4498	86	1325	109	10.83	2.66	655	90	1318	0.11	5.79	18.43	0.72	17.9	21.2	76.28
	4105	9531	10469	5453	80	1339	142	15.65	3.49	670	178	1540	0.35	6.37	46.78	0.9	19.6	18.4	39.6
	3182	5971	10191	4791	75	894	113	11.06	3.52	502	121	485	0.84	6.12	10.07	0.82	14.1	17.3	56.78
	2932	4435	9335	3869	76	1186	112	9.869	2.8	245	62	938	0.85	5.41	26.58	0.69	14.9	19.3	101.9
	4111	10800	8012	4895	84	917	111	9.814	2.74	240	60	917	0.83	5.29	25.96	0.67	14.5	18.8	89.53
	3235	7048	8163	4295	75	740	84	9.628	2.82	915	79	592	0.83	5.5	23.4	0.78	14.7	17.8	70.06
	3333	8006	10454	4928	71	1147	167	8.896	3.58	1863	68	322	0.78	6.45	11.85	0.79	14.7	16.2	103.5
	3604	7914	11936	6059	82	1233	224	9.984	4.36	469	71	543	0.99	7.01	19.82	0.82	15.2	15.7	114.2
	3770	7629	8600	5419	89	827	151	11.25	3.7	338	94	578	1.16	6.7	57.57	0.85	15.1	18.9	61.51
	4146	8132	18543	5233	91	1748	229	14.64	3.11	346	69	1076	0.11	5.96	16.69	0.73	31.5	40	181
Mean	3583	7579	10584	4944	81	1136	144	11.16	3.28	624	89	831	0.68	6.06	25.72	0.78	17.2	20.4	89.43
S. D.	435	1799	3046	634	6.6	302	50	2.231	0.55	484	36	394	0.36	0.58	15.17	0.07	5.31	7.06	39.76
S. E.	137	568.5	962.5	200	2.1	95.4	16	0.705	0.17	153	11	125	0.11	0.18	4.794	0.02	1.68	2.23	12.56
Treatment pH 4.1																			
	3378	6008	14013	5610	91	1050	104	8.489	4.2	849	99	625	0.84	7.23	9.079	0.9	21.4	28.8	95.56
	3522	4898	10809	3068	84	846	106	12.18	2.27	225	147	433	0.33	4.98	19.37	0.69	20	26.4	49.54
	3017	9491	8237	4708	78	889	121	7.562	3.06	1493	49	447	0.86	6.24	15.02	0.79	8.2	7.55	114.2
	3516	6596	8611	5086	84	1010	97	10.77	3.82	461	74	438	0.83	6.44	32.76	0.69	15.2	20.4	78.29
	4573	9299	6457	5693	102	1293	131	10.73	4.35	907	170	704	1.05	7.05	23.85	0.93	8.98	11.2	25.57
	2631	5191	12029	4279	75	1009	123	6.554	3.78	325	46	979	1.08	6.29	14.98	1	19.5	25.8	175.5
	3053	7853	7513	4526	89	741	97	8.616	3.61	492	54	398	0.96	6.48	25.34	1	10.6	13.7	93.44
	3861	8179	9328	5164	81	970	109	13.34	3.82	719	124	755	1.22	6.95	64.55	0.93	14.9	17.2	50.8
	3337	5654	7544	3207	88	842	73	12.29	2.64	241	107	1280	0.57	5.62	21.83	0.58	10.1	11.9	47.75
Mean	3432	7019	9393	4593	86	961	107	10.06	3.51	635	97	673	0.86	6.36	25.2	0.83	14.3	18.1	81.18
S. D.	556	1741	2445	947	8.1	159	17	2.352	0.7	408	45	299	0.27	0.71	16.28	0.15	5.12	7.63	45.4
S. E.	185	579.8	814.2	315	2.7	52.9	5.8	0.783	0.23	136	15	99.6	0.09	0.24	5.421	0.05	1.7	2.54	15.12

Appendix B 36, con't. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Greenhouse Loblolly Pine Seedlings Hapludult.

Treatment pH 5.0

	4214	8644	11288	6173	1061	1147	156	16.01	4.59	840	111	1391	1.18	8.02	60.31	1.01	22.9	30.2	68.42
	4144	11512	6717	5229	98	1746	201	14.35	3.98	1954	166	1358	1.12	7.58	17.72	0.86	7.77	7.02	27.26
	4278	12628	7050	4111	104	950	111	17.85	2.94	1613	343	1338	0.79	5.79	40.54	0.69	6.82	8.57	13.87
	3556	9497	15212	5970	102	1874	249	12.57	3.49	1099	94	1705	0.42	7.85	34.72	1.02	37.5	53.1	108.9
	4121	7588	11709	5418	115	1393	134	17.58	3.94	739	135	428	0.45	7.15	18.89	0.9	20.6	23.8	58.45
	3720	10101	10373	4565	99	1186	102	12.41	3.45	1799	142	1450	1.13	6.68	22.87	6.5	19.6	23.5	49.3
	3906	9281	7521	6625	80	1110	114	13.18	4.47	1608	164	1066	0.96	7.74	26.01	1.15	12.2	13.2	30.96
	4320	7887	11083	6283	82	1243	124	16.3	4.45	722	211	1469	1.12	8.23	36	1.16	22.7	30.3	35.47
Mean	4032	9642	10119	5547	98	1331	149	15.03	3.91	1297	171	1276	0.9	7.38	32.13	1.66	18.8	23.7	49.08
S. D.	277	1735	2893	880	12	322	51	2.197	0.59	503	78	385	0.31	0.81	14.1	1.96	9.95	15	29.92
S. E.	98.1	614.2	1024	311	4.2	114	18	0.778	0.21	178	28	136	0.11	0.29	4.991	0.69	3.52	5.3	10.59

Appendix B 37. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Greenhouse Loblolly Pine Seedlings: Paleudult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 3.5 treatment									mg/Kg										(mol)
	1923	3258	11985	4232	63	1338	92.7	9.109	2.87	92.8	2015	0.61	6.6	8.545	3.77	0.7	33	29	87.18
	2595	5330	9136	4385	76.2	2652	139	8.777	3.41	531	1639	0.96	7.2	19.22	4.92	1.07	24	21	11.61
	2820	5437	10907	5433	93.1	1949	146	10.69	3.49	166	2025	1.14	7.8	7.882	4.92	0.79	25	21	44.31
	2687	6689	10983	5150	83.4	1742	77.5	15.69	3.45	281	1659	1.33	7.4	21.78	5.57	1.11	30	25	26.39
	2781	5937	11264	4417	98.9	2532	173	10.7	3.55	242	2368	1	8.2	9.577	6.1	1.17	24	20	31.36
	3205	7900	9367	5633	105	2444	172	11.98	4.17	408	2146	1	8.4	11.71	5.68	0.97	21	14	15.51
	3089	5197	5353	3219	92.2	1207	80.3	11.59	2.19	217	1064	0.44	5.6	7.859	3.69	0.5	6.5	3.2	16.63
	2785	6191	10347	5090	86.6	2203	126	10.38	3.64	231	1450	1.05	7.7	8.347	5.46	1.05	23	15	30.17
	2507	3914	11802	4399	76.6	2676	128	8.372	3.29	303	2088	1.28	7.7	19.35	5.08	0.87	25	21	26.27
Mean	2710	5539	10127	4662	86.1	2083	126	10.81	3.34	275	1828	0.98	7.4	12.7	5.02	0.91	24	19	32.16
S. D.	369	1392	2040	744.3	12.9	556.7	36.1	2.208	0.55	130	407	0.29	0.9	5.733	0.83	0.22	7.4	7.5	22.88
S. E.	123	464	679.4	247.9	4.3	185.4	12	0.735	0.183	43.29	136	0.1	0.3	1.909	0.28	0.07	2.46	2.5	7.619
pH 4.1 treatment																			
	2106	5409	12455	4262	84.5	1536	95	8.9	3.06	96.8	2025	0.83	7.6	6.986	5.39	0.8	31	29	86.85
	2607	4968	9814	4664	82.8	1725	122	10.8	3.19	201	1770	0.83	7.4	7.616	7.02	1.02	25	21	32.92
	2449	6050	11623	4805	87.6	2910	201	9.768	4.1	230	2716	1.11	8.3	8.905	6.1	1.41	41	34	34.1
	2270	4465	9726	4137	73.9	1388	105	9.103	2.62	254	1893	0.5	6.4	5.662	3.56	0.63	28	32	25.84
	2315	4365	10891	4229	86.7	2032	87.2	9.255	3.52	308	2310	0.99	7	7.641	5.9	1.23	31	31	23.9
	2249	5131	8352	4804	74.3	1629	97.1	9.003	3.27	101	2223	0.83	7.3	6.846	4.57	0.85	12	8.9	55.56
	2724	4829	11811	4526	89.8	2303	214	10.03	3.19	102	1759	0.58	7.4	6.027	4.81	0.89	16	11	78.45
	2685	6332	7995	4446	108	1803	147	10.45	3.17	204	2373	0.7	7	8.005	4.85	0.79	15	13	26.44
	2187	6061	8138	3881	82.2	1462	169	8.245	2.49	89.6	2136	0.69	6.7	7.531	5.02	0.63	12	8.6	61.28
Mean	2399	5290	10089	4417	85.6	1865	138	9.505	3.18	176	2134	0.79	7.2	7.247	5.25	0.92	23	21	47.26
S. D.	226	720	1695	316	10.2	486	47.7	0.817	0.47	81.1	312	0.19	0.6	0.995	1	0.26	10	11	24.04
S. E.	75.3	240	564.3	105.2	3.4	161.8	15.9	0.272	0.157	27.01	104	0.06	0.2	0.331	0.33	0.09	3.33	3.66	8.005

Appendix B 37, con't. Effects of treatment pH on foliar concentrations of selected elements in greenhouse treated loblolly pine seedlings. Paleudult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 5.0 treatment									mg/Kg										(mol)
	2542	6711	9322	4377	68.6	1236	87.2	9.161	2.92	104	1795	0.82	6.6	12	5.22	0.87	26	19	60.8
	2604	5548	9489	5370	98.2	2337	104	10 27	3.74	298	2548	0.77	8.9	8.28	5.61	1.11	26	25	21.47
	2980	6538	10601	5718	92.4	1846	167	11.24	4.16	189	2082	1.13	9.5	7.9	6.32	1.04	28	20	37.82
	2517	4888	11984	5520	91.8	1887	118	11.57	3.37	102	2337		9.2	7.82	6.02	1.16	34	31	79.3
	2192	3046	18997	5155	102	2964	183	10.39	5.33	163	2105	1.04	9.1	6.53	·5.8	0.89	48	53	78.43
	3499	6922	13066	5873	151	2667	159	12.97	4.58	636	2686	1.37	9.6	18.3	7.69	1.56	33	31	13.87
	3375	8236	11005	5738	134	2956	192	12.96	4.59	521	2404	1.81	9.6	20.2	7.68	1.75	32	25	14.26
	3211	5164	12651	4877	102	2773	186	11.76	3.56	167	2311	0.91	8.8	7.44	5.25	0.95	35	35	51.15
	3745	6909	19059	5565	118	3366	309	12.62	4.41	337	2806	1.03	9.9	8.08	6.59	1.37	68	69	38.19
Mean	2963	5996	12908	5355	106	2448	167	11.44	4.07	280	2342	1.11	9	10.7	6.24	1.19	37	34	43.92
S. D.	528	1514	3697	480.1	24.6	678.4	65.4	1.316	0.74	189	317	0.34	1	5.07	0.93	0.31	13	16	25.34
S. E.	176	504	1231	159.9	8.19	225.9	21.8	0.438	0.246	62.94	106	0.11	0.3	1.69	0.31	0.1	4.33	5.33	8.438
NBS	4379	9929	14886	3802	460	2464	68.6	11.53	3.66	1508	1187	0.6	12		42.3	1	16	22	6.662

Appendix B 38. Effects of Treatment pH on Foliar Content of Selected Elements in Greenhouse Loblolly Pine Seedlings: Hapludult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Cd	Sr	Ba
pH 3.5 Treatment										mg/plant								
	86	159	254	113	2.16	33	2.73	0.27	0.067	16.4	2.26	33.04	0.003	0.145	0.46	0.018	0.45	0.531
	56	129	142	74	1.09	18	1.93	0.21	0.047	9.09	2.42	20.9	0.005	0.086	0.64	0.012	0.27	0.249
	84	158	270	127	1.99	24	3	0.29	0.093	13.3	3.21	12.86	0.022	0.162	0.27	0.022	0.37	0.46
	68	103	216	89	1.76	27	2.59	0.23	0.065	5.66	1.43	21.69	0.02	0.125	0.62	0.016	0.34	0.446
	101	266	197	120	2.07	23	2.73	0.24	0.067	5.91	1.48	22.57	0.02	0.13	0.64	0.016	0.36	0.463
	81	176	204	107	1.87	18	2.08	0.24	0.07	22.8	1.97	14.78	0.021	0.137	0.58	0.019	0.37	0.444
	81	194	253	119	1.72	28	4.04	0.22	0.087	45.1	1.65	7.799	0.019	0.156	0.29	0.019	0.36	0.393
	73	160	241	122	1.65	25	4.51	0.2	0.088	9.45	1.43	10.94	0.02	0.141	0.4	0.017	0.31	0.317
	33	67	75.1	47	0.78	7.2	1.32	0.1	0.032	2.95	0.82	5.046	0.01	0.058	0.5	0.007	0.13	0.165
	74	145	330	93	1.62	31	4.08	0.26	0.055	6.16	1.23	19.16	0.002	0.106	0.3	0.013	0.56	0.712
Mean	74	156	218	101	1.67	23	2.9	0.23	0.067	13.7	1.79	16.88	0.014	0.125	0.47	0.016	0.35	0.418
Std. Dev.	19	53	70.9	25	0.43	7.5	1.03	0.05	0.019	12.5	0.69	8.276	0.008	0.032	0.15	0.004	0.11	0.152
pH 4.1 Treatment																		
	84	149	347	139	2.25	26	2.58	0.21	0.104	21	2.45	15.48	0.021	0.179	0.23	0.022	0.53	0.713
	49	68	150	43	1.17	12	1.47	0.17	0.032	3.13	2.04	6.019	0.005	0.069	0.27	0.01	0.28	0.368
	57	179	155	89	1.47	17	2.28	0.14	0.058	28.1	0.92	8.426	0.016	0.118	0.28	0.015	0.15	0.142
	87	164	214	126	2.09	25	2.4	0.27	0.095	11.5	1.84	10.88	0.021	0.16	0.81	0.017	0.38	0.508
	68	137	95.4	84	1.51	19	1.93	0.16	0.064	13.4	2.51	10.4	0.016	0.104	0.35	0.014	0.13	0.166
	66	131	303	108	1.89	25	3.1	0.17	0.095	8.18	1.16	24.64	0.027	0.158	0.38	0.025	0.49	0.648
	59	152	146	88	1.73	14	1.88	0.17	0.07	9.55	1.05	7.725	0.019	0.126	0.49	0.019	0.21	0.265
	68	143	163	90	1.42	17	1.91	0.23	0.067	12.6	2.17	13.23	0.021	0.122	1.13	0.016	0.26	0.302
Mean	67	140	197	96	1.69	19	2.19	0.19	0.073	13.4	1.77	12.1	0.018	0.129	0.49	0.017	0.3	0.389
Std. Dev.	13	33	86.2	29	0.37	5.5	0.5	0.04	0.024	7.82	0.64	5.904	0.007	0.035	0.32	0.005	0.15	0.214

Appendix B 38, con't. Effects of Treatment pH on Foliar Content of Selected Elements in Greenhouse Loblolly Pine Seedlings: Hapludult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Cd	Sr	Ba
pH 5.0 Treatment																		
	67	136	178	97	1.67	18	2.46	0.25	0.072	13.3	1.75	21.95	0.019	0.127	0.95	0.016	0.36	0.477
	74	206	120	94	1.76	31	3.6	0.26	0.071	35	2.98	24.35	0.02	0.136	0.32	0.015	0.14	0.126
	67	197	110	64	1.62	15	1.73	0.28	0.046	25.2	5.35	20.87	0.012	0.09	0.63	0.011	0.11	0.134
	44	116	187	73	1.25	23	3.05	0.15	0.043	13.5	1.15	20.9	0.005	0.096	0.43	0.013	0.46	0.65
	68	125	193	89	1.89	23	2.2	0.29	0.065	12.2	2.22	7.041	0.007	0.118	0.31	0.015	0.34	0.391
	78	212	218	96	2.08	25	2.14	0.26	0.073	37.8	2.99	30.48	0.024	0.14	0.48	0.137	0.41	0.495
	61	145	118	104	1.25	17	1.79	0.21	0.07	25.2	2.57	16.7	0.015	0.121	0.41	0.018	0.19	0.206
	76	139	195	110	1.44	22	2.18	0.29	0.078	12.7	3.71	25.83	0.02	0.145	0.63	0.02	0.4	0.532
Mean	67	160	165	91	1.62	22	2.4	0.25	0.065	21.8	2.84	21.02	0.015	0.122	0.52	0.031	0.3	0.376
Std. Dev.	11	39	42	15	0.3	5.1	0.64	0.05	0.013	10.5	1.29	6.955	0.007	0.02	0.21	0.043	0.14	0.198

Appendix B 39. Effects of Treatment pH on Foliar Content of Selected Elements in Greenhouse Loblolly Pine Seedlings: Papludult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba
pH 3.5 treatment									mg/plant									
	40.81	69	254	89.8	1.34	28	1.97	0.19	0.06	1.97	43	0.013	0.14	0.18	0.08	0.015	0.7	0.62
	40.77	84	144	68.9	1.2	42	2.18	0.14	0.05	8.34	26	0.015	0.11	0.3	0.077	0.017	0.38	0.33
	53.47	103	207	103	1.77	37	2.77	0.2	0.07	3.15	38	0.022	0.15	0.15	0.093	0.015	0.47	0.4
	53.85	134	220	103	1.67	35	1.55	0.31	0.07	5.63	33	0.027	0.15	0.44	0.112	0.022	0.6	0.5
	34.85	74	141	55.4	1.24	32	2.17	0.13	0.04	3.03	30	0.013	0.1	0.12	0.076	0.015	0.3	0.25
	51.38	127	150	90.3	1.68	39	2.76	0.19	0.07	6.54	34	0.016	0.13	0.19	0.091	0.016	0.34	0.22
	53.72	90	93.1	56	1.6	21	1.4	0.2	0.04	3.77	19	0.008	0.1	0.14	0.064	0.009	0.11	0.06
	57.84	129	215	106	1.8	46	2.62	0.22	0.08	4.8	30	0.022	0.16	0.17	0.113	0.022	0.48	0.31
	59.49	93	280	104	1.82	64	3.04	0.2	0.08	7.19	50	0.03	0.18	0.46	0.121	0.021	0.59	0.5
Mean	49.57	100	189	86.3	1.57	38	2.27	0.2	0.06	4.94	34	0.018	0.14	0.24	0.092	0.017	0.44	0.35
Std. Dev.	8.602	24	60.8	20.9	0.24	12	0.57	0.05	0.01	2.14	9	0.007	0.03	0.13	0.019	0.004	0.18	0.17
pH 4.1 treatment																		
	48.99	126	290	99.1	1.97	36	2.21	0.21	0.07	2.25	47	0.019	0.18	0.16	0.125	0.019	0.72	0.68
	69.06	132	260	124	2.19	46	3.23	0.29	0.08	5.32	47	0.022	0.2	0.2	0.186	0.027	0.66	0.56
	54.96	136	261	108	1.97	65	4.51	0.22	0.09	5.16	61	0.025	0.19	0.2	0.137	0.032	0.92	0.76
	60.22	119	258	110	1.96	37	2.79	0.24	0.07	6.74	50	0.013	0.17	0.15	0.094	0.017	0.74	0.85
	54.45	103	256	99.5	2.04	48	2.05	0.22	0.08	7.24	54	0.023	0.17	0.18	0.139	0.029	0.73	0.73
	38.59	88	143	82.4	1.27	28	1.67	0.15	0.06	1.73	38	0.014	0.13	0.12	0.078	0.015	0.21	0.15
	38.46	68	167	63.9	1.27	33	3.02	0.14	0.05	1.44	25	0.008	0.11	0.09	0.068	0.013	0.23	0.16
	60.73	143	181	101	2.44	41	3.33	0.24	0.07	4.61	54	0.016	0.16	0.18	0.11	0.018	0.34	0.29
	41.86	116	156	74.3	1.57	28	3.23	0.16	0.05	1.71	41	0.013	0.13	0.14	0.096	0.012	0.23	0.17
Mean	51.92	114	219	95.7	1.85	40	2.89	0.21	0.07	4.02	46	0.017	0.16	0.16	0.115	0.02	0.53	0.48
Std. Dev.	10.75	24	56.2	18.8	0.4	12	0.85	0.05	0.02	2.28	11	0.006	0.03	0.04	0.036	0.007	0.28	0.29

Appendix B 39, con't. Effects of Treatment pH on Foliar Content of Selected Elements in Greenhouse Loblolly Pine Seedlings: Papludult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba
pH 5.0 treatment																		
	40.7	107	149	70.1	1.1	20	1.4	0.15	0.05	1.67	29	0.013	0.11	0.19	0.084	0.014	0.42	0.3
	55.39	118	202	114	2.09	50	2.21	0.22	0.08	6.34	54	0.016	0.19	0.18	0.119	0.024	0.55	0.53
	33.97	75	121	65.2	1.05	21	1.9	0.13	0.05	2.15	24	0.013	0.11	0.09	0.072	0.012	0.32	0.23
	42.69	83	203	93.6	1.56	32	2	0.2	0.06	1.73	40		0.16	0.13	0.102	0.02	0.58	0.53
	32.13	45	279	75.6	1.5	43	2.68	0.15	0.08	2.39	31	0.015	0.13	0.1	0.085	0.013	0.7	0.78
	48.43	96	181	81.3	2.09	37	2.2	0.18	0.06	8.8	37	0.019	0.13	0.25	0.106	0.022	0.46	0.43
	31.86	78	104	54.2	1.26	28	1.81	0.12	0.04	4.92	23	0.017	0.09	0.19	0.072	0.017	0.3	0.24
	49.77	80	196	75.6	1.58	43	2.88	0.18	0.06	2.59	36	0.014	0.14	0.12	0.081	0.015	0.54	0.54
	47.52	88	242	70.6	1.5	43	3.92	0.16	0.06	4.28	36	0.013	0.13	0.1	0.084	0.017	0.86	0.88
Mean	42.5	85	186	77.8	1.53	35	2.33	0.17	0.06	3.87	34	0.015	0.13	0.15	0.09	0.017	0.53	0.49
Std. Dev.	8.485	21	55.6	17.4	0.37	11	0.74	0.03	0.01	2.45	10	0.002	0.03	0.06	0.016	0.004	0.18	0.23

Appendix B 40. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Loblolly Pine Seedlings: Melton Branch Field Site, Hapludult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Zn	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 3.5 treatment									mg/Kg												mol
	7658	15420	13742	4943	178	2215	113	16.75		3.8	527	2552	856	0	7.75	9.7	7.83	3.4	23	32	3.6
	6086	13871	25323	4959	182	1062	130	14.96	266	3.29	2624	1300	730	0.17	6.45	5.1	4.26	2.3	51	67	13
	6273	17667	9776	4114	199	254	123	13.02	240	2.1	1915	423	772	0	6.18	3.3	0	0.7	22	31	16
	6527	15329	20521	3863	238	3126	109	15.38	256	3.67	2182	3637	857	0	6.77	11	3.52	1.8	35	62	3.8
	7319	15070	14791	4089		3996	148	20.33	190	5.65	1353	5447	3505	1.44	8.55	27	15.5	2.4	21	49	1.8
	9501	17871	13099	7304	261	1224	101	20.58	334	3.73	2275	2010	1171	0	10.2	17	0	2.8	30	55	4.4
	4218	19574	12775	2990	260	1484	102	11.08	157	2.18	2797	2164	1400	0	4.93	6.4	1.19	1.1	26	56	4
	6447	14437	21065	3499	182	1974	72	17.81	245	2.11	1727	2708	571	0	6.36	5.1	0	3.6	40	59	5.3
	7710	16360	17724	4879	507	4432	127	17.28	229	5.82	2067	5259	1682	1.87	9.5	21	12.4	2.2	23	44	2.3
	9990	17485	19624	7952	195	2950	84	11.33	369	5.93	609	2279	534	1.74	9.56	11	5.52	4.9	48	62	5.8
Mean	7173	16308	16844	4859	245	2272	111	15.85	254	3.83	1808	2778	1208	0.52	7.63	12	5.02	2.5	32	52	6
S.D.	1686	1797	4786	1600	104	1341	23	3.356	66	1.51	773	1599	886	0.81	1.77	7.8	5.44	1.2	11	13	4.6
pH 5.0 treatment																					
	4838	17901	14979	3515	208	4600	100	11.99	124	3.8	2492	3149	936	0.26	7.15	7	3.28	0.9	20	45	3.2
	5509	17607	20871	3790	221	3281	104	13.75	187	3.66	2134	2123	2032	0.79	6.88	9.1	8.29	2.1	33	59	6.6
	8917	21079	15448	7145	189	3377	142	19.76	209	6.66	1039	6728	6038	1.41	15.8	21	9.48	2.9	26	47	1.6
	5326	15029	15754	3908	202	2963	87	18.12	261	3.2	1717	2800	1494	0.8	6.41	13	6.53	2.3	28	61	3.8
	5437	15034	16110	3938	289	2724	86	14.55	151	3.89	1887	2843	1202	0.23	6.73	20	6.26	1.5	23	40	3.8
	5580	17370	15620	4051	209	3685	95	15.38	219	4.04	1853	2860	1393	0.34	6.84	15	6.25	2.4	22	56	3.7
	7678	18687	16627	3299	512	3670	124	17.41	200	3.4	1711	2969	2500	0.69	6.93	26	6.72	2	27	58	3.8
	6111	18617	16435	3375	151	1896	97	12.98	125	3.07	1885	2625	1184	0.3	5.15	5.9	7.3	1	29	53	4.2
	6941	19280	15378	4858	329	4234	104	17.23	164	4.67	1353	3139	1416	0.82	7.97	11	5.81	0.9	29	56	3.3
Mean	6260	17845	16358	4209	265	3381	104	15.69	182	4.04	1786	3248	2022	0.62	7.77	14	6.66	1.8	26	53	3.8
S.D.	1330	1934	1772	1194	114	807	18	2.598	46	1.09	418	1341	1579	0.39	3.11	6.9	1.72	0.7	4	7	1.3
NBS Pine	6175	17666	16480	4128	461	3274	105	15.4	185	4	1840	3262	2097	0.6	7.8	15	6.8	2	26	52	

Appendix B 41. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Loblolly Pine Seedlings: Walker Branch Field Site, Paleudult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba
pH 3.5 treatment									mg/Kg										
	5082	14989	9114	4407	154	1574	92	12.4	3.27	1353	3039	737	2.61	4.7	7.5	4.11	2.61	9.568	12.1
	4270	13400	8958	4484	219	2303	100	10.8	3.44	2656	2778	876	0.95	5.7	11	9.83	2.45	19.15	22.4
	6663	16613	6162	3536	133	1527	102	12.2	3.78	1531	3368	889	1.01	4.1	9.2	9.01	1.42	12.85	14.9
	4190	12480	10923	2897	212	2977	110	10.1	4.2	1746	3378	1276	1.36	5.1	6.9	11.7	1.09	24.92	51.7
	6023	13529	9016	4950	257	1217	159	21.7	4.71	626	4544	997	0.97	5	27	15.7	1.71	12.35	13.1
	6091	18908	7875	6402	250	1244	186	12.2	5	1362	2992	1268	1.95	6.2	35	13.2	3.34	15.91	18
Mean	5386	14986	8675	4446	204	1807	125	13.2	4.07	1546	3350	1007	1.48	5.1	16	10.6	2.1	15.79	22
Std. Dev.	1029	2406	1575	1209	50.4	695	38	4.24	0.7	662	629	221	0.68	0.7	12	3.98	0.84	5.546	15
Treatment pH 5.0																			
	5401	14072	8427	4816	214	685	77	12.3	4.21	620	3177	801	1.35	4.9	12	9.86	1.53	10.18	9.19
	5693	15070	13909	6167	213	2787	98	12.9	6.87	933	8487	769	0.83	6.7	12	23.2	2.02	43.87	42.6
	4882	16366	6316	4897	164	971	117	12.8	3.37	2421	3737	923	2.59	4.9	9.8	6.06	1.64	5.411	6.13
	5834	18198	7110	6270	205	1725	149	14.4	5.66	2396	3101	675	0.55	6	15	7.58	1.49	12.59	11.5
	4943	13655	8915	3776	215	2611	100	11.8	4.18	2059	3325	1193	1.01	5	15	9.42	2.67	16.53	13.9
	4166	15200	9928	4419	163	3049	121	10.7	4.26	1859	3984	726	0.6	5	13	10.6	1.98	21.08	15.1
	5793	16764	10555	4564	185	3332	115	15.1	4.61	4139	3500	1059	0.61	6.3	7.5	8.18	2.45	18.45	19.4
	4980	16101	7884	5937	244	2008	105	14.5	5.42	798	3699	925	1.54	6.3	23	12.5	2.76	7.595	11.7
	3713	12495	11158	4165	209	2238	78	10.9	3.6	1495	2618	1217	1.42	5	7.7	11	2.5	17.23	18.2
	4623	13576	9894	3255	157	2570	99	12.2	3.95	1758	2932	805	1.08	4.7	9.2	9.83	1.8	23.39	60.5
Mean	5003	15150	9410	4826	197	2198	106	12.8	4.61	1848	3856	909	1.16	5.5	12	10.8	2.08	17.63	20.8
Std. Dev.	705	1739	2199	1020	28.4	864	21	1.51	1.07	1028	1678	191	0.62	0.8	4.7	4.72	0.48	10.89	17.2

Appendix B 42. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Hog Peanut: Melton Branch Field Site, Hapludult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Zn	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba
pH 3.5 Treatment									mg/Kg											
	8688	63439	85390	20054	601	1799	192	31	196	11	159	582	3232	3	19.51	29.95	12.37	2.8	342	1022
	10504	54889	89136	20825	600	2783	182	27	296	9.6	167	640	3459	3.7	21.65	37.73	20.32	3.8	349	1199
	15853	58048	62771	17827	554	3451	149	38	270	8.1	117	506	4116	2.4	18.05	38.58	15.18	3.2	256	1018
	13489	51063	71797	16297	615	2491	200	32	236	8.5	108	586	3494	3.1	17.06	28.22	16.19	2.8	274	984
	10300	53068	80525	17017	518	2553	175	34	251	8.5	163	440	3661	3.1	17.81	31.93	15.68	2.7	289	886
	14314	55469	67980	16353	1572	3514	159	37	197	9.6	175	2063	6098	3.8	19.53	34.94	23.29	3	254	956
	10227	61089	98000	22533	1244	4322	222	27	282	12	370	1628	5542	4.8	24.89	46.89	22.2	4.1	407	1481
	12230	48110	87986	17476	583	2332	229	3	214	9.1	216	641	3514	3.4	18.79	35.86	18.59	2.6	321	1010
	10867	51053	67474	17039	658	2665	180	34	244	8.2	534	654	3812	3.7	17.74	45.23	17.09	3.1	266	993
	13834	68156	80875	20138	500	2282	167	41	279	9	318	490	4716	1.8	18.84	28.94	10.38	3.2	298	797
Mean	12031	56438	79193	18556	745	2819	186	30	247	9.3	233	823	4164	3.3	19.39	35.83	17.13	3.1	306	1035
Std. Dev.	2270	6258	11355	2161	361	739	26	11	36	1.2	135	553	975	0.8	2.321	6.479	4.097	0.5	49	188
pH 5.0 Treatment																				
	9618	45109	82255	13609	464	4534	177	25	219	8.3	127	488	2735	3.8	16.35	30.31	19.14	2.7	330	1274
	14403	54097	82042	17458	479	3224	198	31	195	9.5	318	648	3656	3.5	18.78	44.39	19.63	2.6	318	971
	9802	53432	97095	22211	485	2756	222	26	170	11	227	585	6655	4	22.59	35.07	18.19	3	378	1317
	10492	40301	67096	16055	477	1847	161	23	161	8.5	263	588	2916	3	16.71	19.63	14.19	2.5	278	902
	11201	40089	79045	17516	601	2489	209	29	228	9.9	310	746	3118	3.9	18.75	32.09	18	3	338	1122
	14557	54652	76261	22326	463	1928	233	30	195	10	157	482	4139	3.4	22.04	38.22	16.63	3.4	288	1002
	15380	68902	42634	15954	352	1479	105	37	253	7.5	145	269	3005	1.9	14.85	56.2	8.683	2.4	155	483
	17983	59828	1E+05	22690	623	4033	278	42	283	12	373	668	4395	5.2	24.67	48.79	25.21	3.6	439	1468
	11037	57616	86832	18384	1368	3290	194	26	218	11	291	1867	5242	4.7	21.12	39.76	23.58	3.3	357	1284
Mean	12719	52670	80481	18467	590	2842	197	30	214	9.7	246	705	3984	3.7	19.54	38.27	18.14	2.9	320	1091
Std. Dev.	2942	9448	19003	3248	302	1027	49	6	39	1.4	87	457	1295	1	3.273	10.79	4.875	0.4	78	294

Appendix B 43. Effects of Treatment pH on Foliar Concentrations of Selected Elements in Carolina Buckthorn: Walker Branch Watershed Field Site, Paleudult.

	P	K	Ca	Mg	Fe	Mn	B	Cu	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba	Ca/Al
pH 3.5 Treatment								mg/Kg												(mol)
	4558	34896	46657	8821	343	3436	153	15	5.9	1364	452	1346	2.01	10.5	21.46	15.31	2.59	278	683	17.27
	5375	41392	54275	13173	265	4692	127	14	7.2	2518	328	1356	1.55	14.2	20.65	10.61	1.94	318	587	11.1
	5712	29280	40892	7748	267	4303	150	15	5.8	1799	313	980	1.93	10.2	15.16	12.1	1.75	249	586	10.98
	4666	32563	54703	12039	539	3941	136	17	6.8	1970	908	2267	2.72	13.6	19.17	19.56	1.91	316	718	11.16
	4376	37176	55557	12986	411	4953	140	14	7.9	1327	637	1928	2.76	14.9	14.5	17.37	2.26	358	779	18.91
	3894	29670	49612	10107	337	4114	119	15	6.6	1098	421	1248	2.23	12	25.56	14	2.5	313	681	18.24
	5808	28423	45985	9675	392	4183	141	16	6.3	1261	539	1275	2.45	12.1	16.19	17.4	1.99	277	686	15.21
	5259	35612	50230	11748	312	5125	170	19	7.7	2051	349	926	2.59	14	20.58	17.48	2.76	298	670	11.72
Mean	4956	33626	49739	10787	358	4343	142	16	6.8	1674	493	1416	2.28	12.7	19.16	15.48	2.21	301	674	14.32
S. D.	684	4491	5088	1994	89.8	557	16	2	0.8	489	201	459	0.43	1.76	3.723	3.054	0.37	33	63.9	3.469
pH 5.0 Treatment																				
	3988	29488	48796	10294	286	3948	137	14	6.1	1284	362	985	2.4	11.8	21.14	18.25	1.84	337	1090	15.5
	4706	33723	67538	12132	346	4325	156	15	7.3	1882	428	990	2.83	13.7	19.97	16.72	2.58	616	1866	12.1
	4310	37829	51317	13985	487	3510	114	15	6.6	2939	888	2062	2.51	13.6	19.12	10.51	2.32	453	2578	8.688
	4246	39745	45834	11173	418	3690	166	15	6.9	1759	628	1837	2.18	12.5	14.68	13.85	2.01	306	849	15.25
	3722	44000	46392	13114	420	3733	135	13	7.1	1245	663	1797	1.94	13.5	30.8	11.29	2.31	373	1261	23.86
	3788	38158	48719	12328	275	3612	149	12	6.6	1844	346	743	2.46	12.7	21.4	10.39	2.32	408	1612	13.97
	4558	27090	41541	8624	389	2548	144	13	5.7	1410	608	1453	2.39	10.1	18.14	12.16	1.7	356	1151	12.97
	4264	40270	58932	13689	369	4143	151	15	8.1	1746	594	1380	3.07	14.9	21.69	13.78	2.27	465	1396	15.57
Mean	4197	36288	51134	11917	374	3689	144	14	6.8	1764	564	1406	2.47	12.8	20.87	13.37	2.17	414	1475	14.74
S. D.	348	5739	8314	1817	71.1	537	16	1	0.7	538	181	472	0.35	1.45	4.62	2.885	0.29	98	546	4.343

Appendix B 44. Concentrations of Monomeric Aluminum Species in Soil Solution from Site in Spruce-Fir Forest, Great Smoky Mountains as Affected by Treatment pH: May, 1985.

	pH 3.5 Treatment				pH 5.0 Treatment			
Time (Hrs)	TMAl	NLMAl	LMAl[1]	NLMAl/TMAl	TMAl	NLMAl	LMAl	NLMAl/TMAl
	-------(mg/L)------				-------(mg/L)--------			
1	0.69	0.09	0.60	0.13	0.84	0.11	0.73	0.13
1	0.89	0.13	0.76	0.15	1.04	0.16	0.88	0.15
1	1.08	0.20	0.88	0.19	0.93	0.12	0.81	0.13
1	0.36	0.08	0.28	0.22	1.08	0.15	0.93	0.14
1	0.42	0.08	0.34	0.19	n.s.	0.14		
mean	0.69	0.12		0.18*	0.97	0.14		0.14*
s.e.[2]	0.14	0.02		0.02	0.05	0.01		0.01
24	0.50	0.10	0.4	0.20	1.49	0.38	1.11	0.26
24	0.56	0.20	0.36	0.36	0.60	0.22	0.38	0.37
24	1.08	0.36	0.72	0.33	0.46	0.22	0.24	0.48
24	0.40	0.08	0.32	0.20	0.40	0.22	0.18	0.55
24	0.56	0.20	0.36	0.36	0.56	0.20	0.36	0.36
mean	0.62	0.19		0.29*	0.70	0.25		0.40*
s.e.	0.12	0.05		0.04	0.20	0.03		0.05
72	0.68	0.16	0.52	0.24	0.47	0.29	0.18	0.62
72	0.56	0.20	0.36	0.36	0.75	0.16	0.59	0.21
72	1.40	0.16	1.24	0.11	0.57	0.17	0.40	0.30
72	0.50	0.05	0.45	0.10	0.57	0.19	0.38	0.33
72	0.52	0.16	0.36	0.31	0.49	0.16	0.33	0.33
mean	0.73	0.15		0.22	0.57*	0.19		0.36
s.e.	0.17	0.03		0.05	0.05	0.03		0.07
144	2.30	0.20	2.10	0.09	0.7	0.23	0.47	0.33
144	1.34	0.18	1.16	0.13	1.64	0.22	1.42	0.13
144	0.85	0.13	0.72	0.15	0.66	0.20	0.46	0.30
144	0.68	0.19	0.49	0.28	1.05	0.19	0.86	0.18
144	0.54	0.31	0.23	0.57	2.14	0.21	1.93	0.10
mean	1.14	0.20		0.25	1.24*	0.21		0.21
s.e.	0.32	0.03		0.09	0.29	0.01		0.05

[1]IMAl determined by TMAl - OMAl
[2]Standard error.
*asterisk indicates comparison of two values at adjacent times within a treatment are different at $p \leq 0.05$.

Appendix B 45. Concentrations of Monomeric Aluminum Species in Soil Solution from Site in Spruce-Fir Forest, Great Smoky Mountains as Affected by Treatment pH: October, 1985.

	pH 3.5 Treatment				pH 5.0 Treatment			
Time (Hrs)	TMAl	NLMAl	LMAl[1]	NLMAl/TMAl	TMAl	NLMAl	LMAl	NLMAl/TMAl
	-------(mg/L)--------				-------(mg/L)--------			
1	1.60	0.20	1.40	0.12	3.10	0.31	2.79	0.10
1	3.20	0.13	3.07	0.04	1.10	0.27	0.83	0.25
1	1.40	0.16	1.24	0.11	1.26	0.14	1.12	0.11
1	2.05	0.12	1.93	0.06	2.04	0.38	1.66	0.19
1	1.40	0.11	1.29	0.08	0.54	0.23	0.31	0.43
mean	1.93	0.14*a		0.08	1.60	0.27a		0.21
s.e.[2]	0.34	0.02		0.02	0.45	0.04		0.06
24	1.24	0.39	0.85	0.31	1.24	0.13	1.11	0.10
24	1.24	0.21	1.03	0.17	2.00	0.13	1.87	0.07
24	3.90	0.30	3.60	0.08	1.20	0.49	0.71	0.41
24	2.92	0.23	2.69	0.08	1.30	0.49	0.81	0.38
24	1.10	0.26	0.84	0.24	1.14	0.22	0.92	0.19
mean	2.08	0.28*		0.18	1.38*	0.29		0.23
s.e.	0.57	0.03		0.05	0.16	0.08		0.07
72	1.40	0.12	1.28	0.09	4.05	0.29	3.76	0.07
72	0.60	0.10	0.50	0.17	3.65	0.26	3.39	0.07
72	1.40	0.08	1.32	0.06	2.25	0.39	1.86	0.17
72	3.05	0.28	2.77	0.09	2.25	0.06	2.19	0.03
72	1.00	0.36	0.64	0.36	5.40	0.15	5.25	0.03
mean	1.49	0.19		0.15	3.52*	0.23		0.07
s.e.	0.42	0.06		0.06	0.58	0.06		0.03
144	1.90	0.50	1.40	0.26	1.30	0.39	0.91	0.30
144	2.20	0.31	1.89	0.14	3.55	0.31	3.24	0.09
144	3.30	0.30	3.00	0.09	3.80	0.39	3.41	0.10
144	2.10	0.19	1.91	0.09	5.30	0.43	4.87	0.08
144	2.05	0.38	1.67	0.19	3.25	0.22	3.03	0.10
mean	2.29	0.34		0.16	3.44	0.35		0.14
s.e.	0.23	0.05		0.03	0.64	0.04		0.04

[1] IMAl determined by TMAl - NLMAl

[2] Standard error.

*asterisk indicates comparison of two values at adjacent times within a treatment are different at $p \leq 0.05$.

[a] values with superscript indicates when differences between treatments are statistically significant at $p \leq 0.05$.

Appendix B 46. Concentrations (mg/L) of Total Dissolved Elements in Soil Solution of the Spruce-Fir Field Site, GSMNP.

		K	Ca	Mg	Fe	Mn	B	Cu	Zn	Mo	Na	Al	Si	Co	Cr	Ni	Pb	Cd	Sr	Ba
STA	1	54.2	12.2	4.5	0	0.33	52.2	0	0.28	0	202	15.8	26.8	0	0	0	0	0	0	0.23
STA	3	104	36.4	7.86	0.02	0.9	85.3	0	0.88	0	202	66.9	50.7	0	0	0.6	0	0	0.17	0.56
STC	5	78.2	26.3	7.87	0.79	1.47	98.4	0	1.28	0.57	317	28.9	74.8	0	0	6.58	0	0	0.22	0.45
STD	2	39.6	82.9	25.8	0.03	6.85	85.3	0	1.81	0	277	33.3	60.9	0	0	2.32	0	0.01	0.34	0.67
STD	5	91.8	54.6	12.9	0	2.21	123	0	0.88	0	430	48.2	70.8	0	0	0	2.13	0	0.22	0.67
SCD	1	176	71.8	24.2	0	4.57	53.6	0	0.35	0	222	25.4	33.1	0	0	0	0	0.01	0.28	0.67
	2	46.6	83.9	22.5	0	5.87	74.4	0	0.75	0	264	25.4	52	0	0	1.75	2.13	0.01	0.28	0.67
	3	81.7	102	21.4	3.06	7.18	50.2	0	3.68	0	238	14.8	30.5	0	0	1.46	0	0.57	0.34	0.9
	4	0	77.8	30.3	0	6.1	60.7	0	0.68	0	288	31.5	31.8	0	0	0.32	0	0.01	0.28	0.67
	5																			
CSA1		114	58.6	13.5	0	3.27	46.1	0	1.48	0	178	31.2	21.7	0	0	1.46	0.21	0.01	0.22	0.67
	2	56.2	31.4	6.18	2.87	1.39	64.3	0	0.28	0	218	20.5	33.1	0	0	0	0	0	0.22	0.45
	3																			
	4	136	107	17.9	0.6	3.27	98.5	0	3.14	0	334	50.8	45.7	0	0	0	0	0.01	0.67	1.79
CSC	1	58.8	34.4	7.86	0	1.31	88.9	0	5.13	0.29	272	68.4	45.6	0	0	2.02	0	0	0.22	0.56
	2	44.2	43.5	11.2	0.02	2.29	83.5	0	0.74	0	241	52.5	43.1	0	0	0.03	0	0	0.22	0.45
	3	86.2	37.4	7.86	0	1.63	87.3	0	18.8	0	268	39.8	40.6	0	0	0.03	0	0	0.22	0.45
	4	92.2	34.3	8.98	0	1.22	85.5	0	0.86	0	299	34	60.6	0	0	2.84	0	0	0.22	0.44
	5	57.9	26.2	7.86	0	1.22	94.3	0	0	0	281	44.5	61.9	0	0	0.57	0	0	0.17	0.44
TSA	2	110	13.1	4.5	0	1.06	16.3	0	0.75	0	39.3	25.4	6.53	0	0	0.61	5.97	0.29	0.17	0.45
	4	95.9	27.2	10.7	0.79	1.5	71.2	0	0.48	0	202	278	35.6	0	0	2.03	0	0.01	0.22	0.45
	5	72	21.3	7.87	0.03	0.98	61.2	0	2.01	0	179	23.9	21.7	0	0	1.75	0	0	0.17	0.45
TSC	1	53.9	19.2	5.62	0	0.9	84.4	0	0.48	0.03	287	28.4	50.8	0	0	0	0	0.01	0.06	0.45
	2	56.9	18.2	3.93	0	0.25	63.6	0	0.34	0	219	21	40.6	0	0	0	0	0	0.06	0.45
	3	52.3	20.3	5.62	0	0.58	90.1	0	0.75	0	234	30.7	67.2	0	0	0	0	0	0.17	0.45
	4	56.7	40.4	10.1	0	2.53	55.7	0	1.26	0	178	40.1	26.5	0	0	0.28	0	0.28	0.22	0.44
	5	16	66.7	16.9	1.15	4.89	86.8	0	0.74	0	290	27.8	73.4	0	0	0	2.06	0.29	0.22	0.56

Sample Key:

1st letter S = Smoky Mts. plots: May sampling
T, C = October sampling: pH 3.5 and pH 5.0 treatments, respectively

2nd letter T, C = pH 3.5 and pH 5.0 treatments, respectively
S = Smoky Mts. plots

3rd letter A = 1 hour samples
C = 72 hour samples
D = 144 hour samples

Appendix B 47. Soil Solution pH and DOM Values from Site in Spruce-Fir Forest, Great Smoky Mountains as Affected by Treatment pH.

	May				October			
Treatment	pH 3.5		pH 5.0		pH 3.5		pH 5.0	
Time (Hrs)	DOM[1]	pH	DOM	pH	DOM	pH	DOM	pH
1	0.036	3.44	0.353	3.38	0.072	3.34	0.079	3.35
1	0.054	3.56	0.068	3.45	0.022	3.50	0.093	3.46
1	0.153	3.48	0.063	3.45	0.039	3.40	0.032	3.42
1	0.029	3.55	0.066	3.43	0.026	3.36	0.086	3.00
1	0.075	3.47	0.058	3.58	0.030	3.36	0.128	3.23
24	0.025	3.68	0.067	3.69				
24	0.049	3.54	0.054	3.85				
24	0.064	3.65	0.072	3.53				
24	0.036	3.69	0.067	3.47				
24	0.083	3.71	0.042	3.75				
72	0.045	3.75	0.126	3.56	0.022	3.52	0.032	3.43
72	0.061	3.70	0.041	3.62	0.028	3.45	0.046	3.36
72	0.032	3.46	0.036	3.69	0.028	3.55	0.128	3.40
72	0.034	3.73	0.209	3.67	0.37	3.47	0.048	3.46
72	0.052	3.65	0.098	3.31	0.93	3.41	0.23	3.50
144	ns	ns	0.031	3.37	0.072	3.50	0.031	3.58
144	0.035	3.32	0.042	3.27	0.093	3.67	0.029	3.46
144	ns	3.56	0.069	3.22	0.034	3.36	0.125	3.52
144	0.018	3.39	0.037	3.25	0.025	3.45	0.131	3.46
144	0.016	3.39	0.032	3.18	0.054	3.57	0.044	3.54

[1]DOM values as absorbance at 250 nm.

Appendix B 48. Effects of Treatment pH on Concentrations (mg/67 g Soil) of 1N KCl-Extractable Elements in Soils from Spruce-Fir Field Site.

Time (Hrs)	Al	Ca	Cu	Fe	Mg	Mn	P	Si	Al	Ca	Cu	Fe	Mg	Mn	P	Si
May																
pH 3.5 treatment									pH 5.0 treatment							
1	36.2	16.65	0.061	7.03	4.03	1.12	0.41	1.08	7.93	151.3	0.04	1.54	17.2	15.1	3.75	2
1	23.19	38.45	0.052	4.49	5.93	2.24	0.22	1.08	43.2	32.23	0.05	4.67	7.77	2.92	0.33	1.3
1	27.3	65.68	0.058	6.12	11.1	4.24	0.69	1.58	37.3	30.02	0.08	5.61	5.21	1.78	0.6	1.2
1	31.91	15.28	0.055	6.08	4.44	1.16	0.3	1.13	50.7	13.79	0.05	6.12	3.96	0.94	0.52	1.3
1	32.78	15.81	0.05	6.9	4.73	0.83	0.35	1.02	40.8	40.54	0.04	7.93	8.38	2.37	0.45	1.4
144	39.93	19.69	0.066	6.46	4.21	0.92	0.35	0.96	51	11.6	0.05	5.52	3.76	0.9	0.5	1.2
144	47.73	17.49	0.047	6.57	5.22	0.96	0.52	1.2	31.4	64.18	0.07	5.39	7.15	2.76	0.07	1.4
144	32.58	31.09	0.074	6.61	5.39	2.19	0.47	1.13	22.6	75.24	0.05	3.12	13.5	5.48	1.93	1.4
144	22.7	57.85	0.047	5.94	10.8	3.41	0.4	1.26	41.5	36.85	0.05	6.06	6.75	2	0.48	1.3
144	31.87	33.81	0.048	6.63	8.34	4.05	0.29	1.12	24.2	74.3	0.05	4.35	17.9	5.77	2.96	1.4
October																
1	38.09	16.47	0.048	5.21	5.3	1.02	0.3	1.42	50.6	41.94	0.08	3.21	7.76	2.85	1.05	1.7
1	47.54	8.16	0.07	3.93	3.76	0.58	0.44	1.47	34.1	62.17	0.07	3.22	6.4	3.56	0.86	1.7
1	36.93	16.3	0.075	3.73	4.48	0.89	0.34	1.28	53.2	12.5	0.08	3.67	3.35	0.4	0.47	1.4
1	60.46	19.84	0.072	4.18	6.1	0.8	0.74	1.5	52.9	18.04	0.08	4.08	4.36	0.64	0.5	1.3
1	35.45	19.74	0.057	4.81	5.81	1.32	0.33	1.36	43.8	48.29	0.06	3.58	5.05	1.96	0.97	1.3
24																
24									39.6	24.32	0.1	3.29	4.19	0.84	0.69	1.2
24	47.33	20.18	0.072	4.02	4.55	0.84	0.47	1.53								
24									43.6	35.89	0.12	3.09	6.85	1.98	0.72	1.6
24	43.79	35.28	0.094	4.24	6.75	1.33	0.4	1.5								
72	40.19	13.43	0.071	4.57	4.31	0.82	0.33	1.19	45.8	27.08	0.06	3.59	5.76	1.29	0.68	1.3
72	42.24	24.52	0.07	3.69	4.3	0.74	0.47	1.39	45.4	28.03	0.05	3.11	4.32	1.28	0.78	1.6
72	48.68	11.08	0.091	3.08	3.6	0.59	0.43	1.34	53.3	30.46	0.12	3.48	5.97	1.04	0.75	1.6
72	33.36	22.16	0.17	3.61	4.99	1.31	0.39	1.18	65.7	52.7	0.07	3.07	5.85	1.25	1.67	1.5
144	26.88	112.5	0.051	1.95	12.9	3.19	4.4	2.19	47.1	22.81	0.07	5.02	4.56	0.62	0.39	1.3
144	38.43	13.75	0.075	4.05	5.29	0.72	0.5	1.34	58.4	26.63	0.07	3.24	6.35	1.78	0.75	1.7
144	37.82	30.3	0.07	6.17	7.85	1.48	0.36	1.6	31.6	60.74	0.05	2.22	9.29	3.74	1.63	1.6
144	30.11	38.32	0.072	3.78	6.28	1.94	0.48	1.37	44.9	15.02	0.06	4.05	2.93	0.38	0.49	1.2

Appendix B 49. Concentrations (mg/100 g Soil) of 1N KCl-Extractable Elements in Soils from Oak-Hickory Forest Field Sites.

Walker Branch

	Al	Ca	Cu	Fe	Mg	Mn
WTA1	6.519	32.69	0.0347	0.0502	4.307	2.974
WTA2	0.409	77.7	0.0319	0.0363	4.808	0.838
WTA3	2.298	71.51	0.032	0.0442	4.832	1.228
WTA4	3.758	25.54	0.0308	0.0269	3.051	1.709
WCA1	2.329	60.07	0.0547	0.0381	5.497	2.485
WCA3	7.115	48.3	0.0327	0.0815	5.755	2.387
WCA4	1.542	87.73	0.032	0.0526	7.173	5.452
WCA5	5.963	52.51	0.0372	0.0776	4.611	2.647
WCD4	2.494	45.49	0.0315	0.0364	4.783	2.22
CWA2	0.371	102.4	0.0404	0.0736	8.799	0.499
CWA3	6.919	23.48	0.0416	0.0994	4.101	1.934
CWA4	2.789	19.9	0.0392	0.1134	11.78	2.56
CWA5	6.223	28.85	0.0422	0.1091	3.799	2.261
CWB2	4.411	97.44	0.2283	0.1295	8.785	6.651
CWB3	6.366	48.94	0.0458	0.1253	4.84	1.951
CWB4	3.448	57.88	0.1219	0.1043	6.451	1.969
CWB5	0.652	78.1	0.0342	0.1826	5.216	0.284
CWD1	3.399	39.28	0.0783	0.0567	5.903	1.546
CWD2	4.846	30.1	0.1587	0.0561	2.675	1.184
CWD4	8.502	26.38	0.1593	0.1277	3.092	2.406
CWD5	4.097	31.75	0.1026	0.0681	3.459	1.372
TWA1	1.233	76.7	0.0403	0.0705	5.931	0.751
TWA3	3.128	60.71	0.0299	0.065	5.931	0.751
TWA4	0.998	71.95	0.0397	0.0729	7.276	0.785
TWA5	9.93	26.73	0.0439	0.1138	2.203	1.413
TWB1	6.95	19.76	0.0371	0.1167	3.005	1.639
TWB2	2.966	37.96	0.0401	0.0588	4.128	0.847
TWB4	0.865	115.5	0.0931	0.066	10.39	1.261
TWB5	6.586	32.52	0.0323	0.0699	4.164	1.826
TWD2	6.09	26.26	0.1486	0.0576	3.083	1.662
TWD3	1.88	49.18	0.1297	0.051	4.014	0.945
TWD4	7.45	36.72	0.1827	0.0889	5.093	2.608
TWD5	1.792	62.01	0.0831	0.0761	5.571	1.272

Sample Key:

W,C/T: May, pH 5.0/pH 3.5 treatment
T/C,W: October, pH 3.5/pH 5.0 treatment
3rd letter:
A = Hour 1
B = Hour 24
D = Hour 144
Sample # = 1-5

Melton Branch

	Al	Ca	Cu	Fe	Mg	Mn
MTD2	4.762	90.7	0.0301	0.0762	13.74	4.757
MTD3	5.098	88.98	0.03	0.0405	11.69	5.164
MTD4	0.195	366.3	0.029	0.0457	23.77	0.1621
MTD5	0.279	249.8	0.0312	0.054	20.28	0.8756
MCD1	17.35	30.19	0.0347	0.0524	6.104	6.121
MCD2	3.257	89.4	0.0284	0.054	15.62	4.033
MCD3	0.284	212.5	0.0279	0.0496	27.1	0.901
MCD5	7.595	72.42	0.0301	0.0662	10.63	6.268
TMA1	0.279	193.5	0.0826	0.0522	18.97	0.1638
TMA2	1.093	122.3	0.0605	0.0547	16.15	1.468
TMA4	0.288	252.5	0.0579	0.0722	21.61	0.1241
TMA5	0.249	202.6	0.0633	0.0547	18.87	0.1999
TMB1	0.553	143.7	0.0519	0.0892	19.34	1.179
TMB2	0.28	240.8	0.0739	0.0681	21.58	0.127
TMB4	13.65	63.25	0.1613	0.0856	10.8	3.347
TMB5	0.72	275.8	0.044	0.2223	32.18	1.943
TMD1	0.361	243	0.0418	0.0596	20.46	0.1003
TMD3	3.935	104.5	0.0418	0.0627	15.95	2.526
TMD4	2.461	107.8	0.0398	0.0534	17.35	2.243
TMD5	5.116	119	0.0551	0.115	15	5.923
TMD5	5.136	116.6	0.069	0.2066	14.59	5.718
CMA1	4.532	94.71	0.0698	0.0634	12.1	2.19
CMA2	1.648	114.8	0.0579	0.0691	18.42	2.893
CMA4	0.42	128.8	0.0578	0.0502	19.92	0.5466
CMA5	10.43	41.96	0.0604	0.0801	8.823	3.548
CMB2	0.476	127.2	0.1037	0.0527	20.65	0.6296
CMB3	9.862	53.19	0.071	0.0744	12.52	3.309
CMB4	0.42	128.8	0.0578	0.0502	19.92	0.5466
CMB5	0.513	91.73	0.0471	0.067	15.92	0.8047
CMD2	9.925	67.24	0.0478	0.0702	10.85	2.007
CMD3	7.324	68.07	0.0484	0.1237	8.832	1.783
CMD4	4.739	102.5	0.0471	0.0975	15.64	2.821
CMD5	8.63	83.64	0.0504	0.0919	13.77	3.938

M,C/T: May, pH 5.0/pH 3.5 treatment
T/C,M: October, pH 3.5/pH 5.0 treatment
3rd letter:
A = Hour 1
B = Hour 24
D = Hour 144
Sample # = 1-5

Appendix B 50. Soil Solution Chemical Parameters from Oak-Hickory Forest: Melton Branch Site

	pH 3.5 treatment						pH 5.0 treatment					
	TMAI	NLMAI	LMAI	NL/TMAI	DOM	pH	TMAI	NLMAI	LMAI	NL/TMA	DOM	pH
		mg/L						mg/L				
May												
Time (Hrs.)												
1	0.07	0.032	0.04	0.45714	1.71	7.99	0.405	0.285	0.12	0.7037	1.95	5.25
1	0.08	0.038	0.04	0.475	1.51	8.31	0.6				2.25	5.68
1	0.405	0.23	0.18	0.5679	2.21	5.94	0.756	0.37	0.37	0.4894		
1	0.135	0.132	0	0.97778	2.25	6.64	0.612	0.182		0.2974		4.39
1	0.176	0.128	0.05	0.72727	1.34	5.07	0.354	0.244	0.11	0.6893		5.31
Mean	0.173	0.112		0.64102			0.545	0.27		0.5449		
s.e.	0.068	0.04		0.109			0.082	0.039		0.095		
24	0.23	0.12	0.11	0.52174	1.33	5.74	0.86	0.65	0.15	0.7558	2.38	5.28
24	0.04	0.05		1	1.45	7.67						
24	0.5	0.33	0.17	0.66		4.72		0.28			1.69	4.55
24		1.08				4.1	0.38					4.38
24	0.012	0.016		1	0.82	7.98	0.64	0.22	0.24	0.3438	0.67	4.24
Mean	0.196	0.319		0.79543			0.626	0.383		0.5498		
s.e.	0.112	0.221		0.121			.12\	0.232				
72	0.17	0.1	0.07	0.58824		4.81	0.5	0.53	0	1	2.32	5.03
72	0.54					4.01	0.26	0.13		0.5		5
72	0.05	0.08		1	2.48	7.22	0.6					
72							0.4	0.29	0.11	0.725		4.13
72	0.064	0.06	0.12	0.9375	2.46	7.35	0.3	0.18		0.6		4
Mean	0.206	0.08		0.84191			0.412	0.2825		0.7063		
s.e.	0.117	0.01		0.0906			0.07	0.089		0.108		
144	0.1					4.21	0.31					3.57
144	0.27	0.25	0.02	0.92593		4.51	0.19					4.16
144							0.28	0.17	0.11	0.6071		5.6
144	0.03	0.032	0	1		7.13	0.64	0.095		0.1484		4.47
144							0.3	0.16	0	0.5333		3.42
Mean	0.137	0.14		0.96296			0.344	0.14		0.4296		
s.e.	0.06	0.075		0.025			0.086	0.021		0.123		
October												
1	0.046	0.05	0	1	0.105	6.67	0.43	0.2		0.4651	0.06	4.55
1	0.2	0.1	0.1	0.5	0.02	4.78	0.77	0.38		0.4935	0.12	5.13
1												
1	0.035	0.045	0	1	0.104	7.1	0.15	0.14		0.9333	0.06	6.22
1	0.138	0.115	0.02	0.83333	0.053	6.92	0.22	0.44		2	0.04	4.59
Mean	0.105	0.079		0.83333			0.393	0.29		0.973		
s.e.	0.039	0.018		0.118			0.139	0.143		0.357		
24	0.31	0.25		0.80645	0.151	5.74	0.77	0.32		0.4156	0.03	4.55
24	0.034	0.02		0.58824	0.055	7.03	0.188	0.23		1	0.14	6.34
24	1.35	0.31		0.22963		4.76						
24	0.58	0.07		0.12069	0.017	4.08	0.12	0.228		1	0.13	6.87
24	1.8	1.25		0.69444	0.588	4.75	0.56	0.23		0.4107	0.05	4.48
Mean	0.814	0.38		0.48789			0.437	0.251		0.7066		
s.e.	0.368	0.25		0.149			0.138	0.023		0.169		

Appendix B 50, con't. Soil Solution Chemical Parameters from Oak-Hickory Forest: Melton Branch Site.

	pH 3.5 treatment						pH 5.0 treatment				
Hour	TMAI	NLMAI	LMAI	NL/TMAI	DOM	pH	TMAI	NLMAI	LMAI	NL/TMA	DOM	pH
		mg/L						mg/L				
72	0.27	0.15		0.55556	0.12	4.39	0.75	0.28		0.3733	0.05	4.87
72	0.28	0.15		0.53571	0.067	4.09	0.27	0.19		0.7037	0.03	4.58
72	0.82	0.2		0.2439	0.025	4.21	0.12	0.14		1	0.07	5.53
72	0.04	0.06		1	0.052	6.77	1.7	1.4		0.8235	0.14	4.47
72	1.38	1.2		0.86957	2.57	4.12	0.84	0.47		0.5595	0.05	4.33
Mean	0.442	0.268		0.64095			0.736	0.496		0.692		
s.e.	0.135	0.145		0.149			0.32	0.26		0.12		
144	0.032	0.015		0.46875	0.074	7.73	1.5					
144	0.13	0.13		1	0.027	5.56	1.6	1.5		0.9375		
144	0.28	0.14		0.5	0.018	4.38	0.76	0.19		0.25		
144	0.36	0.21		0.58333	0.061	4.59	0.19	0.17		0.8947		
144	1.3	0.68		0.52308	0.049	4.45	0.52	0.24		0.4615		
Mean	0.42	0.235		0.61503			0.914	0.524		0.6359		
s.e.	0.254	0.129		0.159			0.308	0.325		0.167		

Appendix B 51. Soil Solution Chemical Parameters from Oak-Hickory Forest: Walker Branch Site.

	pH 3.5 treatment				pH 5.0 treatment			
	TMAI	NLMAI	DOM	H2O pH	TMAL	NLMAI	DOM	H2O pH
May	------mg/L------				------mg/L------			
Time (Hrs.)								
1	1.06	0.4		4.06	0.69	0.53		4.01
1	0.97	0.53	2.14	3.77	0.98	0.76		4.3
1	0.42	0.35			0.65	0.6	1.82	4.2
1	0.53	0.53	1.96	4.36	0.87			
1	1.1		2.13	3.73	0.96	0.52	2.09	4.4
24	1.24	0.62		4.07	1.38	1	2.4	4.22
24	1.44	0.6		4.29		0.5	1.41	4.1
24	1.28	0.57	2.12	4.11	1.32	0.52		
24	0.96	0.5		4.08	0.8	0.71		4.12
24		0.45	2.16	4.01	1.12	0.64	2.26	4.43
72	1.1	0.28	1.38	4.21	0.28	0.1	1.85	5
72	0.79	0.48	1.35	4.18	1.88	1		4.42
72	0.4	0.28	1.6	4.51	1.2	0.94		
72	0.64			4.53	1.08	0.52		4.33
72	0.98	0.55		4.23	0.94	0.24		4.41
144	0.68	0.58		4.28	1.9	0.83		4.03
144	1.34			4.25	3	1.14		
144	1.25	0.29		4.81	1.28	0.43		4.24
144	1.05	0.27		4.49	1.8	0.98		4.11
144	0.58	0.24			1.06	0.66		5poor
October								
1	0.77	0.37	1.96	4.41	0.04	0.02		6.73
1	0.87	0.5			0.71	0.53		
1	0.55	0.3	1.4	4.42	1	0.47	0.89	4.19
1	1.32	0.77	1.87	4.11				
1	0.73	0.5	1.71	4.6	0.46	0.36		4.78
24	2.1	1.12			7.8?	1.21	2.19	3.96
24	0.39	0.28		4.45	1.35	1.14		
24	1.14	0.58	2.28	4.79	3.44	1.02	2.34	3.8
24	0.63	0.5			1.25	0.81		4.44poor
24	0.9	0.55		4.51	0.78	0.71	2.25	4.64
72	1.05	0.65		4.01	1.56	0.72		4.13poor
72	0.42	0.27		4.34	1.14	0.58		4.07
72	0.37			4.14				
72	0.2	0.2		4.52	2.78	0.94		3.96poor
72	0.42	0.12		4.07	0.9	0.66		
144	1.04	0.5	1.58	4.14	0.63	0.47		3.76
144	0.91	0.47			1.3	0.96		4.05
144	0.64	0.39	1.44	4.38	0.65	0.5	1.63	4.43
144	1.24	0.69		3.85	2.64	2.6	2.29	4.04
144	0.89	0.49		4.21		0.07	1.31	4.11

Appendix B 52. Concentrations (mg/0.10 L)Total Dissolved Elements in Soil Solutions from Oak-Hickory Forest Field Sites.

Melton Branch

	Ca	Mg	Fe	Mn	Cu	Al
MCC1	5.464	1.654	0	0.15	0	2.732
MCC2	5.464	1.703	0	0.116	0.057	3.85
MTC3	16.82	2.628	0	0.055	0.388	4.104
MTC5	18.1	2.87	0	0.041	0.057	1.086
TMA1	13.34	2.64	0	0.021	0	0.892
TMA2	3.27	1.246	0	0.028	0	1.153
TMA4	16.44	2.84	0	0.028	0	0.554
TMA5	12.37	3.038	0	0.056	0	1.324
TMC2	8.084	1.966	0	0.066	0	4.164
TMC3	3.035	1.01	0	0.082	0	1.739
TMC5	111.8	31.79	0	2.308	0	5.755
TMD2	6.67	1.854	0	0.009	0	1.44
TMD3	4.949	1.644	0	0.021	0	1.108
TMD4	5.568	1.644	0	0.021	0	0
TMD5	10.51	3.482	0	0.106	0	1.961
CMA1	5.041	1.595	0	0.099	0	1.192
CMA2	9.015	3.787	0.05	0.113	0	0.92
CMA4	6.01	2.093	0.14	0.169	0	1.197
CMA5	4.442	1.655	0	0.082	0	2.436
CMC1	5.862	1.798	0.08	0.09	0	2.013
CMC2	4.247	1.236	0	0.033	0	1.987
CMC3	5.56	1.741	0	0.033	0	2.052
CMC5	4.547	1.067	0	0.033	0	1.733
CMD1	4.949	2.142	0	0.134	0	0.499
CMD2	12.36	3.987	0	0.331	0	1.558
CMD3	3.535	1.295	0	0.084	0	0.864
CMD4	3.889	1.196	0	0.042	0	0.521

WalkerBranch

	Ca	Mg	Mn	Cu	Al
WTA 2	6.89	1.25	0.14	0	1.186
WTA 4	4.15	1.05	0.12	0	0.45
WTA 5	3.8	1.2	0.16	0.16	2.76
WTC1	2.83	1.2	0.17	0	1.05
WTC3	5.04	1.45	0.08	0	3.2
WTC2	2.73	1.121	0.226	0.02	3.592
WCA2	3.18	0.85	0.19	0.09	2.32
WCA3	3.09	1.05	0.11	0	0
WCA5	3.71	0.85	0.08	0	1.02
WCB3	0.44	0.15	0	0	0.8
WCC1	3.89	0.8	0.11	0	0.68
WCC2	10.43	2.39	0.35	0	3.39
CWA3	8.359	2.528	0.415	0.242	3.57
CWA4	10.61	3.34	0.94	0	2.9
CWD3	5.92	1.59	0.05	0	1.43
CWD4	10.08	2.49	2.1	0	2.46
CWD5	5.12	1.45	0.08	0	0.61
TWA1	6.055	1.361	0.054	0.056	2.591
TWA3	4.442	1.314	0.068	0.001	2.759
TWA4	10.32	2.82	0.204	0.027	3.236
TWD1	5.3	1.94	0.25	0	1.77
TWD3	10.25	1.801	0.096	0.015	2.608
TWD4	6.1	2.09	0.36	0	1.64

Sample Key:

M,C/T: May, pH 5.0/pH 3.5 treatment
T/C,M: October, pH 3.5/pH 5.0 treatment
3rd letter:
A = Hour 1
B = Hour 24
C = Hour 72
D = Hour 144
Sample # = 1-5

W,C/T: May, pH 5.0/pH 3.5 treatment
T/C,W: October, pH 3.5/pH 5.0 treatment

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