EXPORT OF NUTRIENTS THROUGH SIMULATED ACID RAIN OF AN ULTISOL FOREST SOIL

By

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EXPORT OF NUTRIENTS THROUGH SIMULATED ACID RAIN OF AN ULTISOL FOREST SOIL

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CHAPTER I

INTRODUCTION

The acidity of precipitation in the southern United States has increased since the 1950's. Industrial and internal combustion emissions are suspected to be the largest contributing factors, with emissions of sulfuric and nitrous oxides having increased by a factor of nearly 2.5 between 1955 and 1978. Additional increases in acidity may be due to migration of sulfuric and nitrous oxide emissions produced in the northeastern United States (Barrie et al., 1984).

Although the acidity of wet and dry deposition in Arkansas is not as low as in more industrialized regions of the world, it does receive a mean annual precipitation pH of 4.6 to 4.7 (Wagner and Steel, 1982). Precipitation pH levels as low as 3.5 have been observed for individual storms. Average annual pH values of less than 4.6 have been documented throughout the southeastern United States and parts of the Midwest (Cowling, 1983). In more industrialized regions, such as the northeastern United States, mean precipitation ranged from 4.0 - 4.6 with individual storms as low as 2.1 (Likens et al., 1979).

The pH of unpolluted rainwater is approximately 5.0 (Likens et al., 1979). This pH level is believed to be a function of the chemical equilibrium between the bases and acids found naturally in rainwater, excluding exotic sources of nitric and sulfuric acids (Likens et al, 1979).

Increased sulfuric acid in bulk precipitation may result in additional nutrient leaching of forest soils (Richter et al., 1983). A 20% reduction in base saturation and a pH drop of .6 units in the A1 horizon is projected to occur in a typical forest soil after 100 years of acid precipitation of 4.0 pH, if no addition of basic materials are added (Mcfee et al., 1976). However, losses produced by additional leaching could be offset by cation production through increased weathering caused by greater acidity (Johnson et al., 1982).

The ability of soils to adsorb sulfate is an important property in determining nutrient cation movement within the soil. Soil with a high capacity to adsorb sulfate can exhibit increased cation exchange capacity which can restrict nutrient leaching (Fuller et al., 1985; Johnson et al., 1982; Richter et al., 1983). Sulfate adsorption is dependant on iron and aluminum oxides. However, organic matter coatings appear to reduce sulfate adsorption, while lower pH enhances sulfate adsorption (Johnson et al., 1984; Fuller et al., 1985). At lower pH levels, humic acids are not soluble, resulting in increased organic matter coatings (Krug et al., 1983). Leaching of iron and aluminum oxides to a lower soil horizon is enhanced by the presence of soluble fulvic acids.

Coniferous and deciduous vegetation vary in the types and amounts of organic acids produced (Fuller et al., 1985; Hay et al., 1985).

There are other possible effects of acid deposition on the ecosystem in addition to nutrient leaching. Transport of hydrogen and aluminum ions from the soil to surface waters could cause detrimental effects to the aquatic ecosystem through low pH and aluminum toxicity (Fuller et al., 1985; Krug et al., 1983; Council for Agriculture Science and Technology, 1984). Toxic metals may accumulate near the root zone, decreasing the trees' ability to uptake nutrients and increase the susceptability to disease (Hutterman, 1985; Binns et al., 1982; Johnson et al., 1984). Mature pine plantations of high density are considered especially sensitive to acid rain if grown on shallow acid soils (Johnson, 1981). Many Oklahoma and Arkansas forests fit this description.

The soils under study are considered potentially sensitive to acid deposition as they have low cation exchange capacities, base saturation, alkalinities, available nutrients, and are acidic. The parent materials of these soils are sandstone and shale (Pettyjohn et al., 1983; USDA SCS, 1974).

Objectives

The primary objective of this study was to determine if sulfuric acidity contributed to additional leaching of nutrients from a forested ultisol soil. Secondary objectives were as follows:

1) To determine the ability of the soil to adsorb sulfate.
2) To determine the physical and chemical properties of each soil horizon beneath a conifer and hardwood forest stand.
3) To determine the changes in leachate chemistry resulting from acidic and nonacidic rainfall.

This study is important in providing additional understanding of basic soil chemistry under conditions of acid deposition. In combination with other studies of a similar nature it will help answer questions such as; what are the mechanisms involved for acid rain to leach nutrients, and what soil properties are able to retard the leaching of nutrients? If a decrease in pH of acid deposition continues, will fertilization be needed to supplement nutrients lost due to the combination of leaching, erosion, and biomass removal? Will it be economically feasable to manage these soils for timber in the future if rainfall pH decreases? Are these soils able to neutralize acid rain before it enters the aquatic ecosystem?

This study will contribute information that will add to the knowledge already existing on the effects of acid deposition on the soils of a forest ecosystem. However, because acid deposition has many interactions and is accumulative over a long period of time, it is a difficult area to research. Thus, there is a great need for basic research on acid deposition effects on the forest canopy, soil microorganisms, plant nutrient uptake, metal toxicity, and plant disease, in addition to nutrient leaching.

CHAPTER II

LITERATURE REVIEW

Acid Deposition

Acid deposition constitutes a problem that is complex and not well understood, in part because the mechanisms are complex and diverse and the effects on forests, soils, and aquatic ecosystems are cumulative over long periods of time.

Acid deposition is defined as wetfall and dryfall that contains sulfuric and nitrous oxides produced by fossil fuel combustion and internal engine combustion emissions (Smith, 1980). These sulfuric and nitrous oxides react with water to produce sulfuric and nitric acids (Fowler, 1980).

The major areas of the world where acid deposition is a recognized problem are the industrial regions of Japan, Europe, eastern Canada, and northeastern United States. The pH of rainfall in these regions is approximately 4.0 (Gravenhurst et al., 1980).

In the United States it has been hypothesized that the source of acid deposition in the South and Midwest originated from emissions carried by air currents from the industrial Northeast. However, this is based on limited data and it can only be concluded that acid deposition has increased since the 1950's. Reduction of pH from the 1950's to the 1970's in some regions has been as great as 1 pH unit which is a 10 fold increase in acidity (Barrie et al., 1984).

In the southern United States emissions from industry and internal engine combustion are suspected to be the largest contributing factor in precipitation pH reduction. Emissions of sulfuric and nitrous oxides have increased by a factor of nearly 2.5 between 1955 and 1978 (Barrie et al., 1984).

It has been estimated that emissions released 27 million metric tons of sulfur dioxides and 23 million tons of nitrous oxides in the United States during 1977. This level is expected to increase as much as 25% due to power generating plants shifting from oil to coal as a source of energy (U.S. Environmental Protection Agency, 1980).

Although Arkansas and southeast Oklahoma do not receive as much acid deposition as more industrialized regions, the pH of precipitation ranges from 4.6 to 4.7 (Granillo and Beasly, 1985; Wagner and Steel, 1982). Precipitation pH as low as 3.5 has been observed in individual storms. Average annual pH values of less than 4.6 have been documented throughout southeastern United States and parts of the Midwest (Cowling, 1983). In more industrialized regions, such as the northeastern United States, mean precipitation ranged from 4.0 to 4.6 with individual storms as low as 2.1 (Likens et al., 1979).

Recent literature indicates that the pH of unpolluted rainwater ranges from 4.5 to 5.6, depending on natural occuring acids resulting from CO_2, S, N, and organic compounds found in the atmosphere (Likens et al., 1979). An example of naturally ocurring atmosphere nitrogen is the NO_2 produced through nitrification caused by lightning (Likens et al., 1979; Galloway et al., 1984). In the past, it had been estimated that unpolluted rainfall would have a pH of 5.6, which takes into account CO_2 in equilibrium with the atmosphere (Smith, 1980; Hornbeck 1981; Council for Agriculture Science and Technology 1984).

Effects of Acid Deposition

Acid deposition has been suspected of contributing to the dieback of conifers in Europe and northeastern United States (O'Sullivan 1985; Johnson and Siccama, 1984). Although there is no scientific proof that acid deposition is the cause of this forest decline, evidence indicates that emissions containing SO_2 and NO_2 may be an important factor (Ulrich, 1982). However, in the northeastern United States, this forest decline may be the result of other more important factors such as stress created by drought (Council of Agriculture Science and Technology, 1984).

Acid deposition may cause toxic metals to accumulate near the root zone decreasing the trees ability to uptake nutrients and increasing the susceptability to disease (Hutterman, 1985; Binns et al., 1982; Johnson et al., 1984). Damage to the forest canopy may result in early leaf fall, growth disturbance, increased susceptability to frost and pests, disturbance of stomatal function, and increased transpiration (O'Sullivan, 1985). Direct damage to the canopy can be caused from nitrous oxides reacting with hydrocarbons in the atmosphere to form ozone gas (Mohr, 1983). Simulated acid rain experiments with pH values below 3.8 have produced visual damage to foliage after five or more treatments. However, at pH levels presently occuring in the United States, there has been no evidence that indicates direct damage to the canopy (Council of Agriculture Science and Technology, 1984).

Acid deposition can cause damage to the aquatic ecosystem through transport of H^+ and Al^{+3} from the soil or direct input of H^+ to surface waters. Low pH and aluminum toxicity have been shown to cause direct injury or reproductivity failure in fish (Fuller et al., 1985; Krug et al., 1983; Council for Agriculture Science and Technology, 1980).

Acid rain can cause additional nutrient loss through leaching of the soil and foliage by NO_3^-, $SO_4^=$, and H^+ (Council for Agriculture and Technology, 1980).

Damage to beneficial soil microorganisms can also be a result of acid deposition (Francis, 1982).

Nutrients

A soil gains available nutrients through the weathering of minerals and parent material, recycling of biomass, nitrogen fixation, and from atmospheric deposition (Johnson et al., 1968). In fact acid deposition may be benificial to forest soils deficient in nitrogen and sulfur. This is generally true in the case of nitrogen. However, soils deficient in sulfur are normally only found in remote regions far from an atmospheric pollution source (Johnson et al., 1982).

When excess sulfate input from acid deposition leaches through the soil profile, it may export nutrient cations with it (Richter et al., 1983; Johnson et al., 1982). Nutrients are also lost from a forest ecosystem by timber harvesting, stormflow, leaching of the canopy, litter, and soil by natural precipitation.

Previous studies on nutrient leaching found a sharp increase in calcium loss at pH less than 4.0, where 500 mm/month of sulfuric acid was leached for 40 days on a 40 cm deep column lysimeter (Bache, 1980).

Field experiments on the effects of sulfuric acid were conducted on five podzolic soils. Sulfuric-acid simulated rain was leached through soil profiles at 50 mm/month at pH levels from 2 to 6. Significant reductions in base saturation occurred after 2 years at a pH of 3. However, predicting how a soil will react to a moderate pH over a long period of time cannot be represented by using a large input of strong acid over a short period of time, as this process artificially lowers the pH and buffer capacity (Bache, 1980). This may initiate a process of increased chemical weathering that may not occur at a higher natural pH level (Bache, 1980).

Sulfate

The ability of soils to adsorb sulfate is an important property in the soils response to acid deposition. Soils with a high capacity to adsorb sulfate may show increased cation exchange capacity and decreased transport of nutrients on exposure to acid precipitation (Fuller et al, 1985; Johnson et al., 1982; Richter et al., 1983). At low pH, iron and aluminum oxide minerals within the soil have a net positive charge to which anions can attach. Anions such as sulfate may have only one of its two negative charges neutralized by the iron or aluminum oxide, thus, the cation exchange capacity could be increased, and nutrient cations adsorbed by the unneutralized negative charge (Johnson, 1980).

Organic matter contains fulvic and humic acids. Fulvic acids are soluble at low pH levels. However, humic acids precipitate at a pH less than 6.5 (Schnitzer, 1980). Organic matter appears to block sulfate adsorption (Johnson et al., 1984; Fuller et al., 1985). Thus, in acid soils, humic acids will precipitate, restricting sulfate adsorption (Krug et al., 1983). However, lower pH levels increase the net positive charge on iron and aluminum oxides. Thus, pH has a positive and negative effect on sulfate adsorption depending on the amount of humic acids present and the degree of H^+ concentration.

Fulvic acid, the major acid produced by decomposing coniferous litter, is dissolved in weak alkali and acid solutions, and can leach iron and aluminum oxides through a process called chelating (Fuller et al., 1985; Hay et al., 1985). As the fulvic acid dissolves iron and aluminum while moving downward through the soil, the iron and aluminum charge becomes neutralized and iron and aluminum oxides precipitate. Thus, a zone of accumulation occurs. This is most evident in sandy soils low in iron and aluminum oxides (Peterson, 1980).

Thus, sulfates which result from sulfuric oxide in emissions can play a major role in nutrient leaching in some soils (Matzer and Ulrich, 1985). The input of sulfate through acid deposition, in excess of the needs of the forest ecosystem, will leach nutrient cations or adsorb on aluminum and iron oxides in the soil (Johnson et al., 1982).

Studies have shown that soils that have mechanisms created by iron and aluminum oxides to retain sulfate prevent excessive nutrient cation leaching (Wiklander, 1975; Johnson, 1980). Soils without iron and aluminum oxides have no means of retaining exotic sulfate inputs, thus, cation nutrients and toxic aluminum ions are allowed to leach from the soil into lakes and streams (Likens et al., 1977).

Soils of the Ouachita Mountains of Arkansas and Oklahoma are not characterized to have the capacity to immobilize sulfate inputs, therefore, they are considered potentially sensitive to nutrient losses due to sulfate in acid deposition.

CHAPTER III

METHODS AND MATERIALS

Study Area

Soil and forest litter samples were collected from a loblolly pine (*Pinus taeda* L.) stand and an oak - hickory forest stand located on the Alum Creek experimental watersheds in the Ouachita National Forest, 35 km north of Hot Springs, Arkansas. The conifer and hardwood sampling sites were 1/4 mile apart. The basal area of the hardwood site was estimated at 80 square feet/acre while the conifer site was estimated at 120 sqaure feet/acre.

The soils of this area are classified as Typic Hapuldults and have parent materials comprised of bedded standstone and shale of the Atoka, Stanley, and Jackfork geologic formations. The parent materials in this mountain region have been faulted, severely folded, and eroded over geologic time. The mountain soils range from shallow rocky soils on the ridges to deep colluvial and alluvial soils at the toe slopes and in flood plains. The predominant soils have loamy surface horizons and very clayey sub-horizons, with shale and sandstone parent material at about 40 in. (James, 1982).

The climate ranges from mild winters to very hot and often dry summers. The average annual precipitation is 50 inches and ranges from 46 to 52 inches. Precipitation as snow is minimal (U.S. Department of Commerce, 1961).

Five distinct soil horizons were identified for the purpose of this study. The O = litter layer, A = dark organic mineral soil, E = leached gray soil, B = high clay accumulation, and C = weathered shale.

Soil depth to the C horizon of the deciduous stand was sightly less than that of the conifer. However the soil of the deciduous stand had a thicker A horizon (Figure 4).

Methods

Field Methods

Six soil sampling plots were randomly located; three in the conifer stand and three in the deciduous stand. The three plots were within a 1/2 acre site within the conifer and deciduous stands respectively, and were uniform in soil profile characteristics. Pits were dug with a backhoe at each sampling plot.

On June 4, 1987, soil and forest litter samples were collected from each soil horizon of the six soil pits. Thus, for every soil pit, soil samples were collected from the O, A, E, B, and C horizons. Forest litter (O horizon) samples were collected with as little disturbance as possible, were placed between pie plates, and then in plastic bags, as they were found on the forest floor. No effort was made to collect samples from the other soil horizons in an undisturbed condition. Enough soil samples were collected to run the required tests needed to characterize the soil and to prepare the soil columns used in the laboratory experiment.

The soil samples were refridgerated and transported to Oklahoma State University where the soils were tested and the laboratory experiment and analysis were performed.

Soil Testing

Soil subsamples were oven dried (105° C) to determine the gravimetric field moisture content (Gardner, 1965).

Soils were air dried and sieved through a # 10 U. S. standard sieve prior to chemical analysis.

Triplicate soil samples from each horizon of each pit were tested for cation exchange capacity, Na, K, Mg, Ca, base saturation, soil pH, exchangeable acidity, and organic matter. Soil samples from respective horizons from the three pits within forest sites were composited (within each site) for each soil horizon to determine texture, soluble sulfate, and sulfate adsorption isotherms.

Exchangeable cations (Na, K, Mg, Ca) were determined for cation exchange capacity and base saturation, by the ammonium acetate method using the buchner funnel procedure (Chapman H. D., 1965). Forty ml of 1 N NH_4OAC were added to 10 g of soil, mixed well, and allowed to stand for 1 hour to allow exchangeable cations to be displaced. The soil was then filtered with a number 42 Whatman filter and rinsed with five-10 ml portions of NH_4OAC. The filtrate was brought to volume of 100 ml. Cation measurements were made with atomic adsorption spectrophotometry.

Soil pH was determined using a 0.01 M solution $CaCl_2$ at a 1:1 soil to solution ratio and glass electrode (Peech, 1965). Ten ml of .01 M $CaCl_2$ were added to 10 g of soil and stirred several times over a 30 minute period. The glass electrode was then placed in the soil solution and pH determined.

Exchangeable acidity was determined using the barium chloride - triethanolamine method (Thomas, 1982). Fifty mls of 0.25 N $BaCl_2$ - 0.055 N triethanolamine adjusted to pH 8.0 was added to 5 g of soil, mixed well and allowed to stand for 1 hour to displace hydrogen ions. The soil was then filtered with a number 42 Whatman filter and rinsed with four-10 ml portions of $BaCl_2$ - triethanolamine. The filtrate was brought to 100 ml volume and titrated with 0.2 N HCl to a pH 5.1 indicator endpoint. Exchangeable acidity was calculated by comparing the volume of 0.2N HCl used in titrating the samples with a blank.

Soil organic matter was determined using the Walkley - Black Method (Nelson and Sommers, 1982). The soil was finely ground to pass through a 0.5-mm sieve. Five mls of 1 N $K_2Cr_2O_7$ was added to 1 - 5 g of soil. The amount of soil sample used was dependant on the estimated percent of organic matter. A small volume of soil was used for samples from horizons estimated to be high in organic matter, such as the A soil horizon, with a greater volume of soil used for soil horizons lower in organic matter, such as the E, B and C soil horizons. This was done to insure an excess of $K_2Cr_2O_7$ which reacts with organic matter. The soil was mixed rapidly with 5 ml of concentrated H_2SO_4 and allowed to cool. Then 15 ml of distilled water and 3 drops of ferroin was added. The mixture was titrated with 0.5 N ferrous ammonium sulfate until the color changed from green to reddish-brown. The percent organic matter was determined based on the amount of Cr_2O_7 reduced to Cr^{+3}.

Texture was determined using the hydrometer method (Day 1965). Forty g of soil was added to 25 ml water and 25 ml (30% H_2SO_4) in order to remove organic matter. The samples were centrifuged and the decant discarded. One hundred ml of calgon (50 g/l) was added to disperse the soil particles. The soil and solution was then transfered to 1000 ml cylinders and agitated with a plunger. Solution density was recorded by a hydrometer and calibrated with a blank. The percent sand was determined after 40 seconds following aggitation, and percent silt and clay were determined after 2 hours.

Soluble sulfate was determined by the water extractable sulfate method following the procedure by NCASI (1983). Eighty ml of distilled water was mixed with 4 g of soil and filtered through a .45 um membrane filter. Soluble sulfate was determined with the Dionex ion chromatograph.

Sulfate adsorption was determined by adding 6, 12, 25, 50, 100, and 200 ppm S in a 1:5 solid/solution ratio with a .01 N KCl background and shaking for 24 hours. The solutions were filtered with a 0.45 um membrane filter and the sulfate in solution was measured with the Dionex ion chromatograph. Sulfate adsorption isotherms were plotted using the sulfate adsorption data.

Soil Leachate

In the Laboratory, simulated acid rain, pH 3.8, and simulated natural rainfall (control), pH 5.6, with no sulfuric or nitric acid, were prepared based on the average ion concentrations of rainfall in the northeastern United States. These rainfall recipies were then applied to soil columns (See Table I and II for rainfall chemistry).

The soil columns were built with polyvinyl chloride pipe with a 8.9 cm diameter. Replicates of each soil horizon had equal volumes of soil which were consolidated by light tamping in the soil columns to approximate soil field densities. Depth of respective horizons simulated field conditions (Figure 4). Simulated rainfall was siphoned from a 5 gallon plastic-covered container to the soil columns where it was allowed to drip for 1 week. The soil columns were drained by a buchner funnel and leachate collected in a 5 litter plastic-covered container (Figure 1). A sample was

TABLE I

ION CONCENTRATIONS FOR RAIN SIMULANT MEQ/L

	pH 5.4	pH 3.8
H^{++}	0.0025	0.1581
Ca^{++}	0.0083	0.0083
Mg^{++}	0.0029	0.0029
K^{+}	0.0008	0.0008
Na^{+}	0.0073	0.0073
NH_4^{+}	0.0143	0.0143
NO_3^{-}	0.0074	0.0458
$SO_4^{=}$	0.0232	0.1404
Cl^{-}	0.0031	0.0031
PO_4^{-3}	0.0002	0.0002

Weighted average ion concentrations for New York, Pennsylvania, and Ohio NADP sites, June through September, 1979.

TABLE II

CHEMICAL COMPOSITION OF RAIN SIMULANTS MG/L

	pH (5.6)	pH (3.8)
NaCl	0.176	0.176
$CaSO_4$-$2H_2O$	0.709	0.709
$MgSO_4$-$7H_2O$	0.355	0.355
K_2SO_4	0.069	0.069
$NaNO_3$	0.368	0.368
$(NH_4)2SO_4$	0.746	0.746
NH_4NO_3	0.243	0.243
H_3PO_4 (85.2%)	0.008	0.008
H_2SO_4 (96.5%)	0	5.941
HNO_3 (70%)	0	3.149

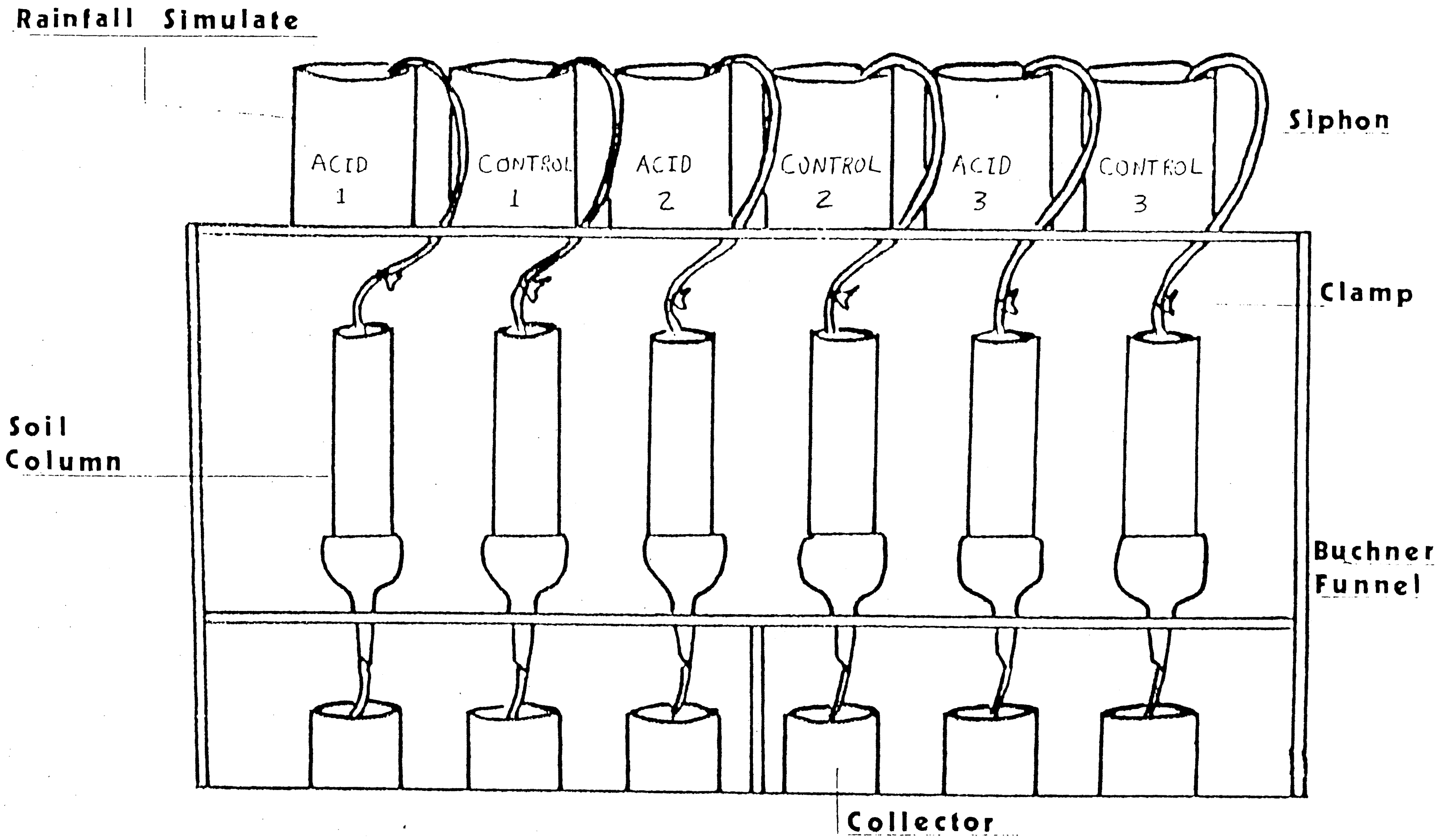

Figure 1. Soil Leachate Column Study.

collected and the volume of the leachate was measured and set aside to be siphoned through the next soil horizon. This procedure was repeated until the leachate was leached through all 5 soil horizons.

The soil columns were prepared by horizon, with rainfall first passing through the O horizon then the A, E, B, and C, simulating the order in which rainfall would encounter the soil profile in the natural environment. Soil leachate samples were collected between each horizon. Ninety seven cm of rainfall were applied to the O horizon. This was estimated to be the amount of rainfall which would annually reach the litter layer. The amount of simulated rainfall was subsequently reduced for the deeper soil horizons based on estimations which account for evaporation, transpiration, and interflow (see Figure 4).

Soil leachate was analyzed for SO_4, NO_3, and Cl with the Dionex ion chromatograph. Atomic adsorption spectrophotometry was used to analyze for Ca, Mg, Na, K, and Al.

Soils were retested for exchangeable acidity and pH following the leaching process.

Statistics

Values of P (probability of a greater F) of .05 or less were considered to indicate significant differences between factor levels. Values of P of .01 or less were regarded to indicate highly significant differences between factor levels. All calculated P values for statistical tests are given in appendix A.

Standard analysis of variance procedures were applied to all the soil and leachate chemistry data. Analyses of variance were also determined by soil horizon and site to detect interactions. The simple linear regression relationships between leachate sulfate and calcium, magnesium, and calcium + magnesium respectively, were determined. Means and standard deviations were determined for graphic presentations and interpretations.

CHAPTER IV

RESULTS AND DISCUSSION

Soil

Soil Texture and Depth

Clay content of the B soil horizon of the conifer stand was significantly greater than the clay content of the B horizon of the deciduous stand. The soil of the deciduous stand had 18% clay in the B horizon, compared to the soil of the conifer stand which had 55% clay. The C soil horizon of both stands were high in clay (60%) while the E horizons were high in sand (greater than 45%). The A horizons had an even distribution of clay, silt and sand (Figures 2 and 3).

Soil horizon depths also varied between sites. The soil of the deciduous stand had a thicker A horizon, while the total depth to the C horizon was slightly less than that of the conifer stand (Figure 4).

It is unknown why the soils differed in texture and depth between vegetation types. Depth and texture differences may be due to past management or that the deciduous trees are more competitive in the shallower droughty soil. It is unlikely that the vegetation had a

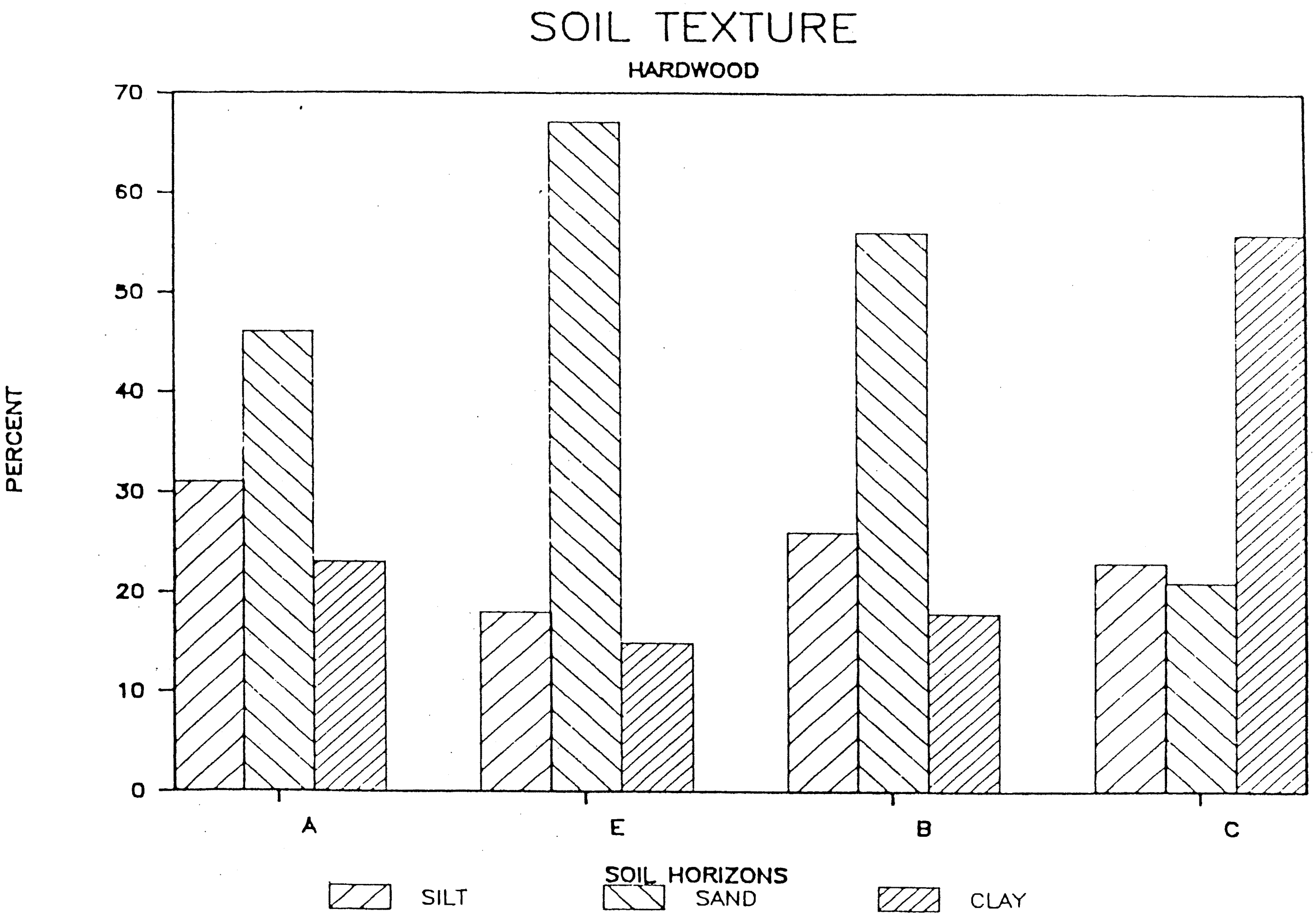

Figure 2. Soil Texture of Hardwood Stand.

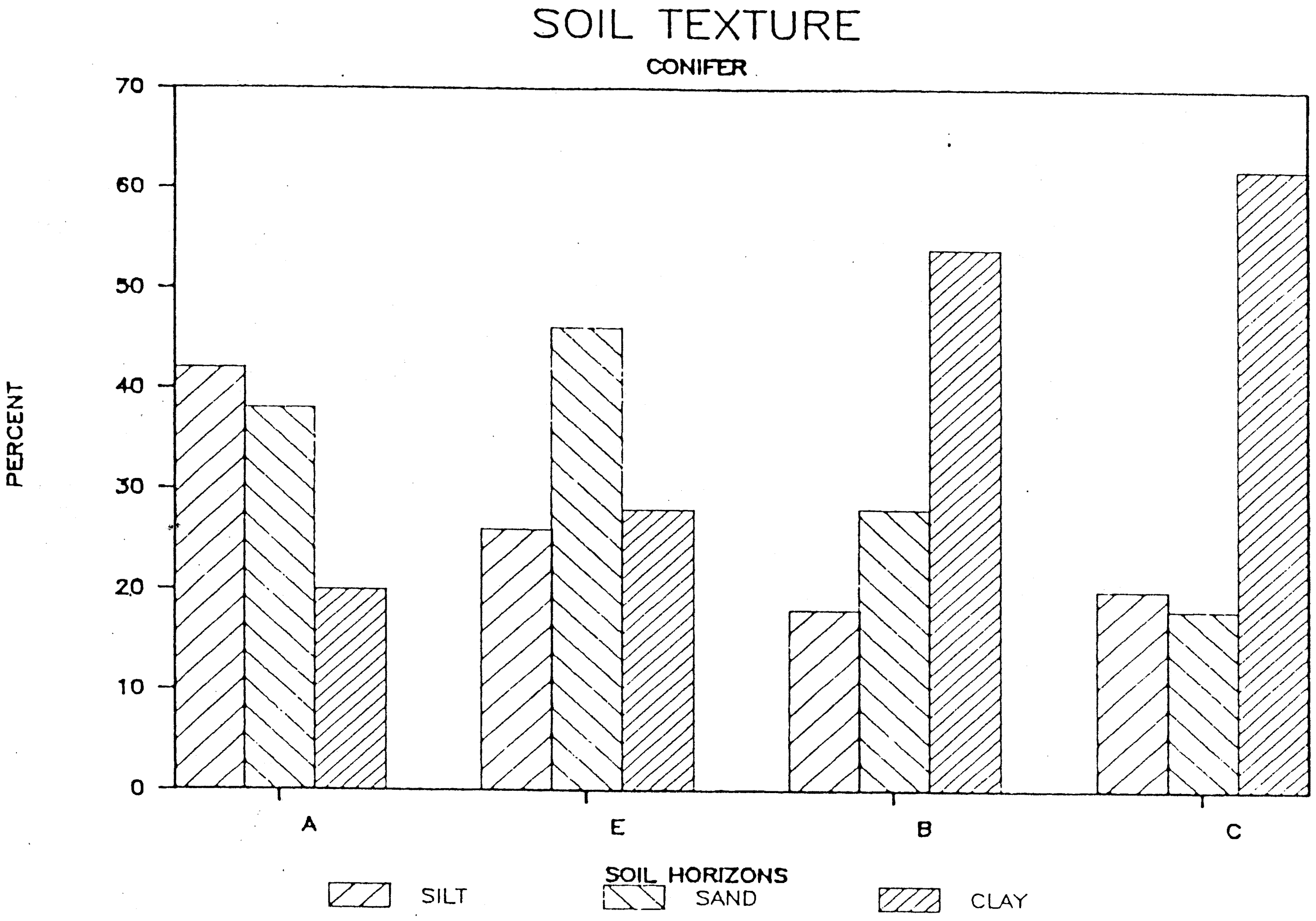

Figure 3. Soil Texture of Conifer Stand.

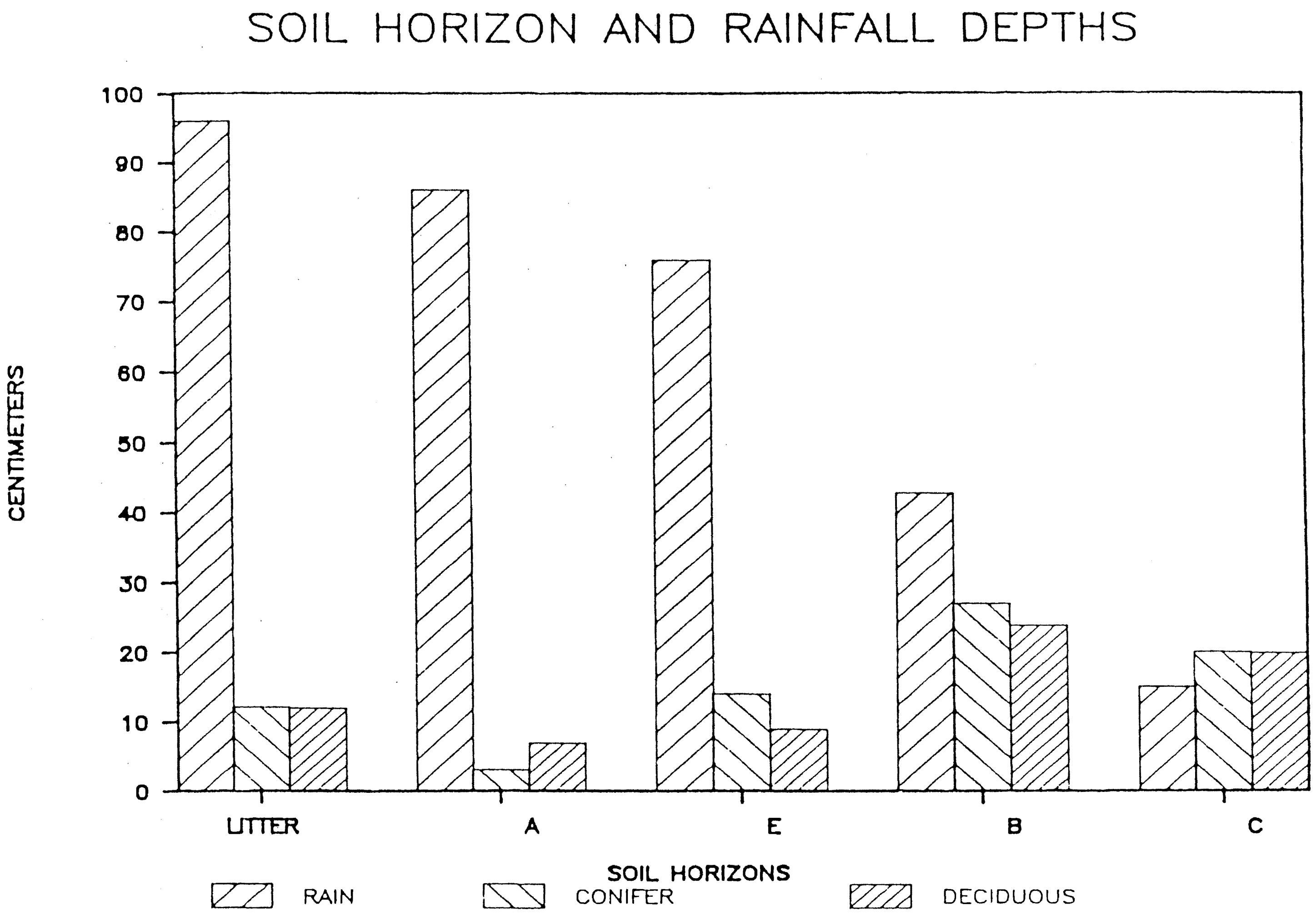

Figure 4. Soil Horizon and Rainfall Depths.

major influence on the measured soil physical properties. An exception to this observation is that the thinner A and thicker O horizon in the conifer stand is probably due to the acidity of the litter produced by the vegetation. This acidic condition slows the rate of litter decomposition and results in a thinner A horizon and a thicker litter layer under the conifer stand.

Soil pH

The soil pH increased slightly with soil depth (Figure 5). This may be due to the replacement of bases with hydrogen ions in the upper horizons and the accumulation of leached bases in the lower horizons. Organic acids produced by decaying organic matter in the upper horizons may also have contributed to the lower pH (Figure 5).

There was a small but significant difference in A horizon soil pH between the conifer site (3.3) and hardwood site (3.5). The differences in soil pH in the A soil horizon was probably due to the decomposition of the more acidic litter. No significant differences in soil pH were found in the other soil horizons.

Soil pH was determined with .01 M $CaCl_2$, thus, all the soil pH values are approximately 1 pH unit lower than if distilled water had been used.

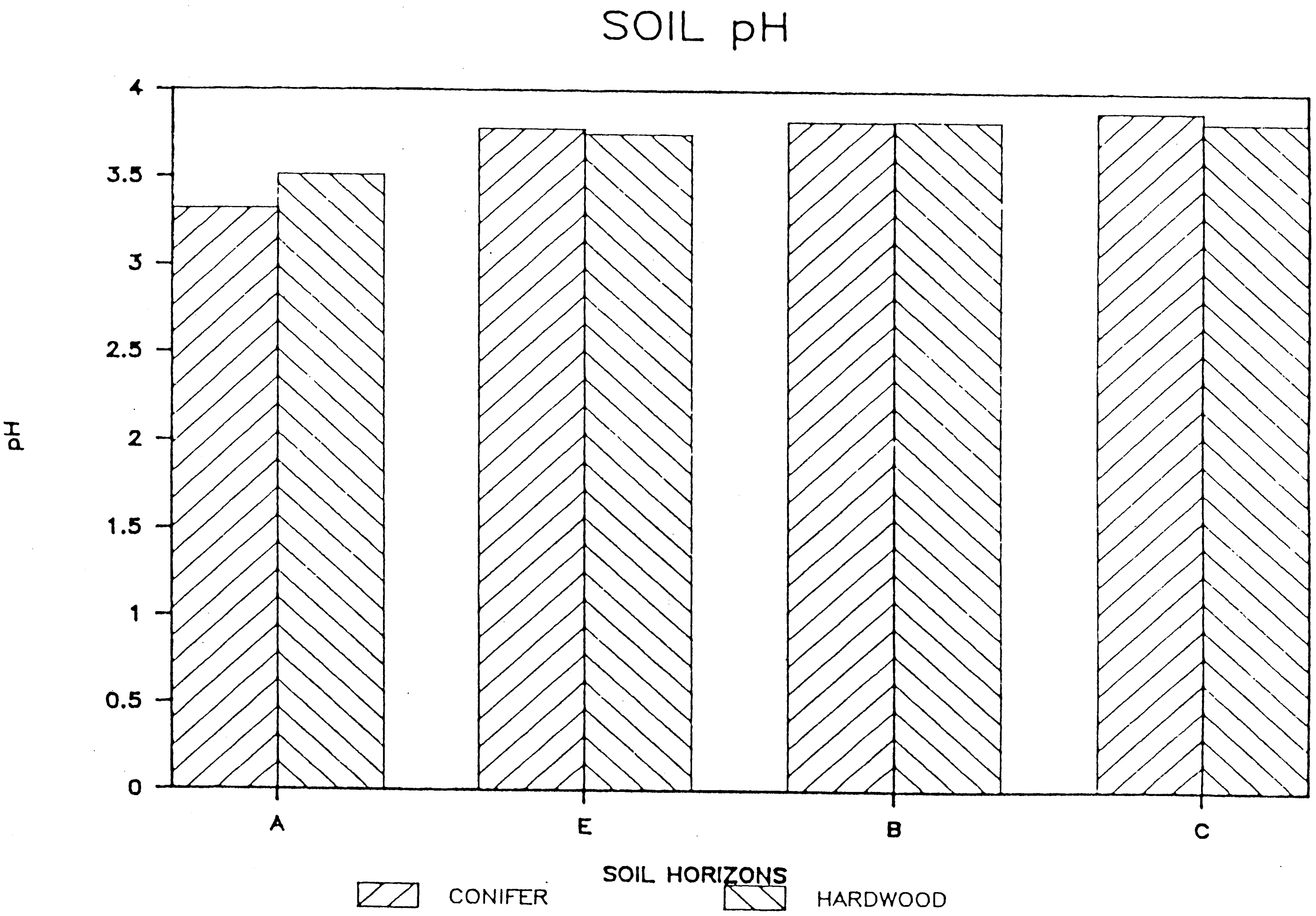

Figure 5. Soil pH.

Exchangeable Acidity

Exchangeable acidity is the sum of the hydrogen ions on the cation exchange sites expressed in meq/g of soil.

Exchangeable acidity is related to the high exchange capacity of organic matter and clays which are capable of retaining more acidity. For this reason exchangeable acidity is highest in the upper and the lower horizons, due primarily to a greater clay content in the C horizon and a higher amount of organic matter in the A horizon (Figure 6).

The soil of the conifer stand had significantly more exchangeable acidity than the soil of the hardwood stand in all soil horizons except the E (Figure 6). As with pH, this is likely due to organic acids produced by the litter and the leaching of bases to lower horizons.

Organic Matter

The A horizon of the conifer stand had significantly more organic matter than the A horizon of the deciduous stand (Figure 7). However, there were no significant differences in organic matter between the other respective soil horizons. The soil of the conifer stand had a high amount of organic matter (10.8%) in the A horizon, with significantly lower amounts of organic matter (< 3%) in the lower soil horizons. This is due to the slower

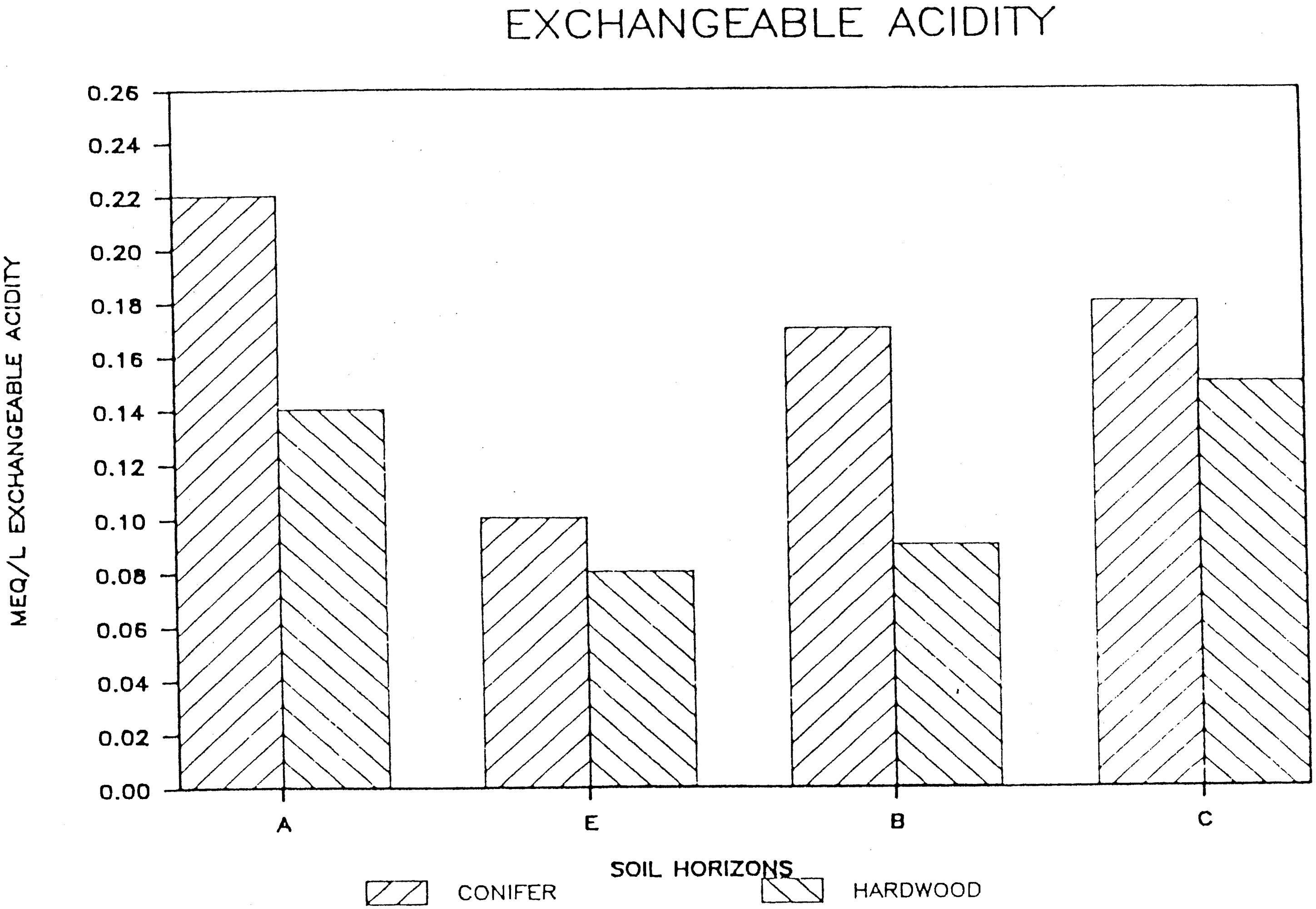

Figure 6. Exchangeable Acidity.

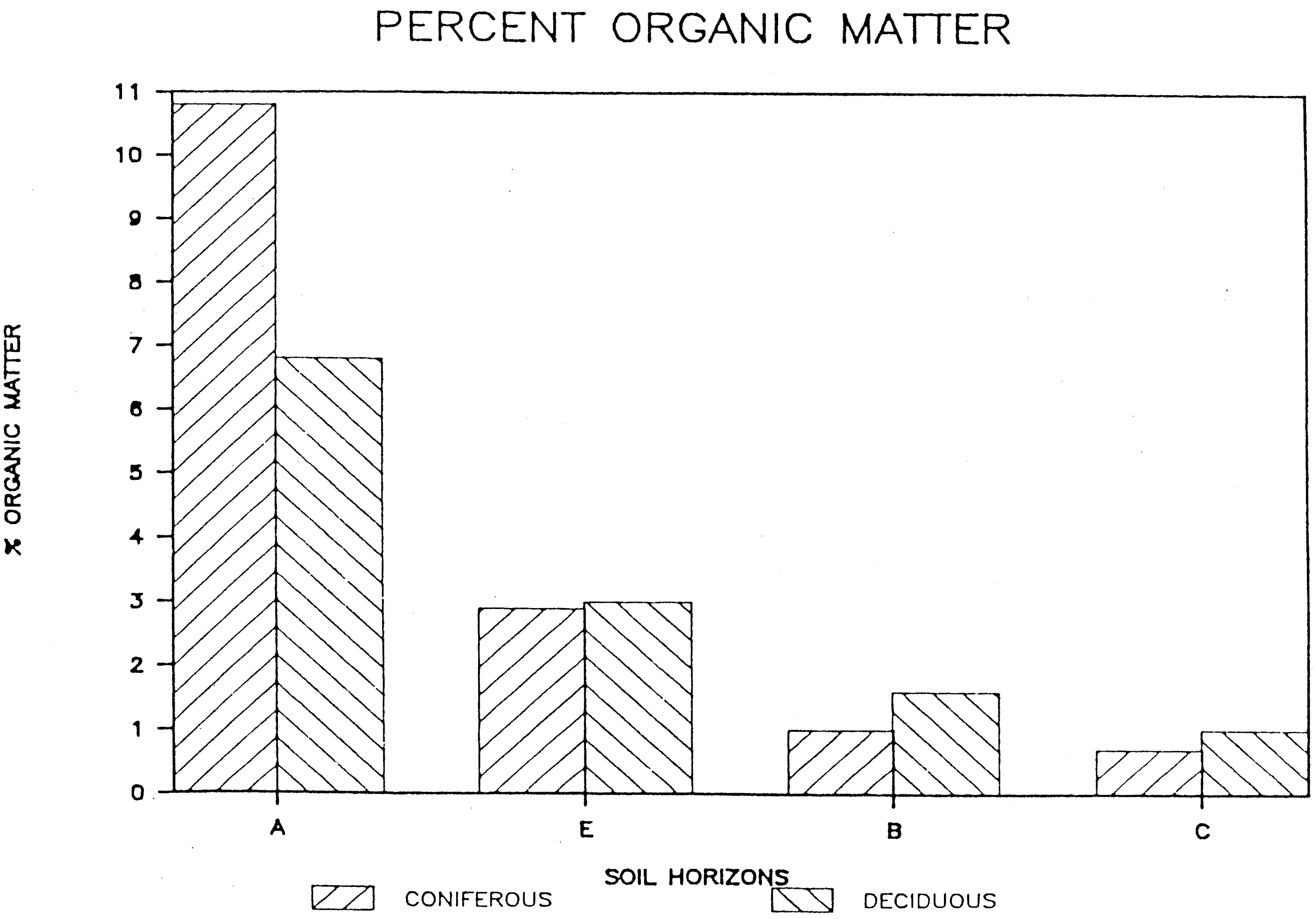

Figure 7. Percent Organic Matter.

decomposition rate of the acidic litter (Pritchett and Fisher 1985). The organic matter of the deciduous stand is more evenly distributed between the soil horizons (Figure 7).

Cation Exchange Capacity

The cation exchange capacities of the soils were relatively low overall (Figure 8). The cation exchange capacity was significantly higher in the A and B soil horizons of the conifer site, than the A and B horizons of the hardwood site. This was primarily due to a greater percentage of organic matter in the A horizon, and a higher clay content in the B horizon of the conifer site. There was no significant difference in cation exchange capacity between the conifer and hardwood sites in the E and C soil horizons. The cation exchange capacity averaged 0.23 meq/g soil for the conifer site and 0.16 meq/g soil for the hardwood site (Figure 8). Most southern soils, such as the soils in this study, are dominated by kaolinite clays and have low cation exchange capacities, while soils in the Midwest are high in illite, and montmorillonite clays have adsorption capacities ranging from 0.5 to 1 meq/g (Brady 1974).

Cation exchange capacity was highest in the A and C horizons of the conifer and hardwood sites. This is due to a high pecentage of organic matter in the A horizon and

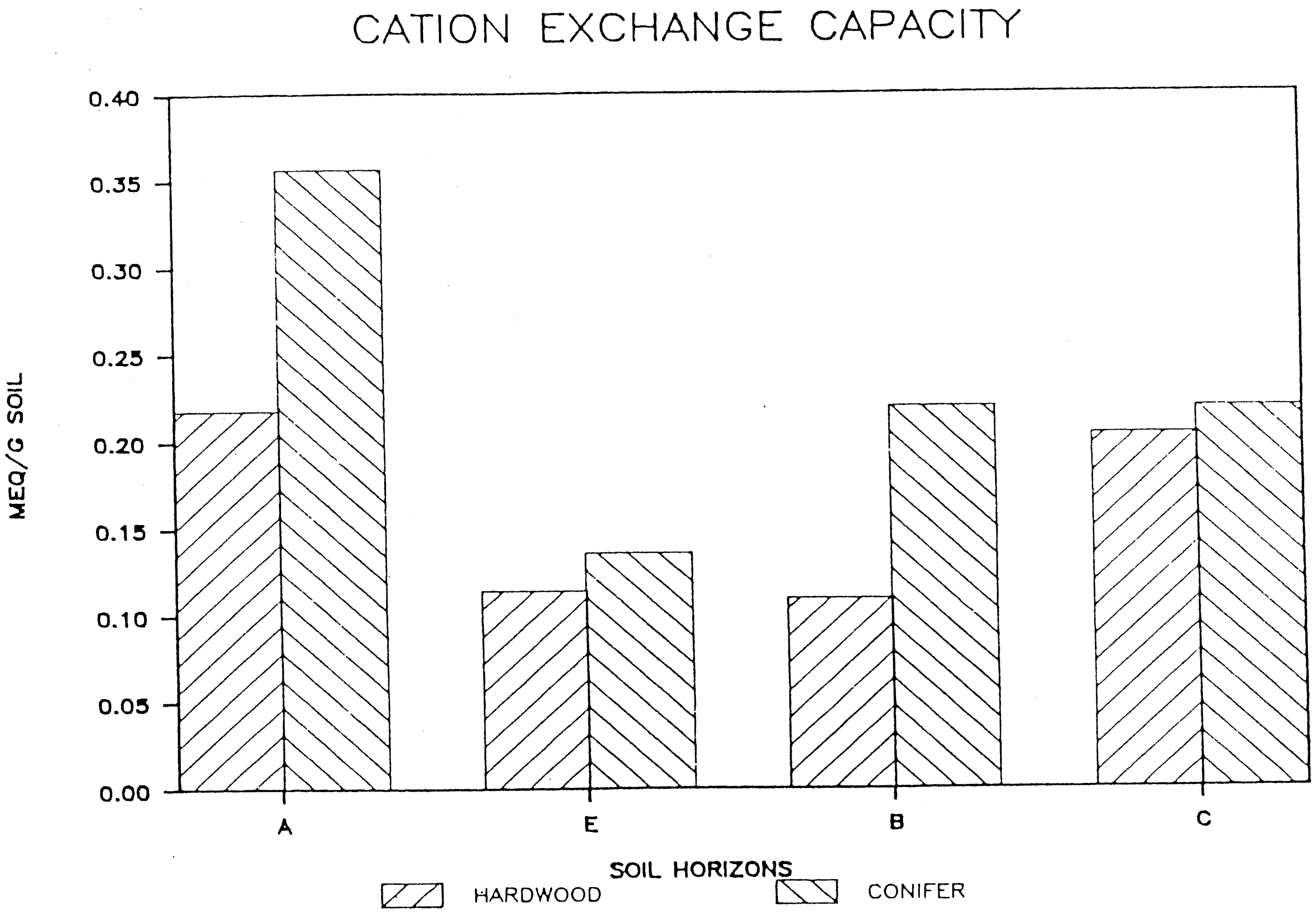

Figure 8. Cation Exchange Capacity.

clay content in the C horizon. The cation exchange capacity was higher in the A horizon of the conifer site than the A horizon of the hardwood site. This is due to the higher percent organic matter (10%) of the conifer site A horizon compared to (7%) organic matter in the hardwood site A horizon (Figure 7).

Nutrients

The base cations measured on the cation exchange sites were calcium, magnesium, potassium and sodium. Calcium dominated the exchange complex in the A and E soil horizons, while magnesium was most abundant in the B and C horizons. Potassium was more abundant in the A horizon, as potassium content of organic matter was high and was released as the organic matter decayed. The amount of sodium on the exchange sites was similar in all horizons (Figure 9 and 10).

The relative levels of calcium, sodium and potassium on the cation exchange sites were similar between the hardwood and conifer sites. However, the hardwood site had significantly more magnesium on exchange sites of the B and C horizons than the conifer site (Figures 9 and 10).

Base Saturation

Ultisols, by definition, have a base saturation less

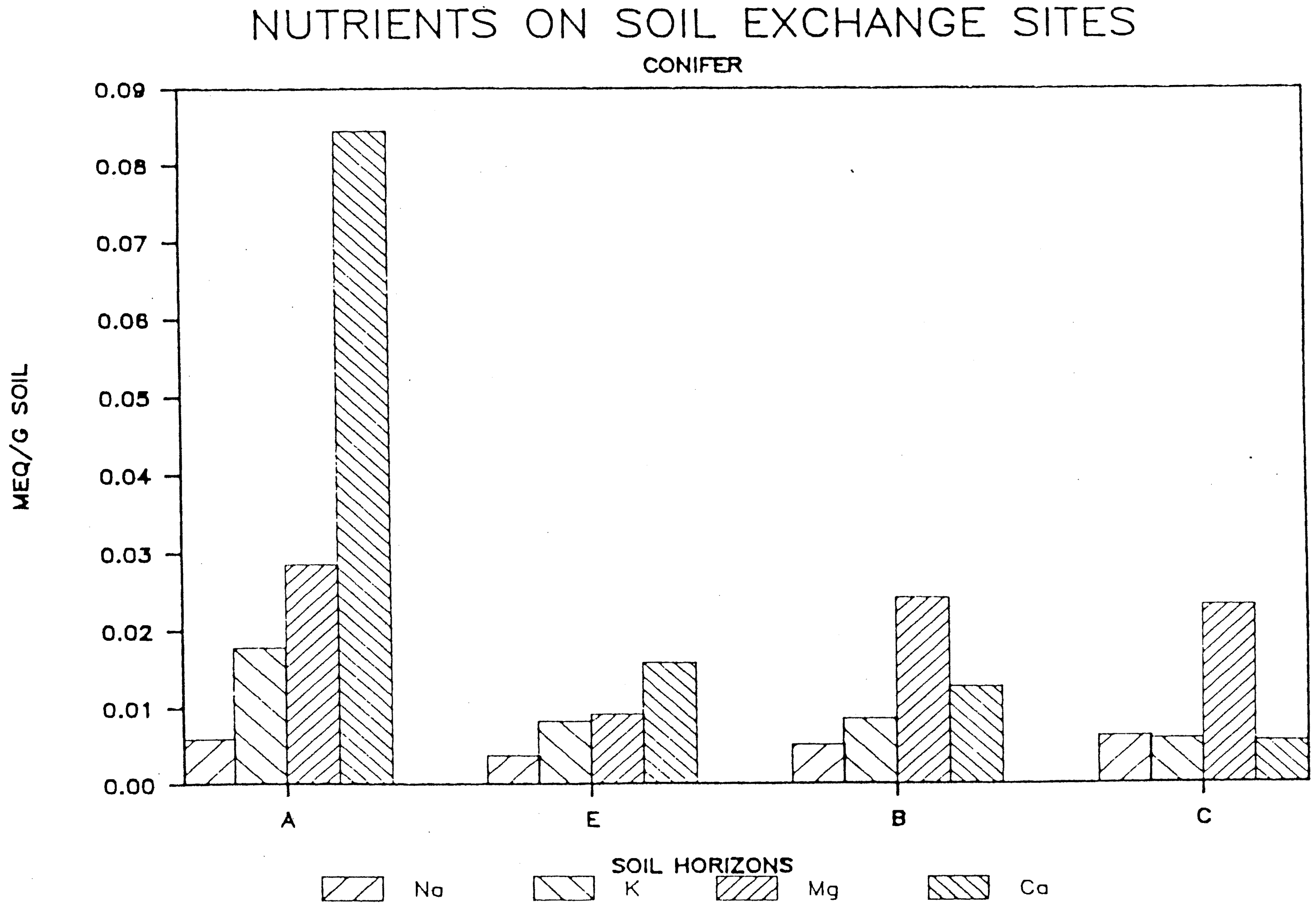

Figure 9. Nutrients on Soil Exchange Sites of Conifer Site.

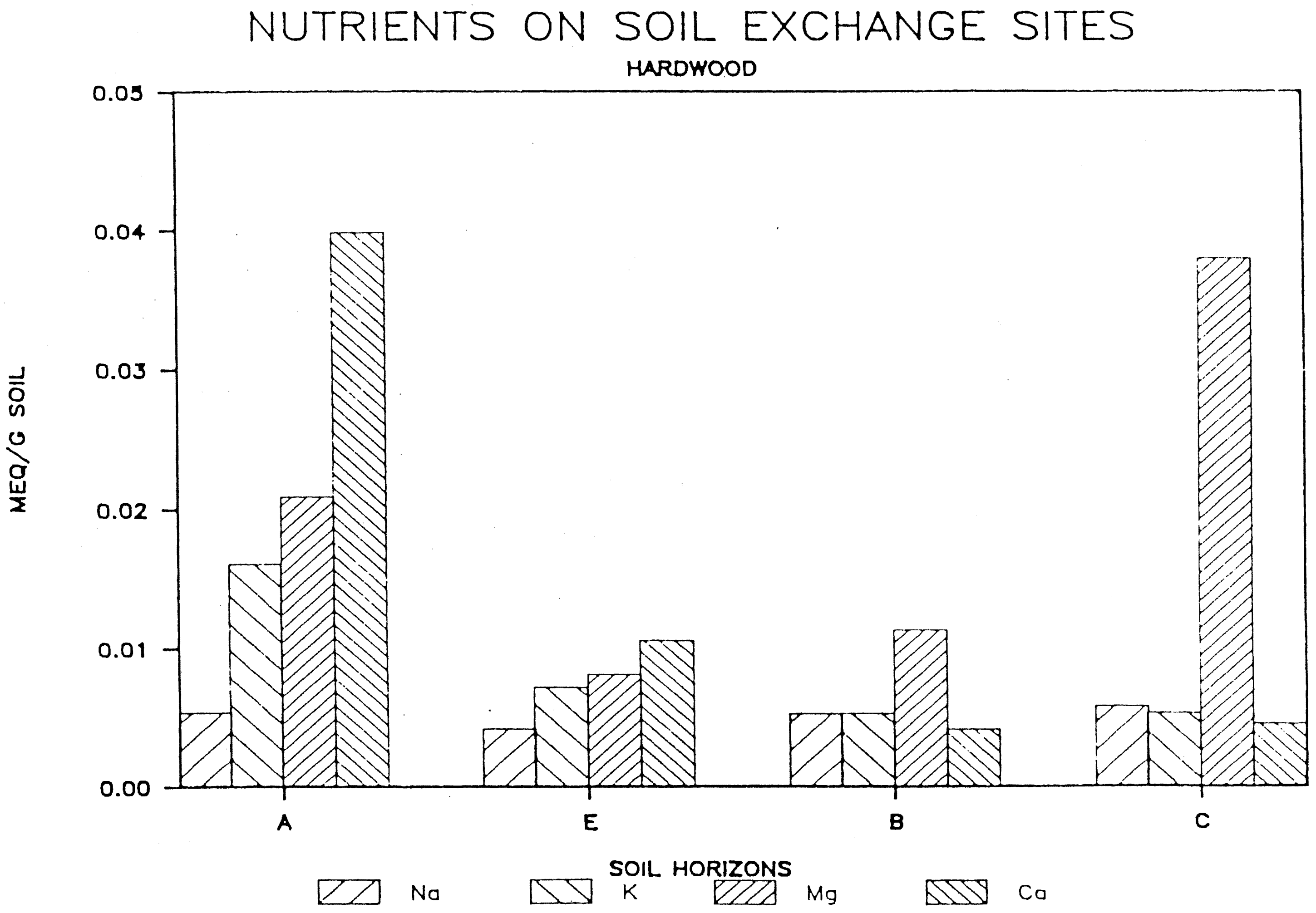

Figure 10. Nutrients on Soil Exchange Sites of Hardwood Site.

than 35% (Soil Survey Staff, 1975). The average base saturation for the soils in this study are 25 to 30%. This means that over 70% of the cation exchange sites of the soils under study are occupied by hydrogen ions (exchangeable acidity). Therefore, only a small percentage of the soils' cation exchange sites are occupied by cation nutrients. The soils under study decreased in base saturation in the lower horizons (Figure 11).

Sulfate Adsorption Isotherms

Sulfate adsorption isotherms were graphed by plotting sulfate adsorption on the Y axis and solution sulfate concentrations on the X axis (Figures 12 - 19). The sulfate level where sulfate adsorption was maximized was represented by the flattening of the curve.

When 100 or more ppm sulfer was added to the soil solution, it is believed that a sulfate precipitate was formed. This unexpected result was detected when precipitate was found in the sample bottles. This could help explain the change in slope in the isotherms at higher equilibrium sulfate values, where the amount of sulfate plotted as adsorbing to the soil actually includes precipitated sulfate.

Another possible explanation for the sharp increase in the adsorption isotherm slope after 100 ppm of sulfer was added is, the high sulfate concentration forced other anions

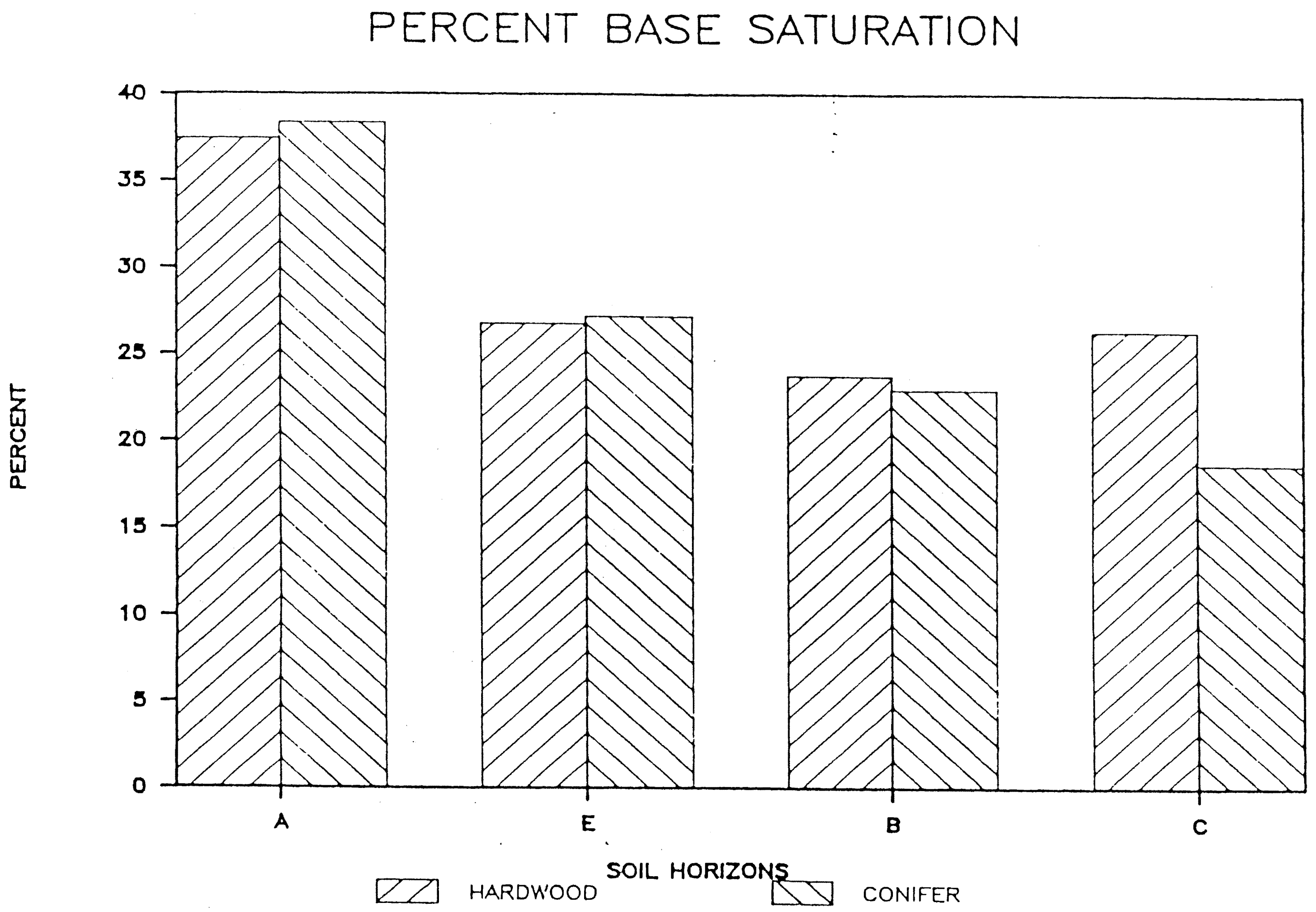

Figure 11. Percent Base Saturation.

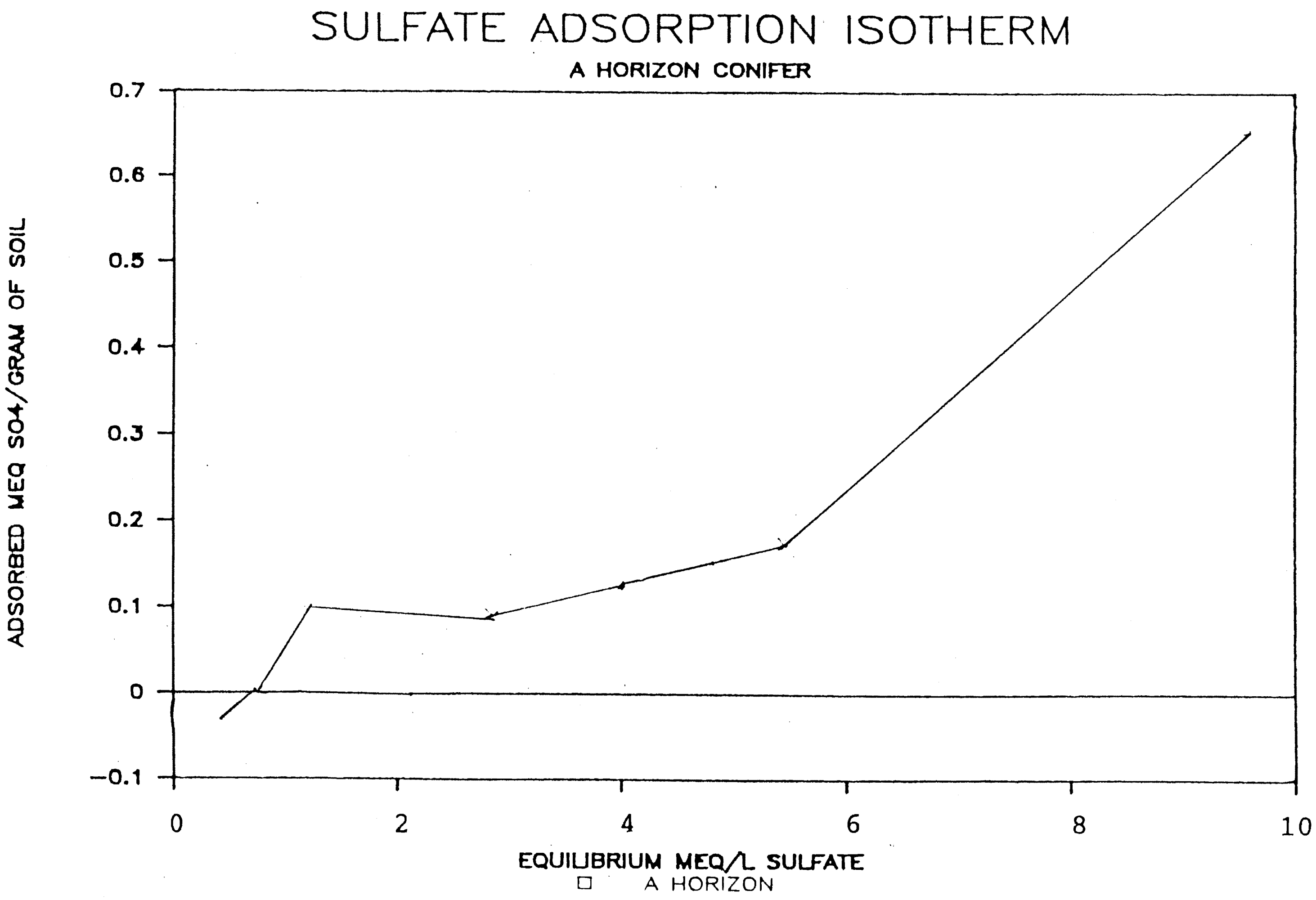

Figure 12. Sulfate Adsorption Isotherm of the Conifer Site A Horizon.

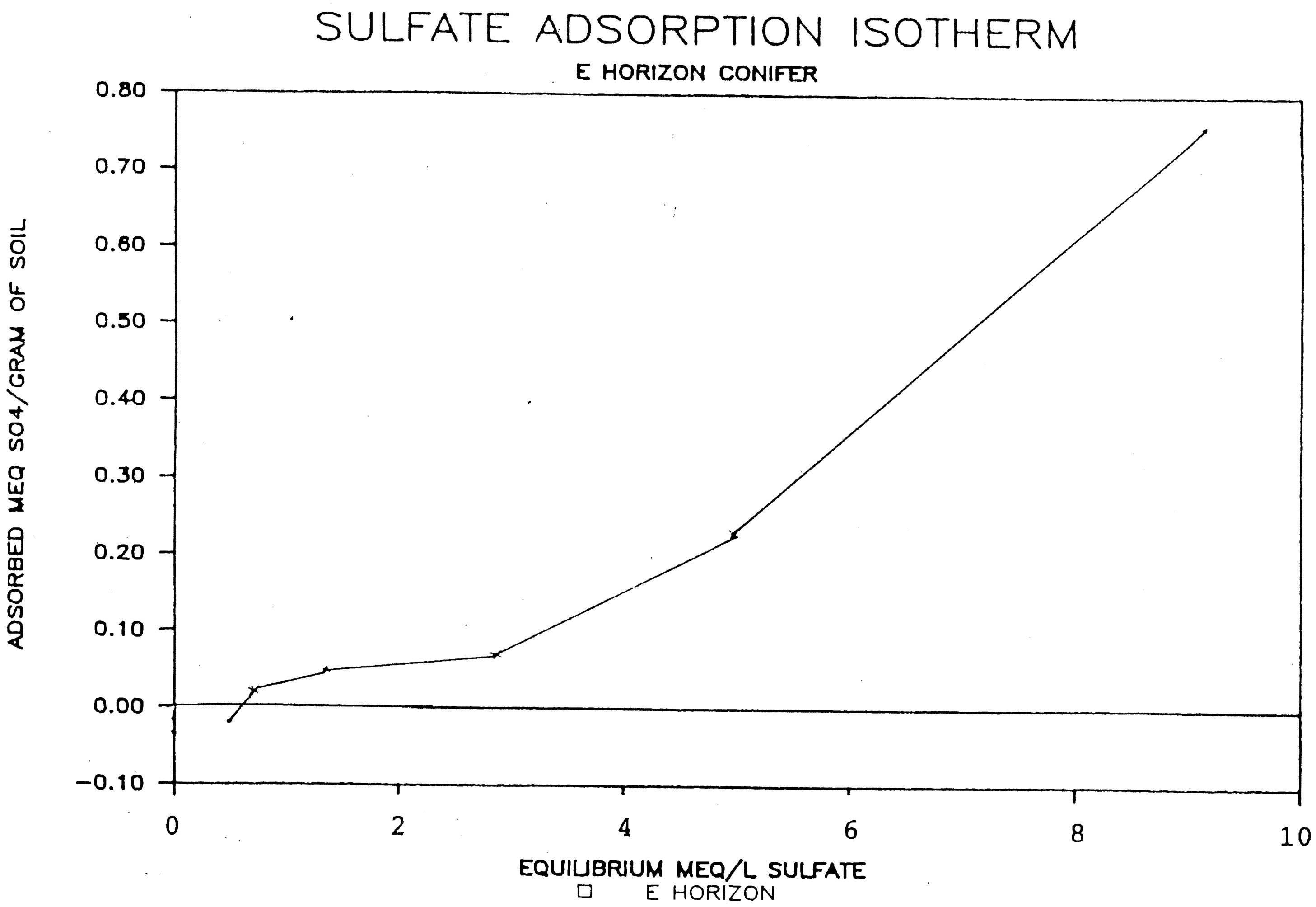

Figure 13. Sulfate Adsorption Isotherm of the Conifer Site E Horizon.

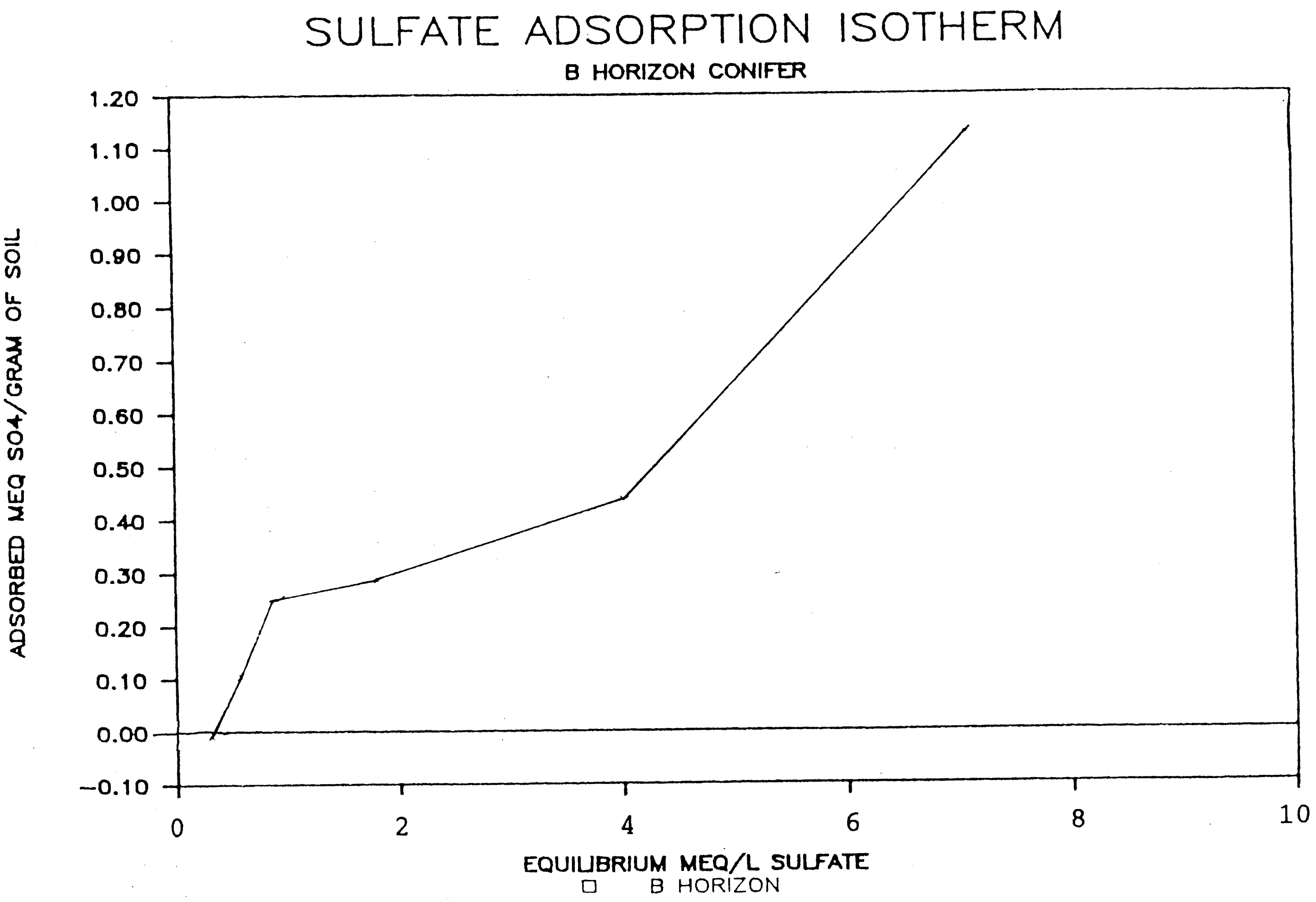

Figure 14. Sulfate Adsorption Isotherm of the Conifer Site B Horizon.

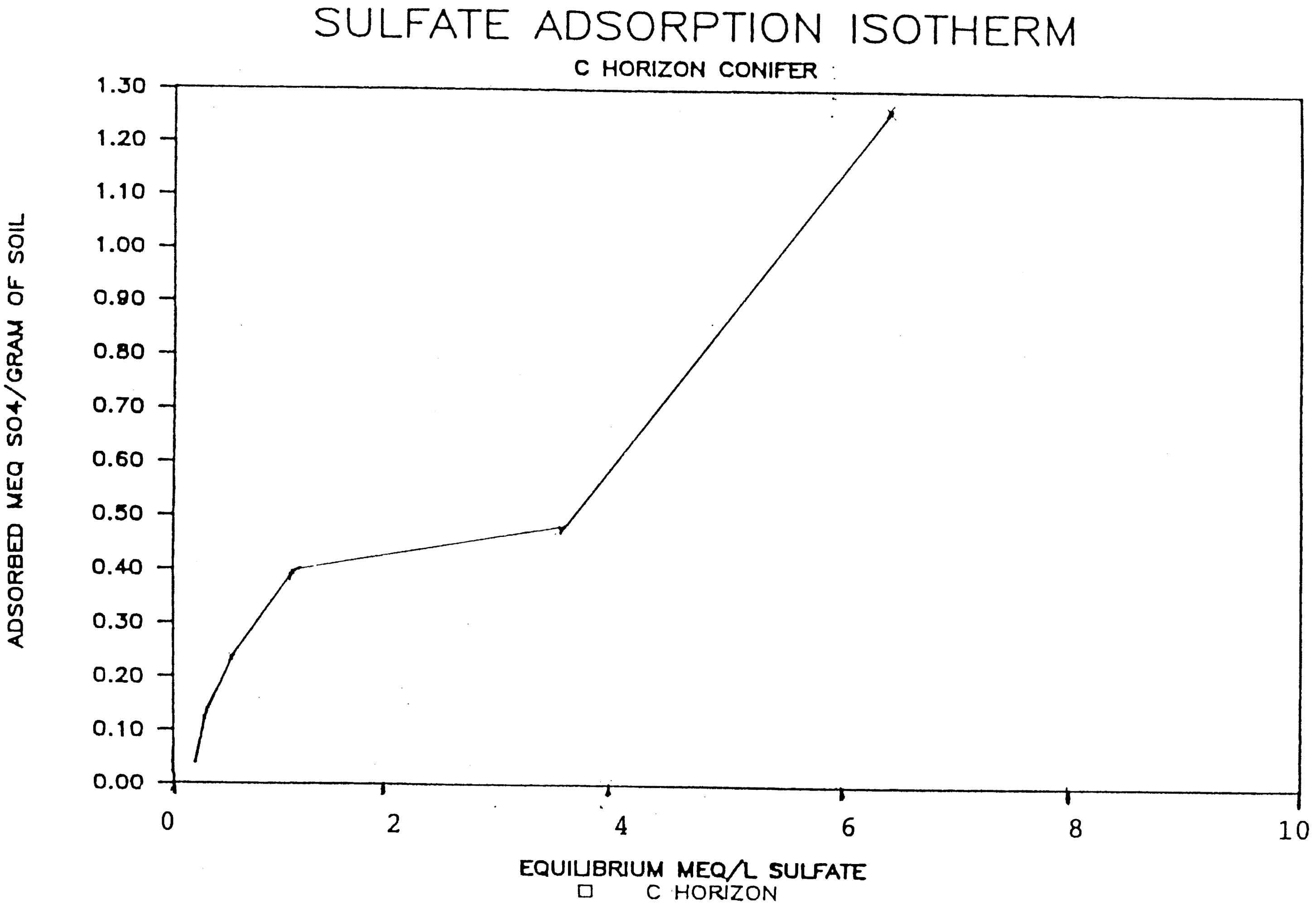

Figure 15. Sulfate Adsorption Isotherm of the Conifer Site C Horizon.

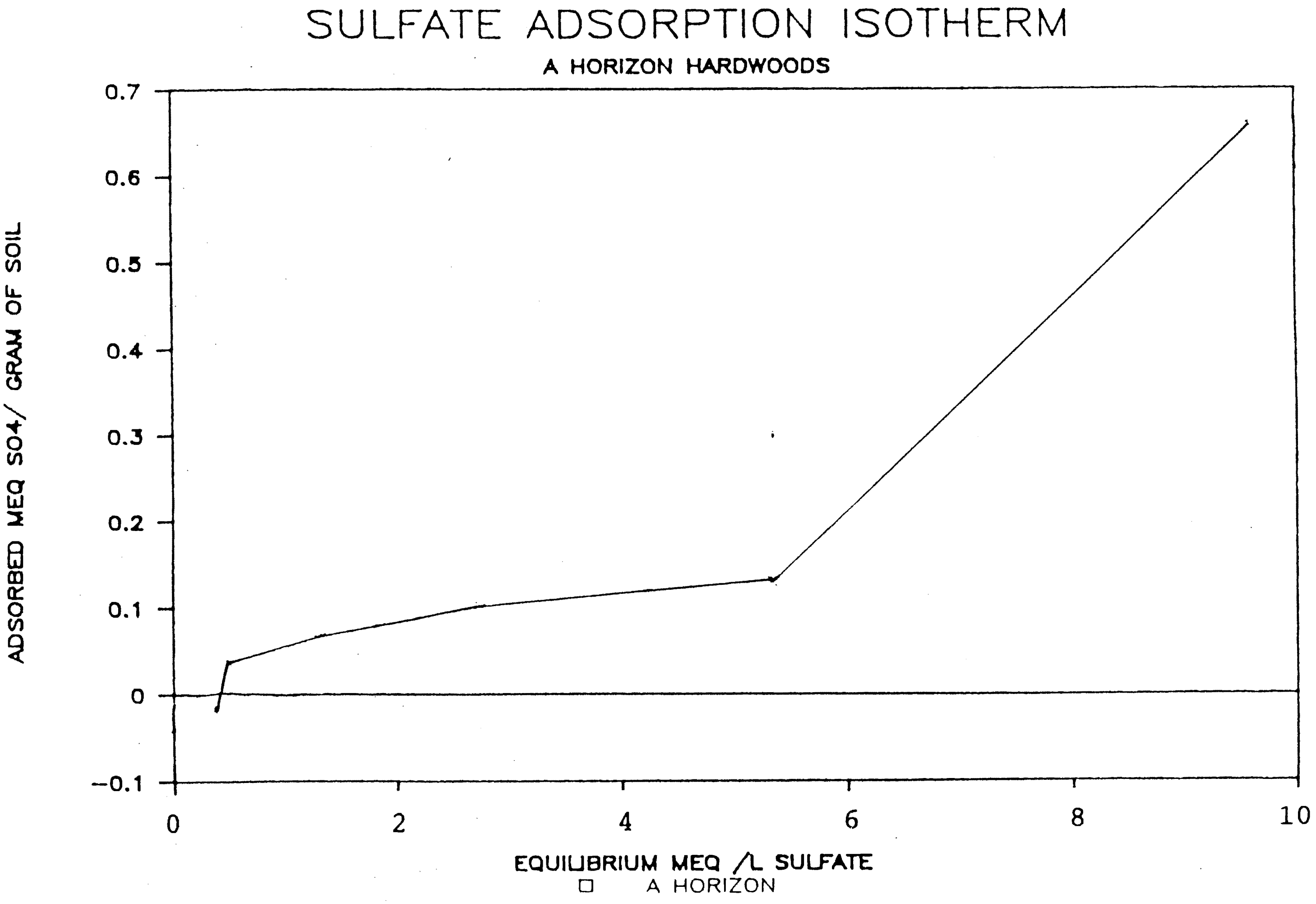

Figure 16. Sulfate Adsorption Isotherm of the Hardwood Site A Horizon.

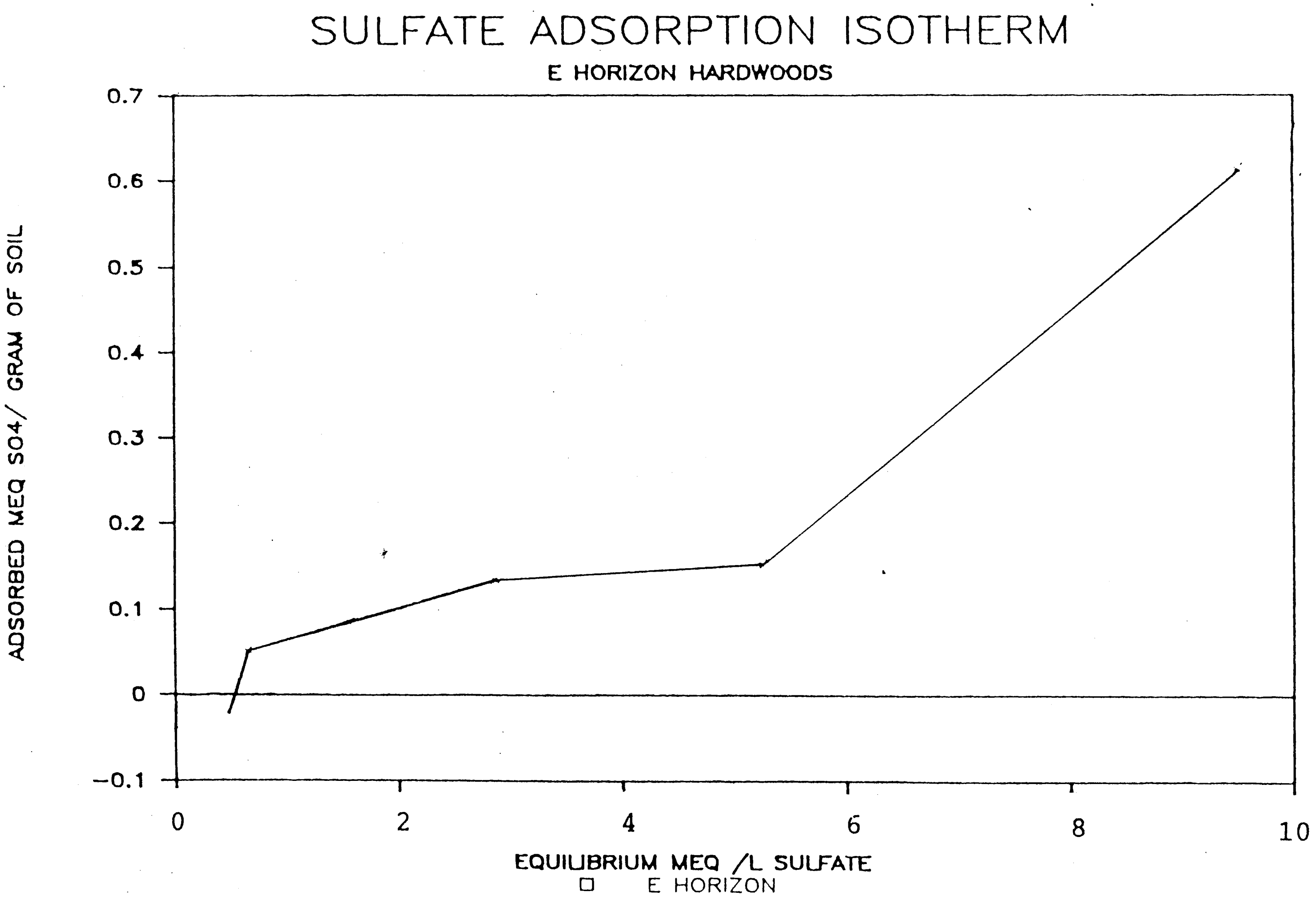

Figure 17. Sulfate Adsorption Isotherm of the Hardwood Site E Horizon.

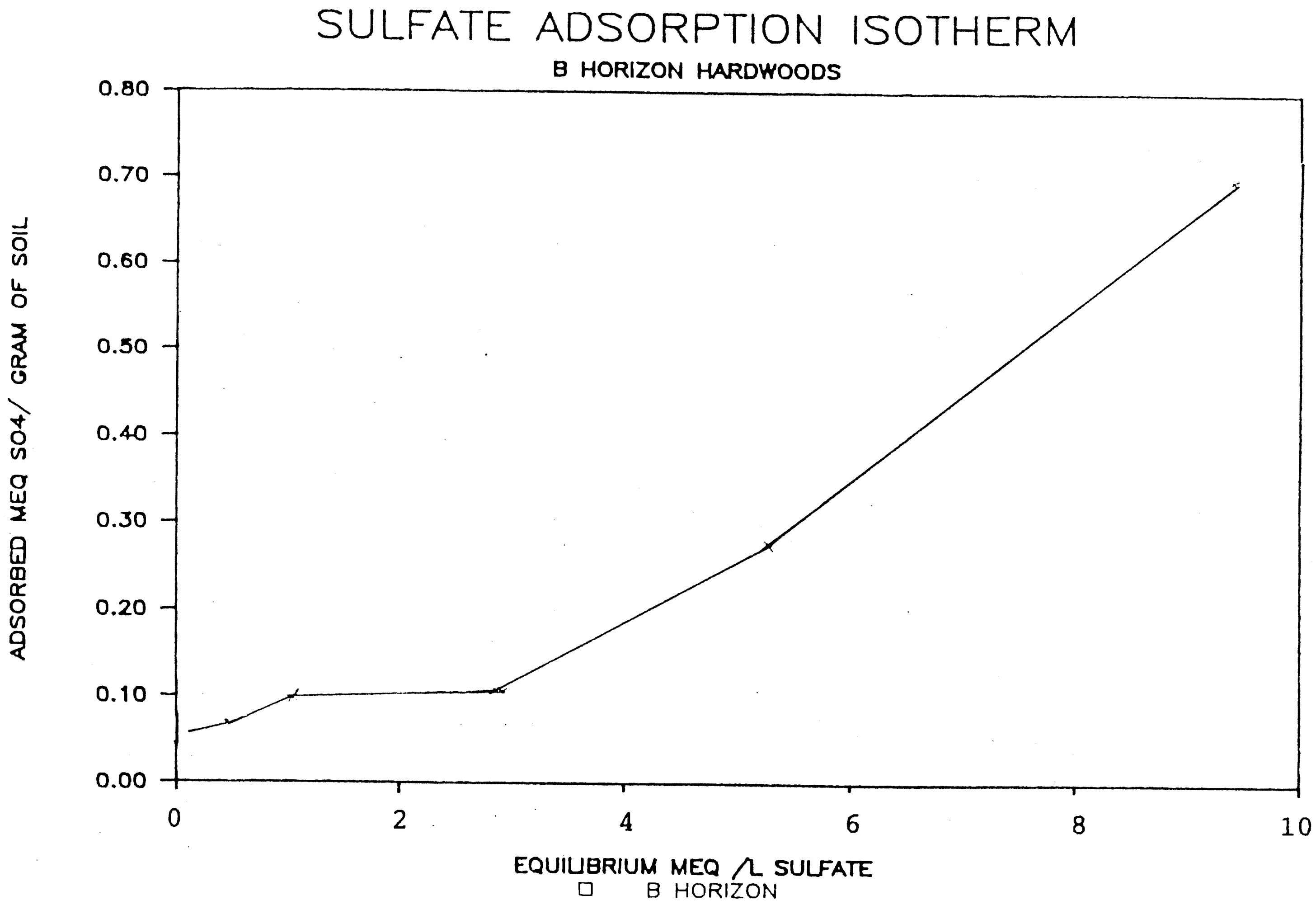

Figure 18. Sulfate Adsorption Isotherm of the Hardwood Site B Horizon.

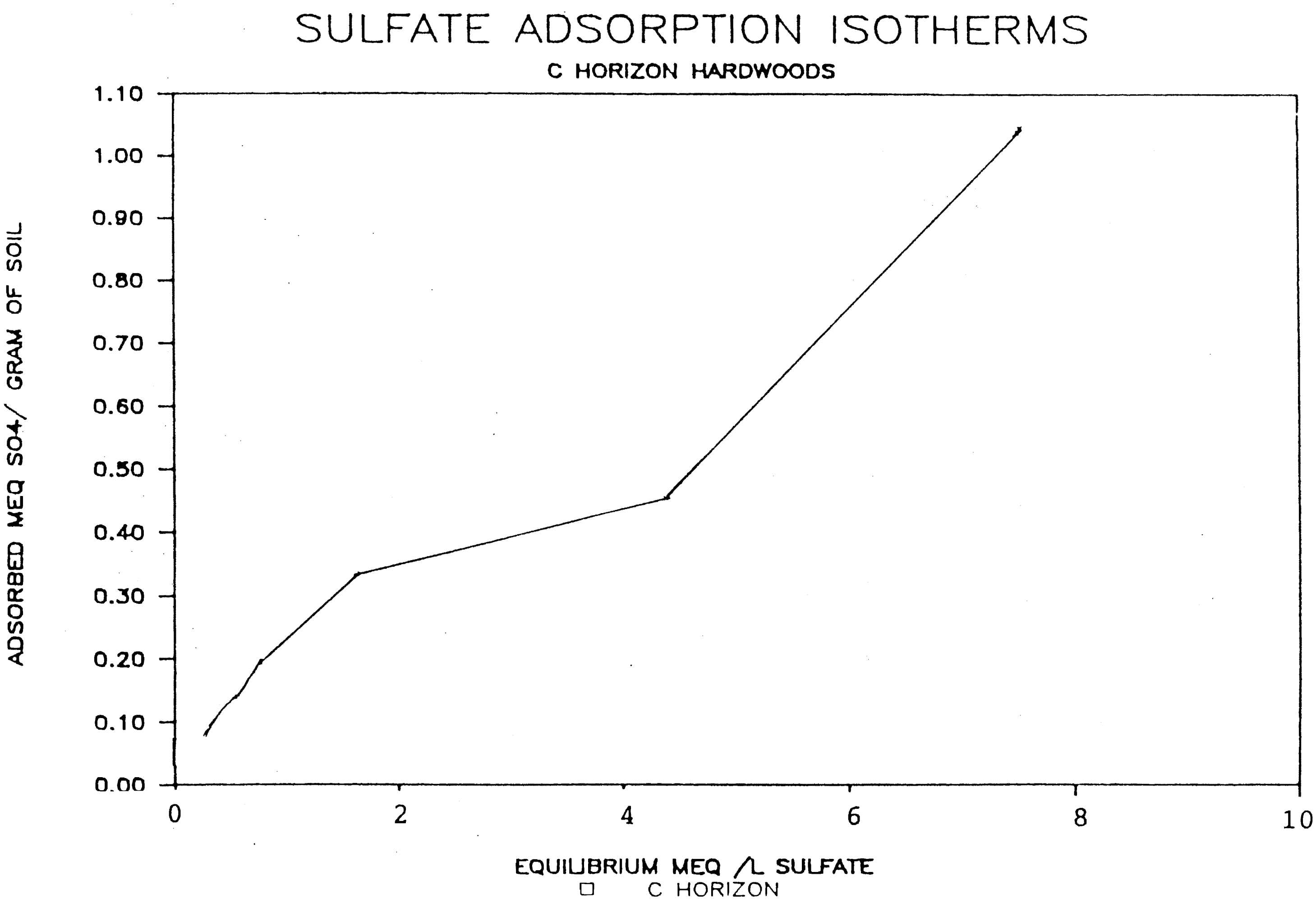

Figure 19. Sulfate Adsorption Isotherm of the Hardwood Site C Horizon.

from the exchange complex, resulting in a greater net positive charge, to which sulfate could adsorb.

The soils of both the conifer and deciduous stands adsorbed 0.8 to 0.12 meq sulfate/g of soil in the A and E soil horizons, which was low compared to the B and C soil horizons of the conifer stand which were able to adsorb 0.3 to 0.4 meq sulfate/g of soil. The B soil horizon of the deciduous stand adsorbed 0.12 meq sulfate/gram of soil which was low compared to the B soil horizon of the conifer site (0.3 meq sulfate/g of soil).

Sulfate adsorption appears to be correlated with clay content.

Soil Leachate

Leachate pH

Simulated rainfall pH levels of 3.8 (acid) and of 5.6 (control) were sequentially applied to the soil horizons. Leachate pH varied significantly between soil horizons. Leachate pH increased a full pH unit after passing through the O soil horizon. Hydrogen ions were adsorbed in the litter layer, raising the leachate pH. However, after passing through the A horizon the pH dropped, as exchangeable hydrogen ions were released into solution until an equilibrium was reached. Leachate pH then gradually increased to approximately 6.0 as it passed through the lower soil horizons.

The acid rain treatment resulted in lower leachate pH levels than those from natural rain as it passed through the upper soil horizons. The differences in leachate pH between acid and control were highly significant for the O, A and E horizons. In the B and C horizons, acidic rainfall became neutralized, and no differences due to rainfall pH could be detected (Figure 20 and 21).

Statistically, there was no significant difference in B horizon leachate pH between conifer and deciduous sites (Table VIII). However, the differences which did occur are noteworthy. The higher leachate pH from the B horizon of the conifer site occurred because the B soil horizon of the conifer site neutralized the acid rain resulting in a higher leachate pH. The B soil horizon of the hardwood site did not neutralize the acid rain resulting in a lower leachate pH. The ability of the B horizon of the conifer site to neutralize leachate acidity was related to the amount of clay and the cation exchange capacity. The soil under the conifer stand had a higher amount of clay and, therefore, a higher cation exchange capacity, and was able to adsorb hydrogen ions.

The O soil horizon of the hardwood stand was less effective in neutralizing the acidity in the acid rain than the O horizon of the conifer stand (Figure 20 and 21). This may be due to the conifer site having a greater volume of O horizon than the Hardwood site.

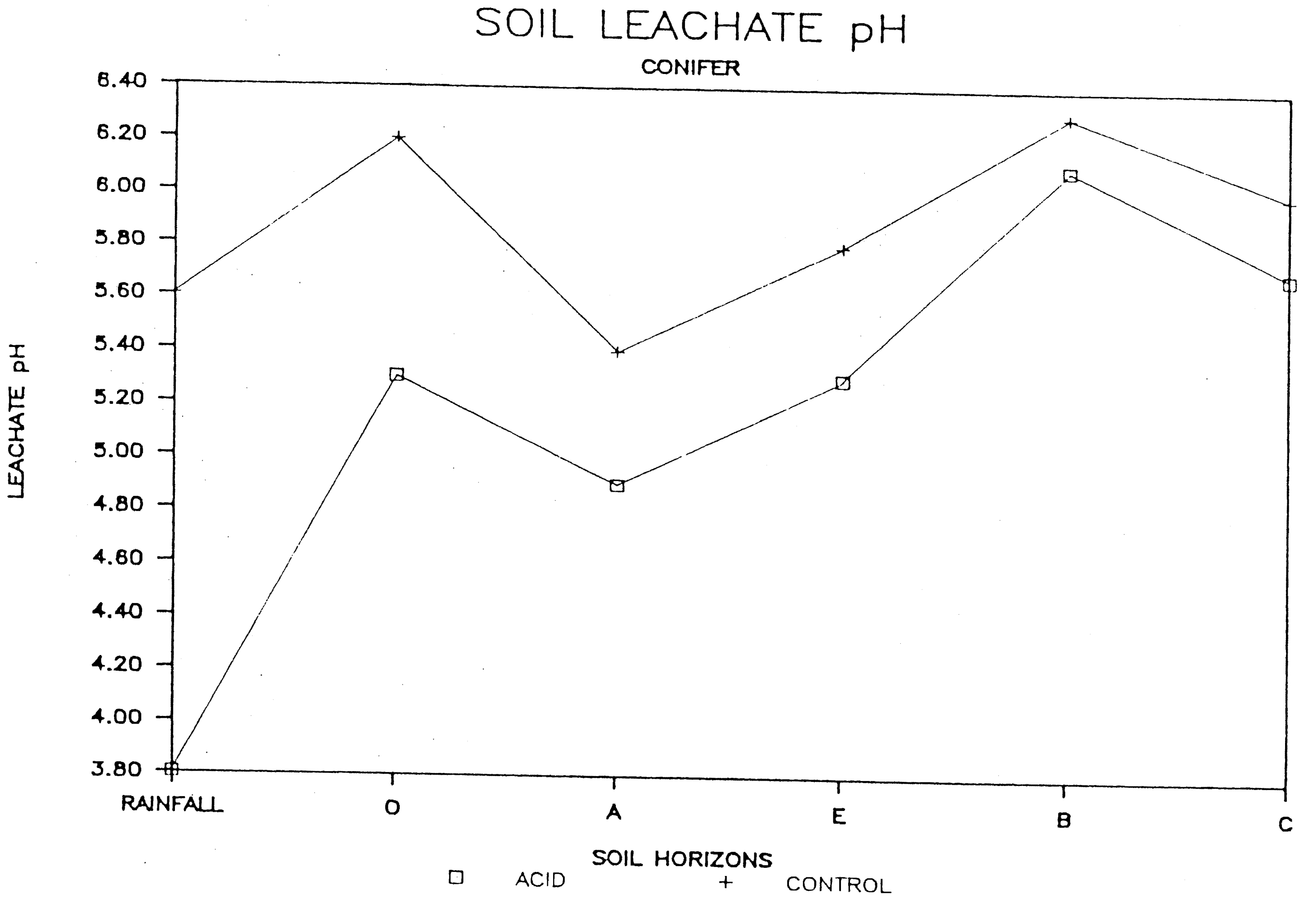

Figure 20. Soil Leachate pH of the Conifer Site.

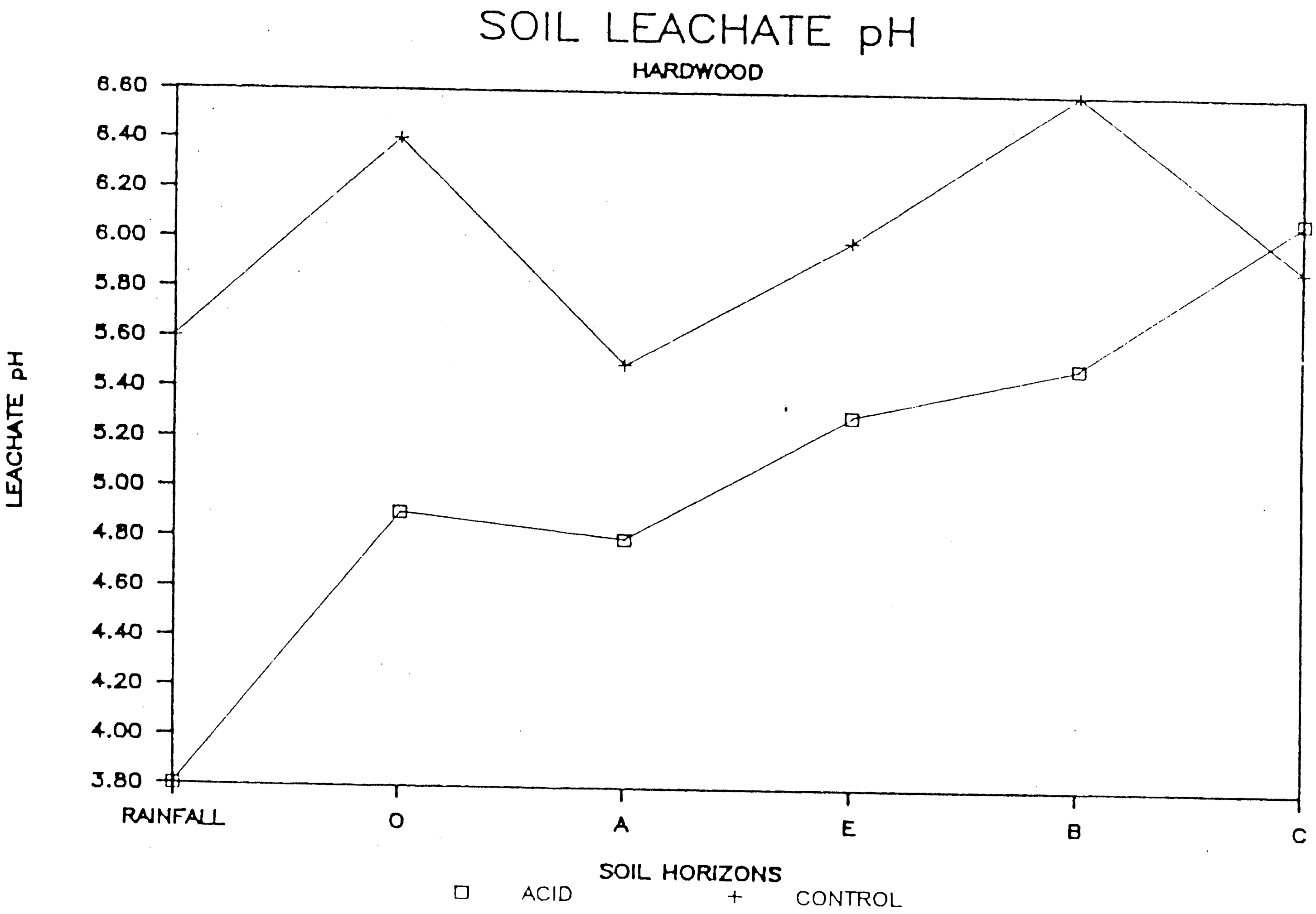

Figure 21. Soil Leachate pH of the Hardwood Site.

Leachate Chlorides

Highly significant increases in leachate chloride concentrations occurred as the simulated rainfall percolated down through respective soil horizons. This was probably due to the high solubility of chlorides and the mobility of the chlorides in the soil solution. The increase in chlorides was additive as the leachate passed through the soil. There were no significant differences in leachate chloride concentrations between acid and natural rain, which was expected as there were no differences in chloride between the acid and control rain recipies. There were also no differences in leachate chloride found between conifer and hardwood stands (Figure 22).

Leachate Nitrates

Nitrates were significantly higher in acid rain leachate in comparison to natural rainfall leachate (Figure 23). No significant differences in leachate nitrates could be determined between the conifer and deciduous stands. The large difference in leachate nitrate levels between acid and natural rainfall was simply explained by the higher nitrate level in acid rainfall in the form of nitric acid.

Nitrates increased slightly in the upper horizons, as soluble nitrate produced by decomposing organic matter was added to the leachate. However, nitrate concentration

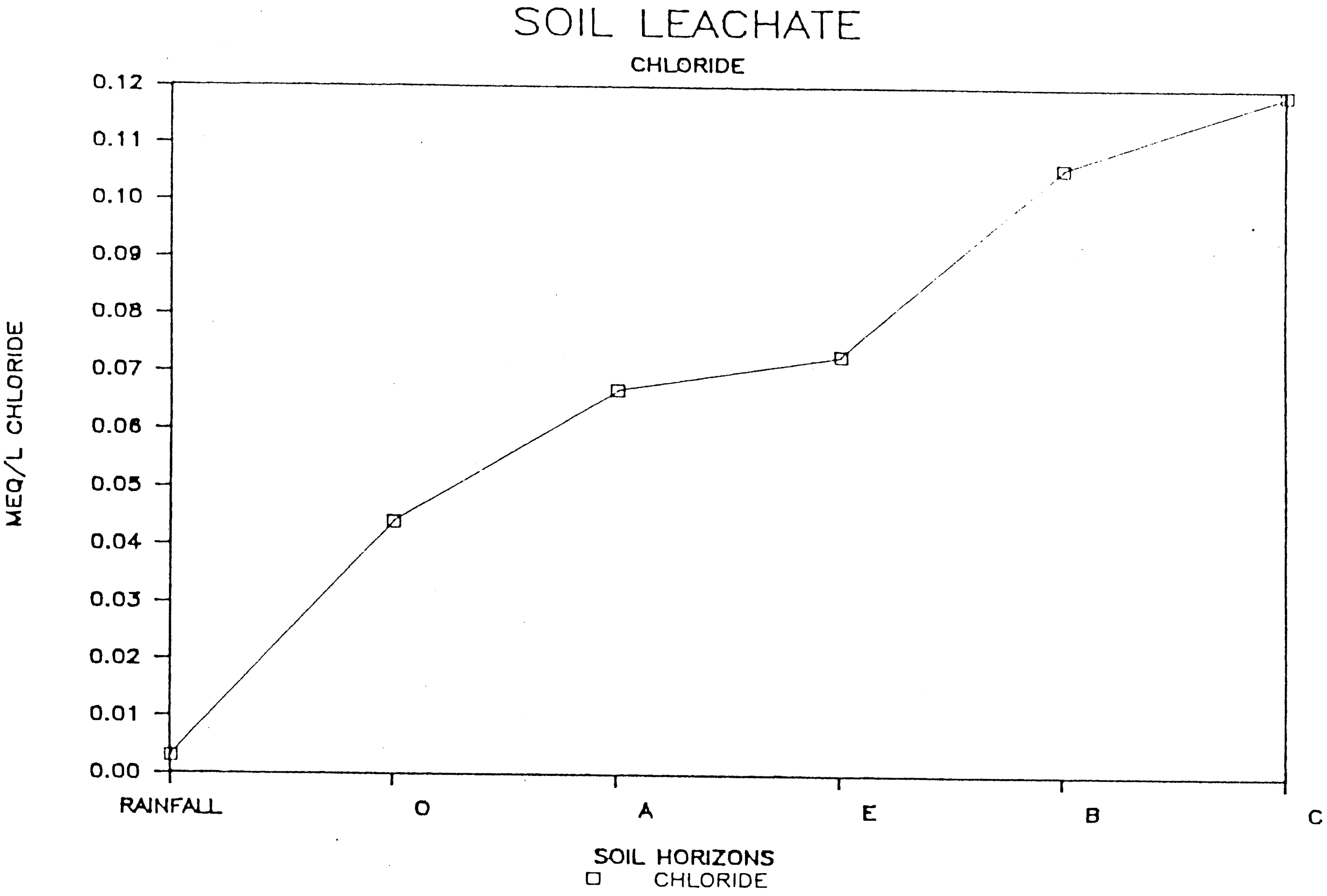

Figure 22. Soil Leachate Chloride

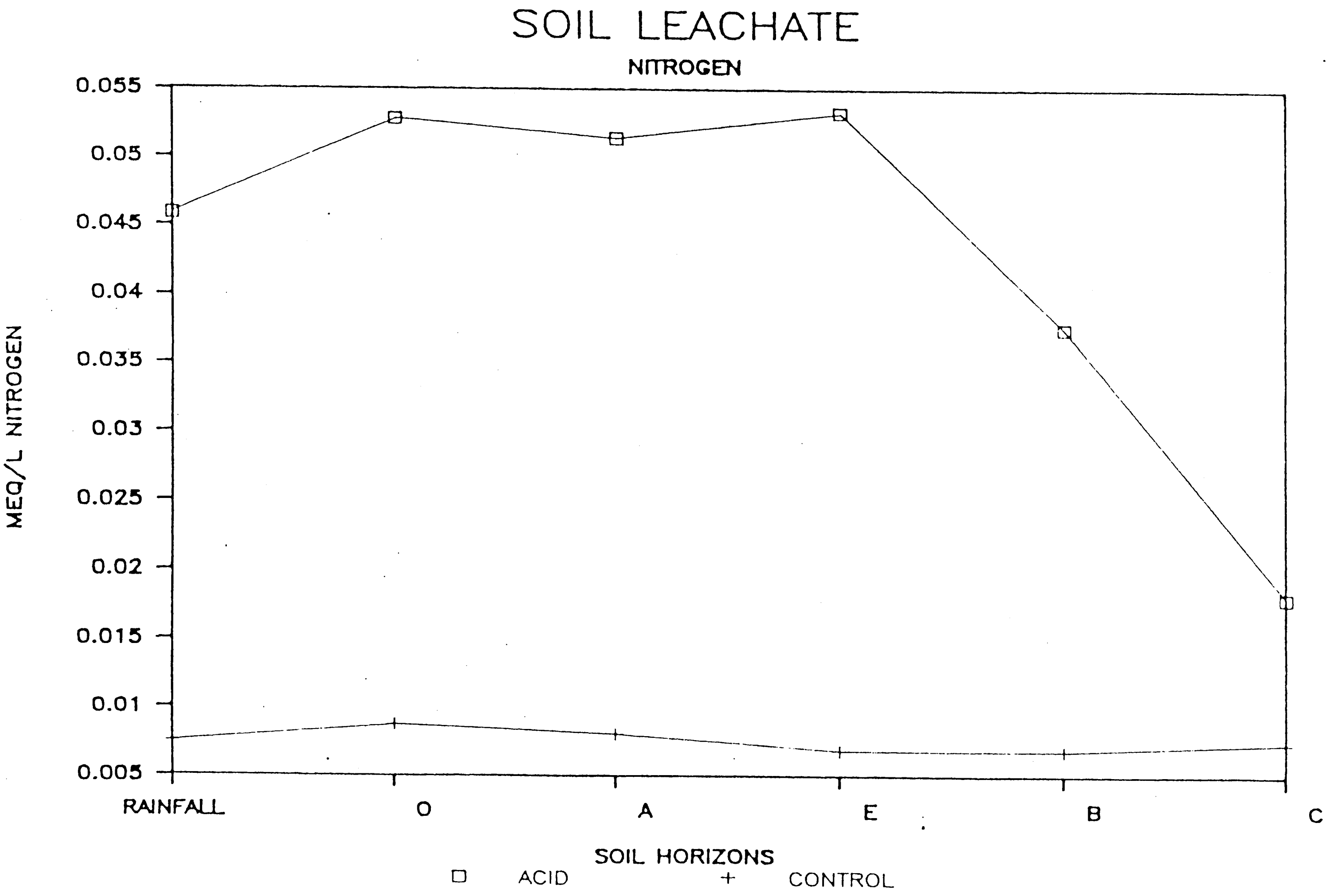

Figure 23. Soil Leachate Nitrate.

was reduced in the acid rain leachate as it passed through the B and C horizons. The nitrate in the acid rain was adsorbed in the B and C soil horizons because of the high nitrate concentration where the solution was not in equilibrium with the soil, and high clay content which has a net positive charge caused by aluminum and iron oxides at low soil pH. The nitrate in the natural rainfall leachate did not adsorb to the soil, as the solution was in equilibrium with the soil (Figure 23).

Leachate Sulfates

Sulfates were significantly higher in the leachate from all soil horizons for the acid rain treatment compared to natural rainfall treatment. The difference in sulfate concentration between rainfall treatments was a function of the sulfate in the acid rain (Figure 24).

Leachate sulfates increased slightly through the O, A and E horizons for the acid rain treatment, as the leachate picked up soluble sulfate. Soluble sulfate for all soil horizons was determined to be in the range .05 to .06 meq/l.

In the B and C horizons the leachate sulfate concentrations were reduced. The sulfate adsorbed to the clay, which had a greater net positive charge caused by aluminum and iron oxides at low soil pH, to which anions such as sulfate can adsorb. For the acid rain treatment,

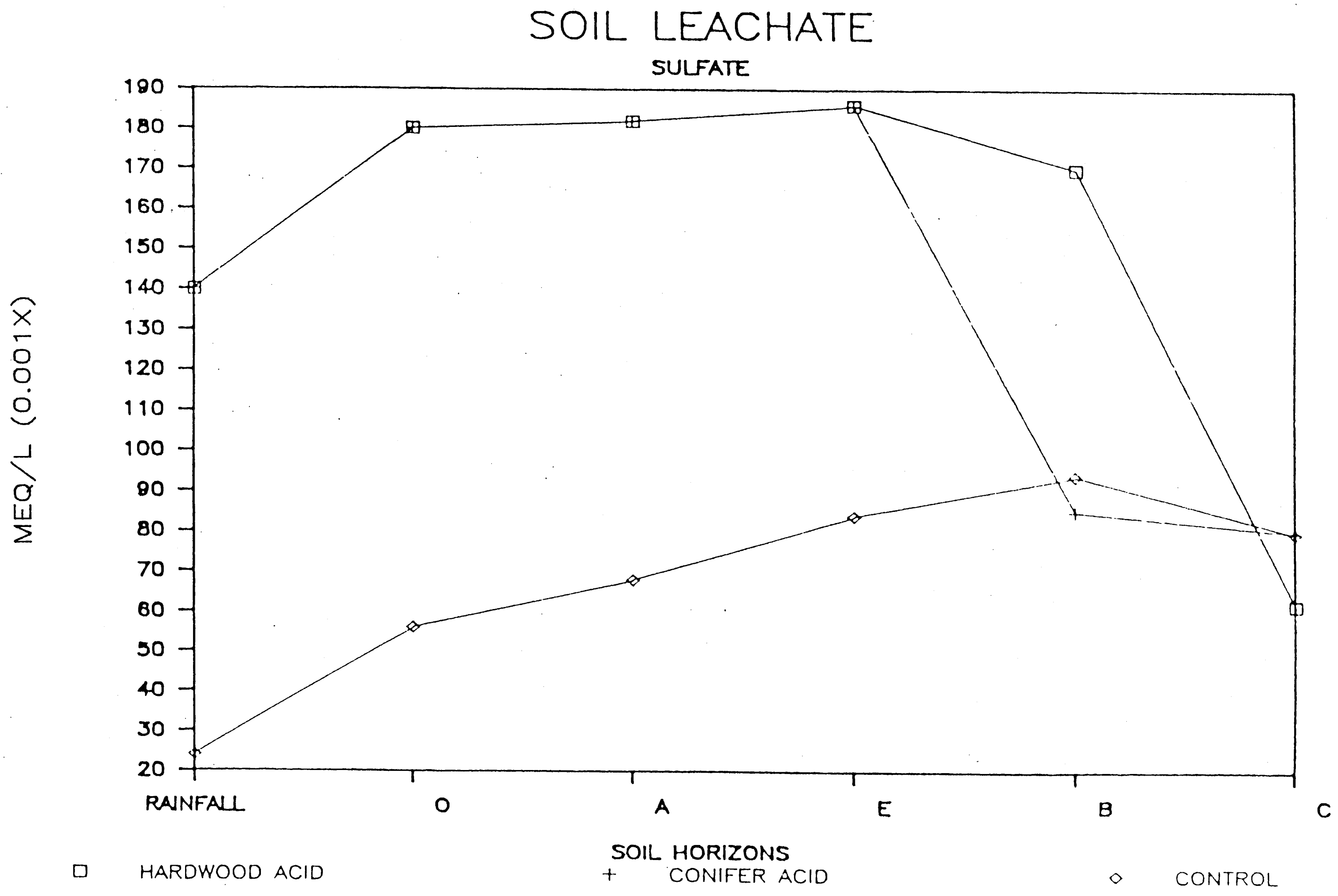

Figure 24. Soil Leachate Sulfate.

the B horizon of the conifer site adsorbed significantly more sulfate than the hardwood site. Again, this was due to a greater percent of clay (Figure 24).

For both the hardwood and conifer sites the leachate of the natural rainfall increased in sulfate concentration as it picked up soluble sulfate and finally reached equilibrium in the B soil horizon.

Leachate Sodium

Sodium was leached from the O, A, and E horizons and adsorbed in the B and C horizons. There were no significant differences in leachate sodium concentrations between the acid and natural rain treatments or conifer and hardwood sites (Figure 25).

Leachate Potassium

The largest proportion of the total potassium leached from the soil profiles was contributed by the O and A horizons (Figure 26 -27). Potassium was not adsorbed in the lower horizons, therefore, leachate potassium concentrations progressively increased while passing through the remaining soil horizons. The source of most of the potassium in the soil is from decaying organic matter (USGS Water Supply Paper 2254).

Acid rain had a very minor influence on potassium

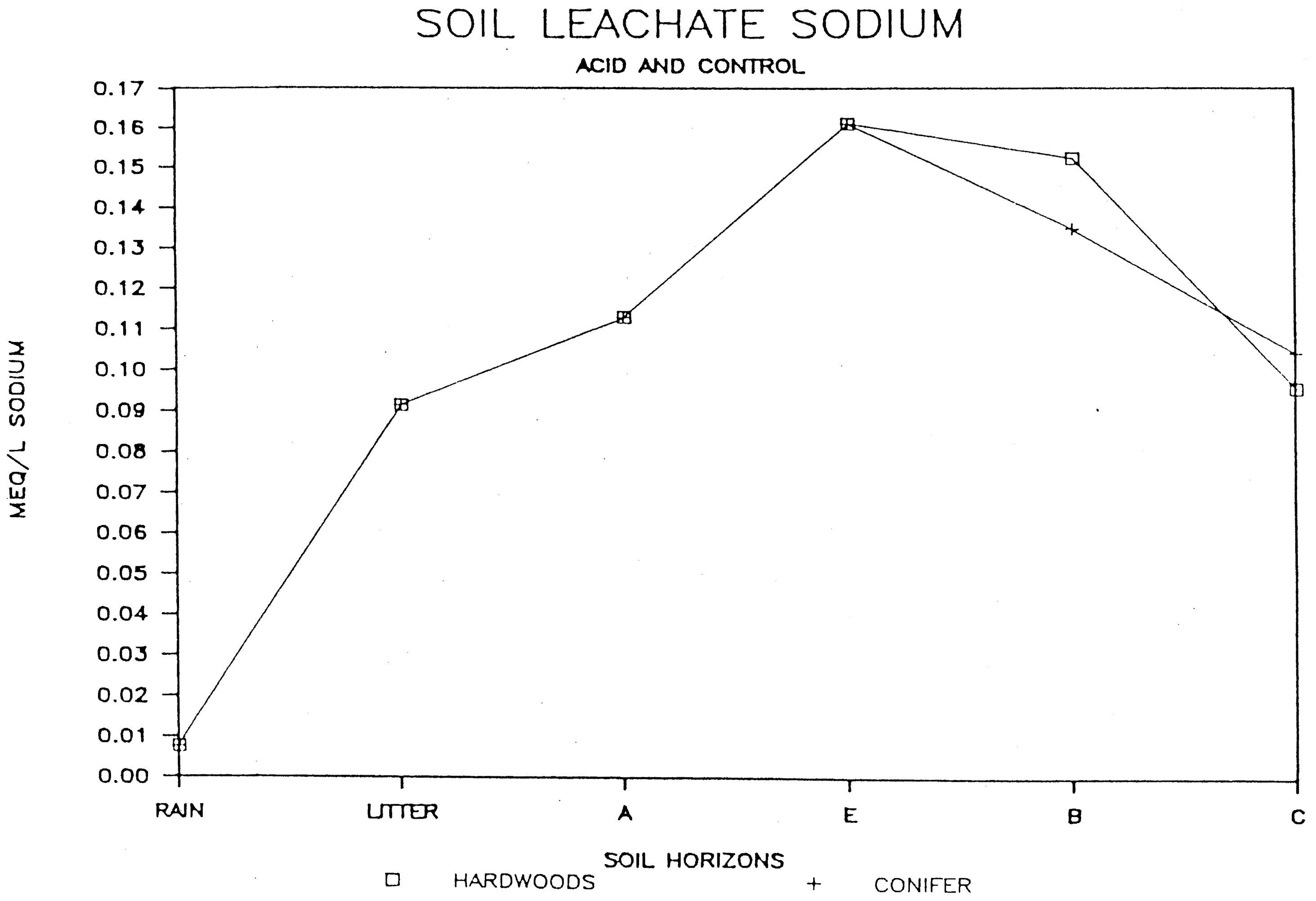

Figure 25. Soil Leachate Sodium.

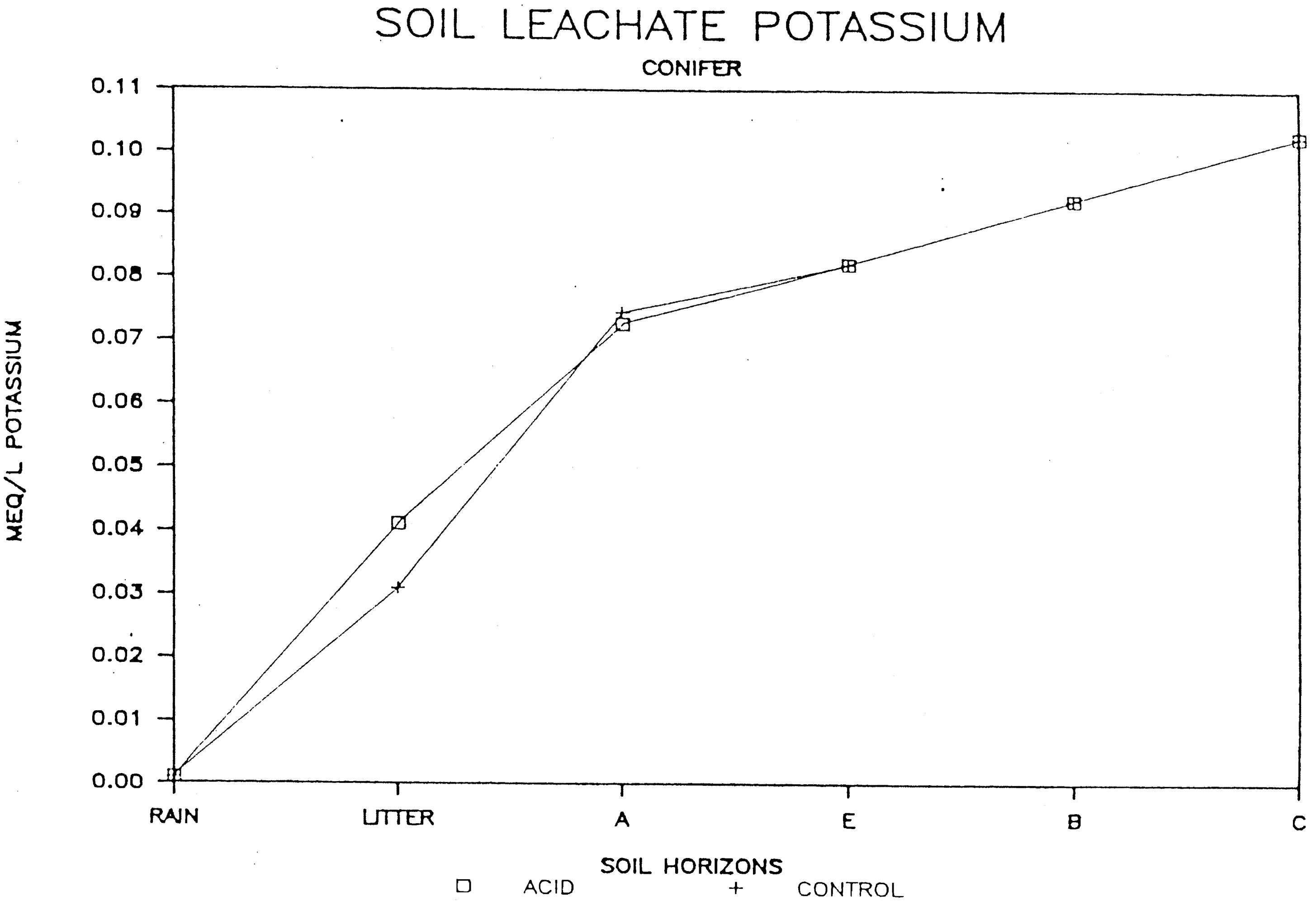

Figure 26. Soil leachate Potassium of the Conifer Site.

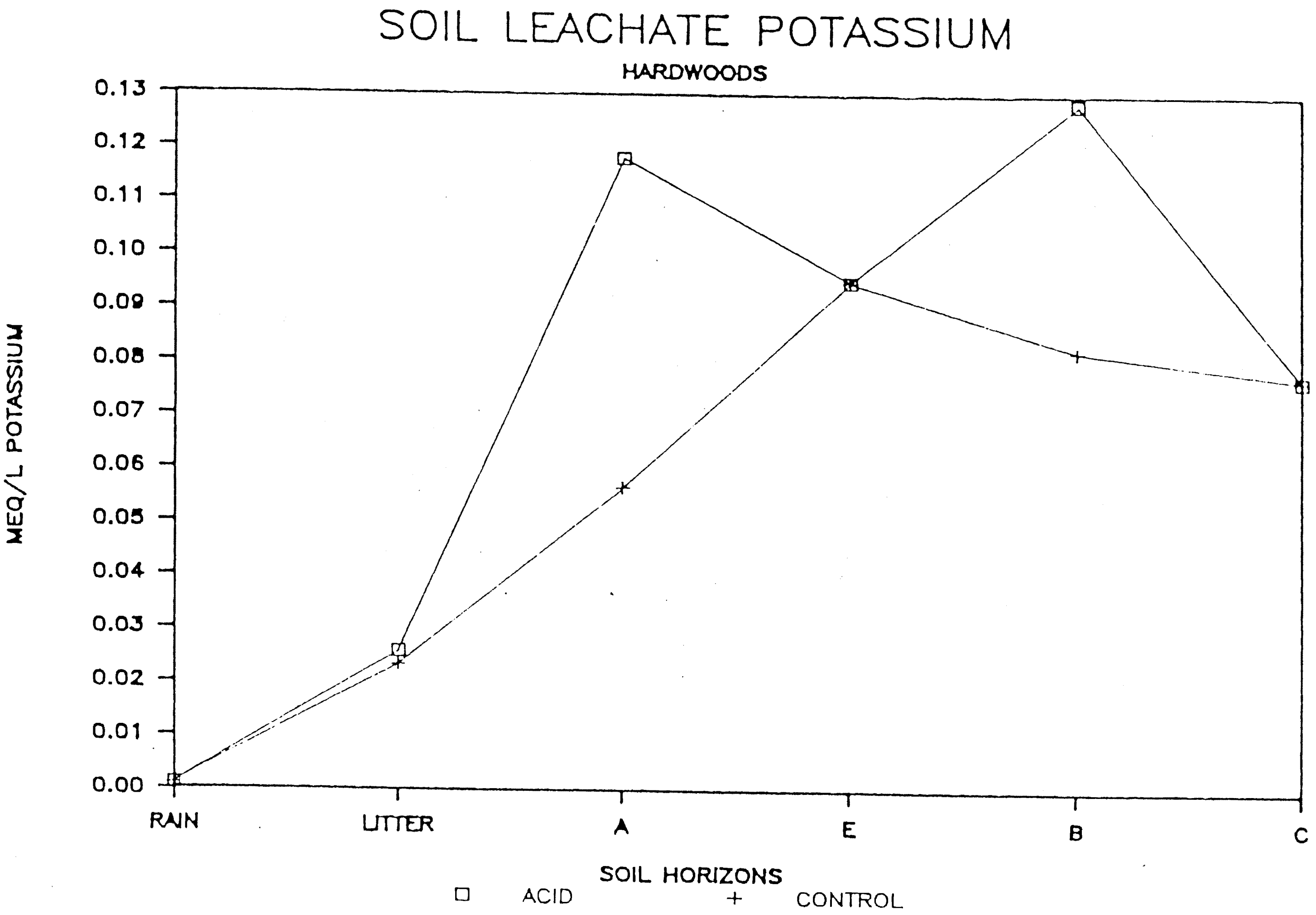

Figure 27. Soil Leachate Potassium of the Hardwood Site.

leaching. The hardwood site showed signs of accelerated potassium leaching by acid rain in the A and B soil horizons, however, differences in leachate potassium due to treatments were not significant.

Leachate Calcium and Magnesium

The litter layer was the primary source of leached calcium (Figure 28 - 29). Calcium was leached from the litter layer and adsorbed by the lower soil horizons. Acid rain (pH 3.8) leached nearly three times as much calcium as did the natural rain. The conifer site had more calcium adsorption in the B horizon than the hardwood site due to higher clay content.

The litter layer and B soil horizon were the primary source of leached magnesium (Figure 30). Magnesium was leached from the litter layer and B horizon before it began to adsorb in the C soil horizon. Acid rain leached nearly three times as much magnesium as did the control. No significant differences in magnesium leaching or adsorbance were found between the conifer and hardwood sites.

The excess calcium and magnesium leached by acid rain was due to the amount of sulfuric acid in solution. When the sulfuric acid came in contact with the litter layer, the hydrogen ions displaced calcium and magnesium from the exchange complex into solution, where they moved in association with sulfate. A correlation between the meq/l

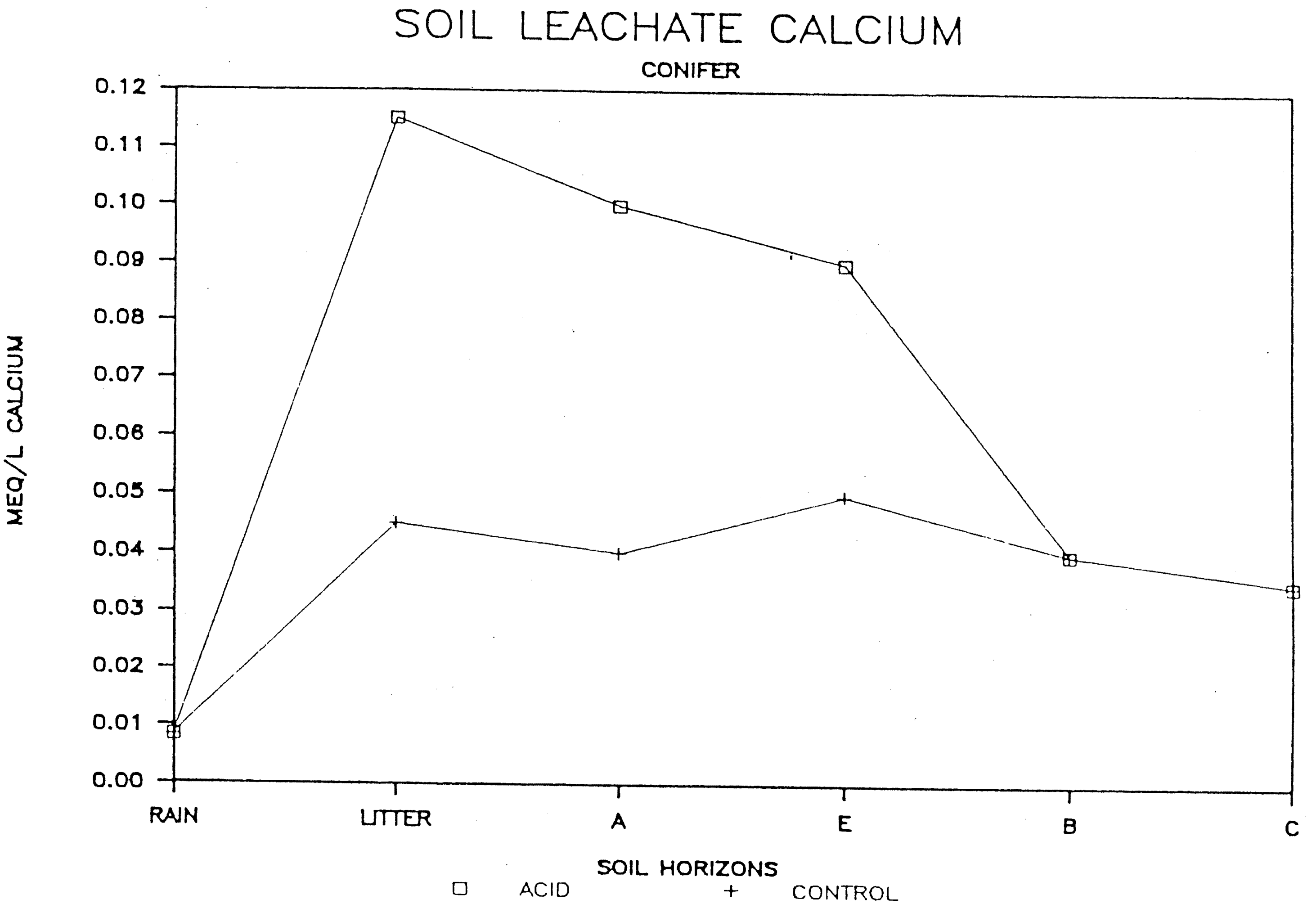

Figure 28. Soil Leachate Calcium of the Conifer Stand.

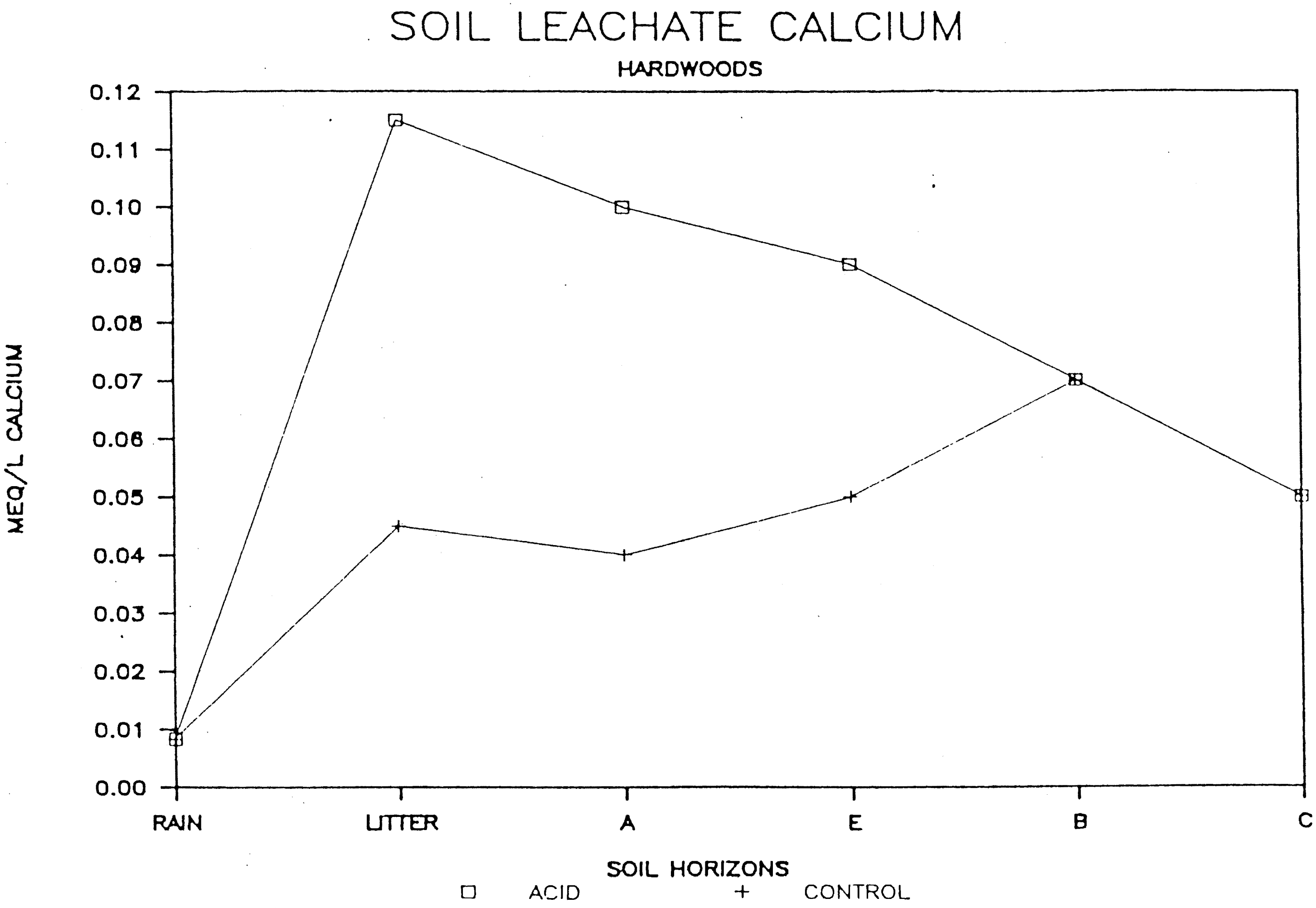

Figure 29. Soil Leachate Calcium of the Hardwood Stand.

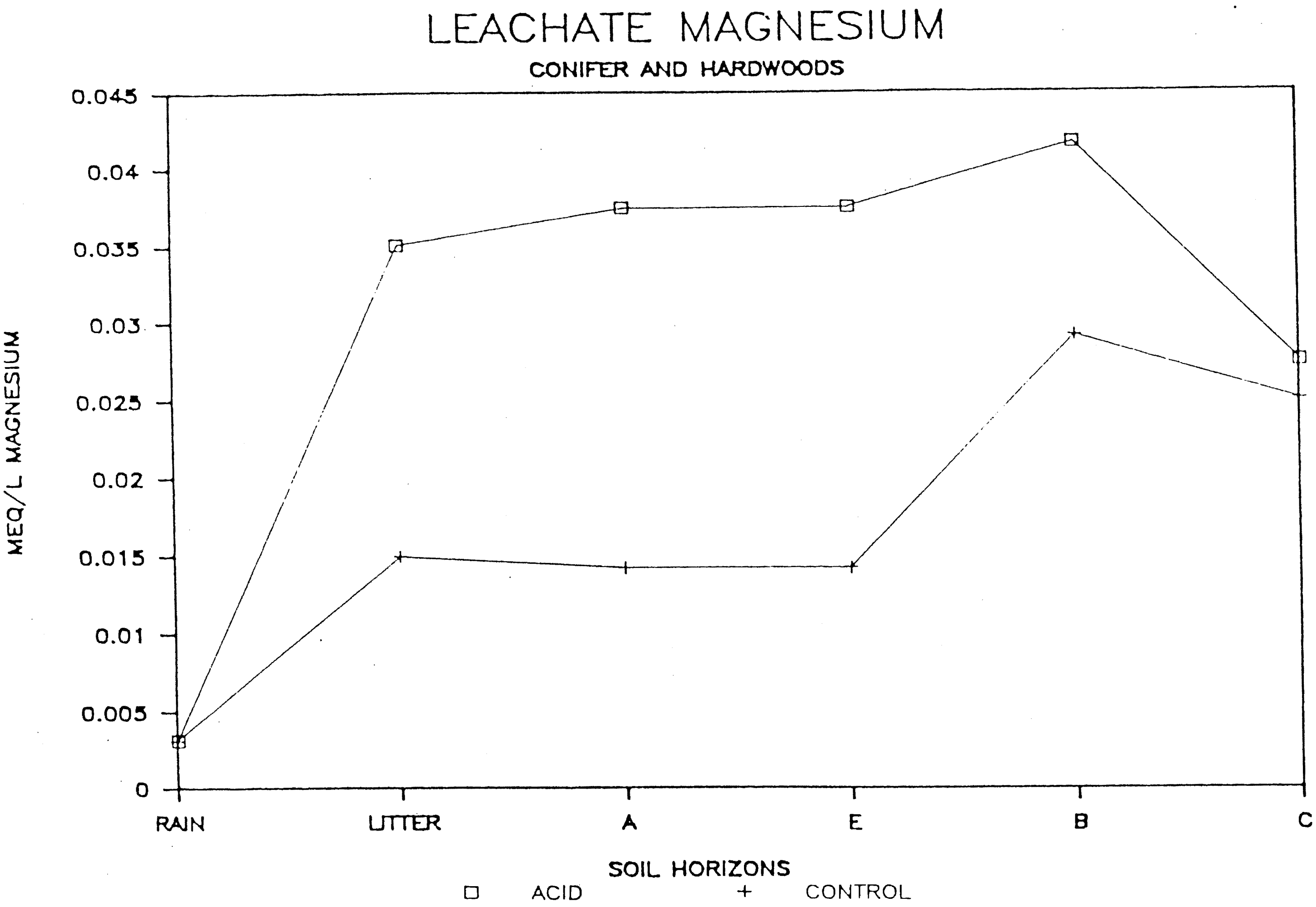

Figure 30. Soil Leachate Magnesium.

sulfate and the sum of meq/l calcium and magnesium in the soil leachate had an R-square of .70 (Figure 31). This indicates that 70% of the variation of the sum of meq/l calcium and magnesium in the soil leachate were explained by the meq/l sulfate in the soil leachate. Only 62% of meq/l calcium and 47% meq/l magnesium in the soil leachate were explained by the meq/l sulfate in the soil leachate.

Leachate Aluminum

No trends could be determined for aluminum due to the high variability of the leachate aluminum concentrations.

Leaching of Calcium and Magnesium by Acid Rain

Calcium and magnesium leaching is increased by acid rain. Estimates of calcium and magnesium leaching rates due to decreasing levels of rainfall pH were made as follows.

An estimation of the amount of calcium and magnesium which would be leached by rain is based on the amount of sulfate in the rainfall, which increases at lower pH levels. The rainfall sulfate concentrations were determined from weighted average ion concentrations for New York, Pennsylvania and Ohio NADP sites June through September, 1979. The amounts of calcium and magnesium that are expected to leach at various pH levels of acid rain are shown in figures 32 and 33.

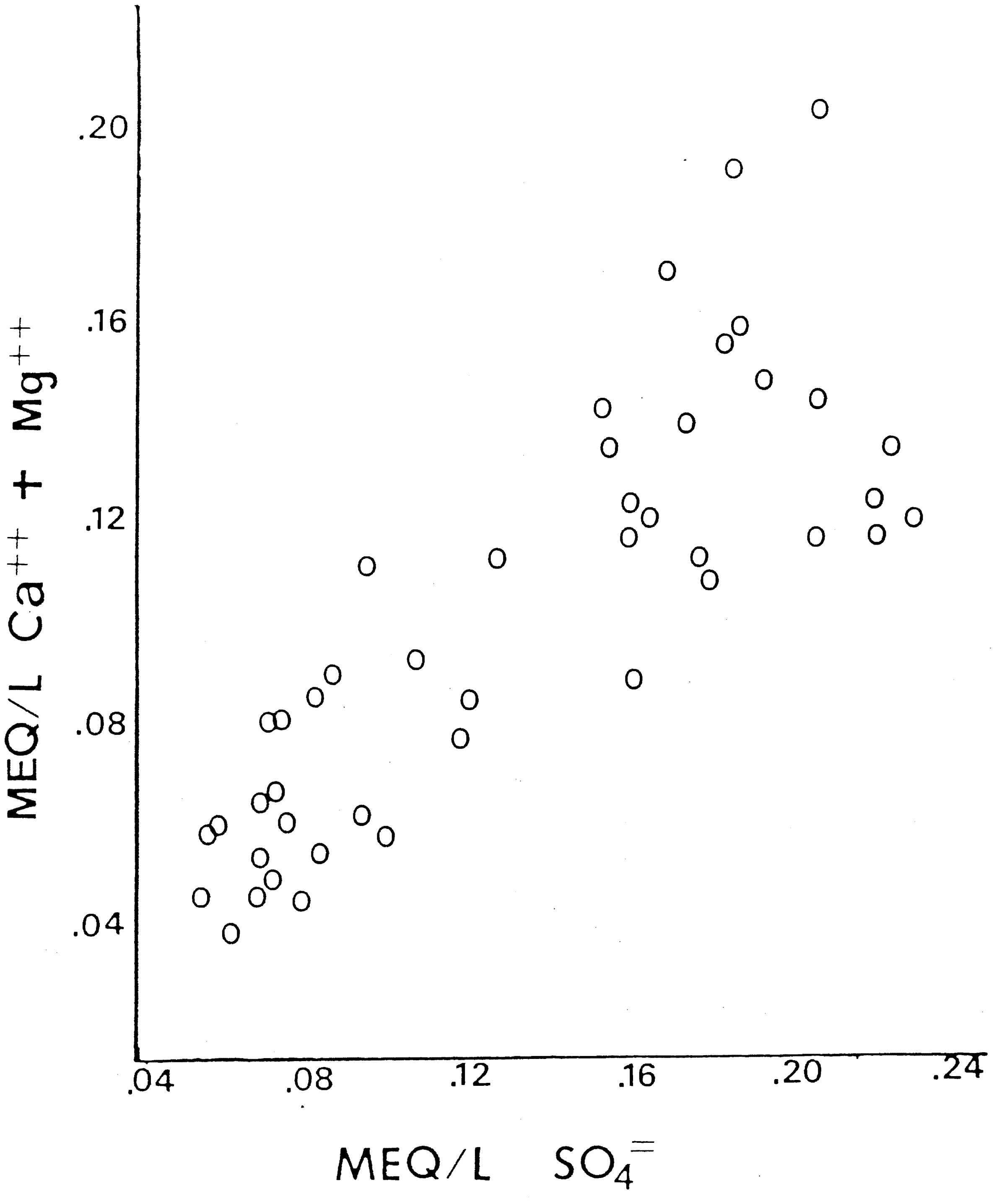

Figure 31. Correlation of Leachate Sulfate with Leachate Calcium + Magnesium.

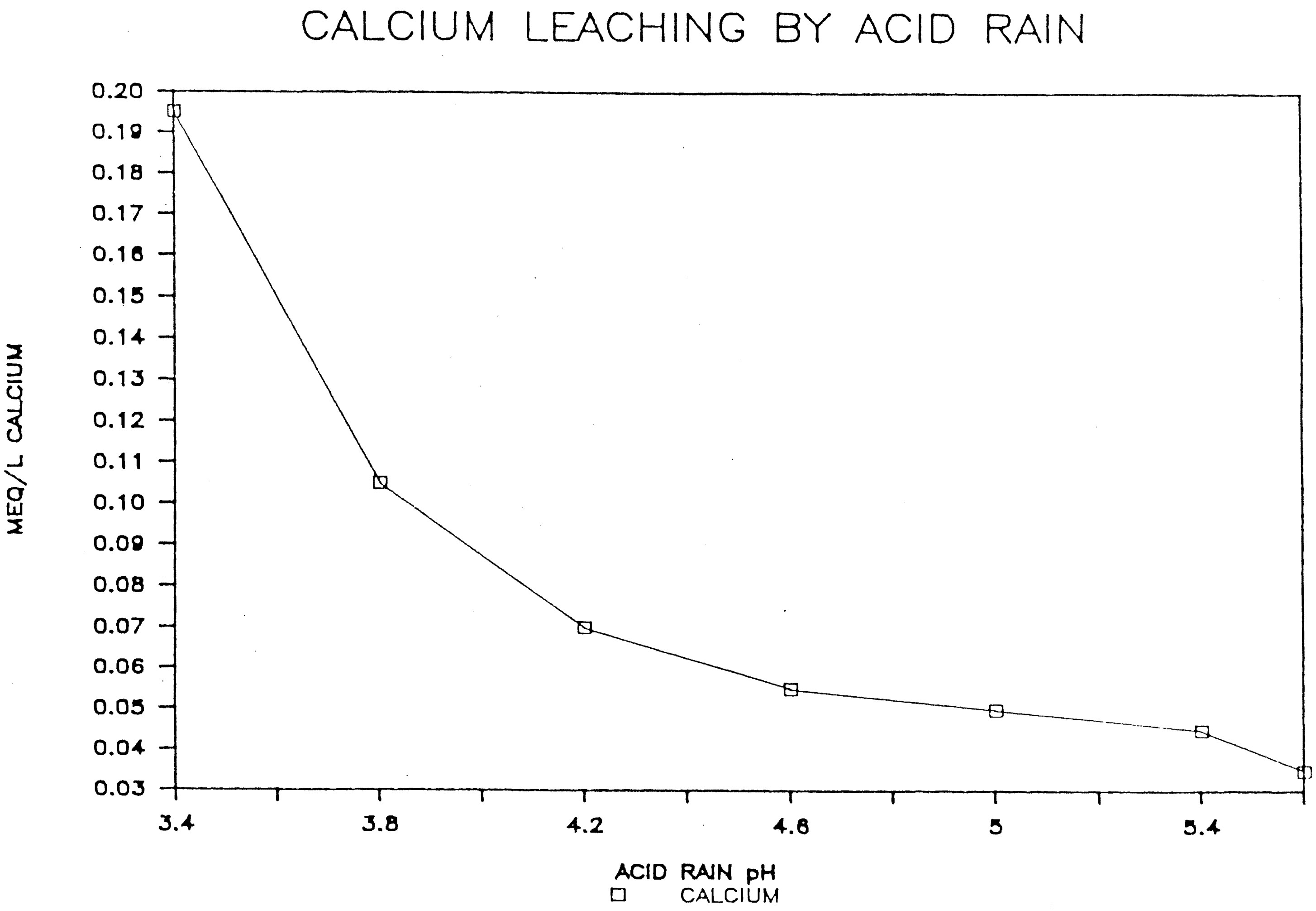

Figure 32. Calcium Leaching by Acid Rain.

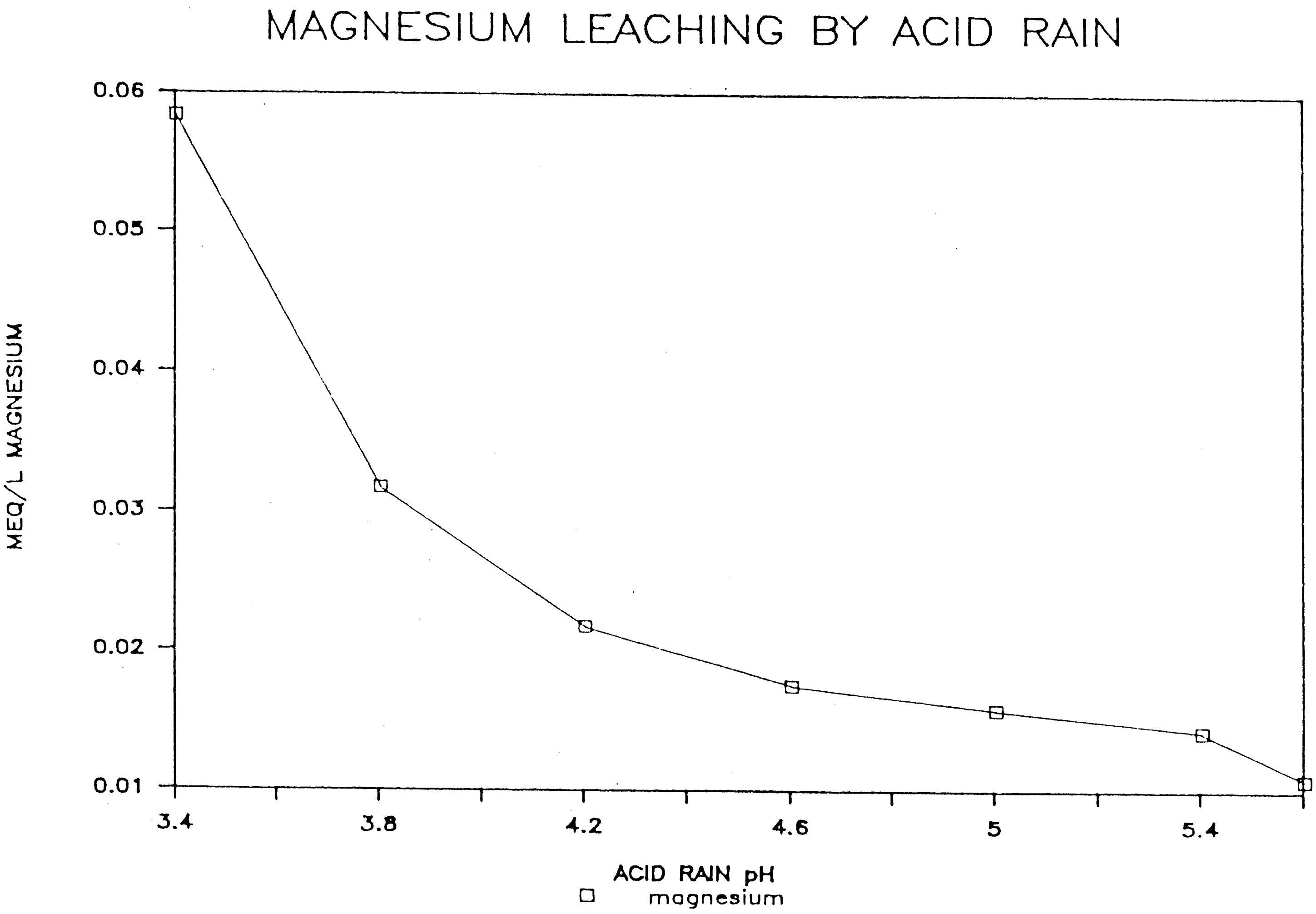

Figure 33. Magnesium Leaching by Acid Rain.

Calcium and Magnesium Losses lbs/acre

Average precipitation in the Ouachita Mountains of Arkansas and Oklahoma is 50 in/yr (U.S. Department of Commerce. 1961). Selected gauging stations on the larger watersheds of the Ouachita Mountains show approximately 45% (22.5 in/yr) of the precipitation occurs as stream discharge (USGS), while the gauging stations on smaller watersheds of the Ouachita Mountains show 26% (13 in/yr) of precipitation as stream discharge (Miller, Beasly and Lawson 1985). Therefore, 19% (9.5 in/yr) of the precipitation that infiltrates small watersheds enters larger order streams as baseflow, below the small watershed gauging stations.

For the following equation an assumption was made that 20% (2.5 in/yr) of small watershed discharge is base flow. The number of area inches of flow in the various components can be expressed:

(Equation (1))

$$A - B + C = D \qquad B - C = E$$

Where A = Discharge of larger watershed = 22.5 in/yr.
B = Discharge of smaller watershed = 13.0 in/yr.
C = Discharge of small watershed baseflow = 2.5 in/yr.
D = Discharge of baseflow (water in contact with B and C soil horizons and parent material = 12.0 in/yr.
E = Discharge as surface runoff and interflow (water in contact with O, A, and E soil horizons) = 10.5 in/yr.

Table (III) gives the average concentrations for calcium and magnesium expected in the base flow and interflow at several pH levels.

Calcium or Magnesium Removed by Acid Rain

The following equation is used to convert calcium and magnesium concentrations to lb/acre/yr.

(Equation (2))

$$(F)(G)(H)(I)(J) + (K)(L)(H)(I)(J) = M$$

Where F = Average concentration (mg/l) of surface and interflow.
G = Annual volume of surface + interflow (.88 acre-ft).
H = 1233000 liters /acre-ft.
I = 1 kg/1000,000 mg
J = 1 lb/.4536 kg
K = Concentration (mg/l) of baseflow.
L = Annual volume of baseflow (1 acre-ft).
M = Pounds of calcium or magnesium removed per acre of watershed per year.

The assumption was made that all water comes in good contact with the soil. In nature this assumption may not hold. The results of calculations made with equations 1 and 2 are twice as large as outputs recorded in the stream discharge by the Oklahoma State University Forest Watershed Laboratory.

The amounts of calcium and magnesium that would be

TABLE III

AVERAGE CONCENTRATIONS OF CALCIUM AND MAGNESIUM AT SEVERAL RAIN pH LEVELS FOR SURFACE AND INTERFLOW AND BASEFLOW

	AVERAGE CALCIUM CONCENTRATION MG/L		AVERAGE MAGNESIUM CONCENTRATION MG/L	
pH	Surface and Interflow	Base Flow	Surface and Interflow	Base Flow
5.6	0.7	0.8	.13	.25
4.6	1.1	0.8	.21	.25
3.8	2.0	0.8	.38	.25

TABLE IV

CALCIUM AND MAGNESIUM EXPORTED THROUGH LEACHING

pH	Calcium lost lb/acre/yr	Magnesium lost lb/acre/yr
5.6	3.8	1.0
4.6	4.8	1.1
3.8	6.8	1.6

lost due to leaching at several pH levels under the preceding scenario are in (Table IV).

At pH (5.6) there is negligable sulfuric acid in the rain. Thus, by subtracting the amount of calcium and magnesium leached at rainfall pH (5.6) from amounts leached at more acid rainfall pH levels, the amount of additional calcium and magnesium leached from the soil due to acid rain can be determined. Thus, at pH (4.6), rain would leach an additional 1 lb of calcium and .1 lb of magnesium than at pH (5.6), and at pH (3.8) rain would leach an additional 3 lb of calcium and .6 lb of magnesium than at pH (5.6). At rainfall pH (3.8) the estimated calcium output is twice as great as with nonacidic rainfall, while magnesium output increases by 1.5 times.

Prediction of Time it would take to Remove 500 lbs of Calcium from a Forested Watershed of the Ouachita Mountains at Several Acid Rain pH Levels

Excluding the litter layer, the A and E soil horizons have the highest percentage of the total exchangeable calcium on their exchange sites. Exchangeable calcium was calculated to be 500 lbs/acre by the following equations.

(Equation (3))

$$N / O = P$$

$$(P)\ ((Q)(R)(S) + (T)(R)(U)(I)(J)) = V$$

Where N = 4047 square meters/acre
O = .0062 square meters/soil column
P = 652,742 soil columns/acre
Q = 123 g soil in the A horizon
R = 0.8 moisture factor
S = 1.7 mg calcium/g soil
T = 711 g soil in E horizon
U = .32 mg calcium/g soil
I = 1 kg/1000,000 mg
J = 1 lb/.4536 kg
V = 500 lb of calcium/acre

The O, A and E soil horizons are very susceptible to losses of calcium through leaching of acid rain because these horizons have little ability to adsorb sulfate.

The B and C soil horizon have a much smaller percentage of exchangeable calcium, in comparison to the other horizons. However, due to a much larger volume, they contain slightly more total exchangeable calcium than the A and E horizons (600/lbs acre). Calcium in the B and C soil horizons is not very susceptible to leaching by acid rain. The B and C soil horizons have a much higher sulfate adsorption capacity and are subject to a smaller volume of rainfall percolation than the upper soil horizons. Therefore, they are less likely to be leached of calcium.

Although magnesium is also leached by acid rain, a much larger total amount is located in the B and C horizons than the A and E horizons (1100 lbs/acre compared 100 lbs/acre).

Thus, only a small amount of the total available magnesium is highly susceptible to leaching by acid rain.

Calcium is most susceptible to leaching by acid rain as it is located in the surface soil horizons which have little to no sulfate adsorption capacity, and the surface horizons have a large proportion of the total annual rainfall leaching through them.

Under the assumptions that (1) at a rainfall pH of 5.6 the amount of calcium leached from the soil roughly equals calcium inputs through weathering and atmospheric wetfall and dryfall, and (2) additional available calcium produced by decaying organic matter from the O soil horizon is quickly recycled into living biomass, one can calculate the time period it would take for 500 lbs of calcium (the amount of exchangeable calcium calculated to be in the A and E horizons) to be leached from the cation exchange complex.

The number of years it would take to deplete 500 lbs of calcium from the forested watershed can be calculated (Equation (4)) using a zero-order reaction in which equal amounts of calcium are leached each year. The zero order reaction was chosen, as it is assumed that an excess reserve of exchangeable calcium currently exists in the forest ecosystem. If and when the forest vegetation should become deficient in calcium, a first order reaction would better discribe the calcium depletion curve.

(Equation (4))

$$W/(Y - Z)$$

Where W = The amount of exchangeable calcium in the A and E horizons, which equals 500 lbs/acre.
X = the mg/l calcium converted from meq/l calcium expected to leach at a selected pH level derived from figure 32 (Calcium Leaching by Acid Rain).
Y = Pounds of calcium leached per acre of watershed per year; derived using the value found for X transfered to equation 2 as mg/l calcium surface and interflow with 0 mg/l calcium used as the baseflow value.
Z = Calcium leached with natural rainfall, which equals 1.67 lbs/acre. This was calculated using pH 5.6 for X and following the procedures of Y.

The results of these calculations are shown in figure 34.

These calculations do not take into account that in nature not all of the rainfall will come into good contact with the soil. Vegetation influences nutrient movement in the soil profile by removing nutrients from the lower soil horizons and supplying the upper horizons with nutrients through leaf fall and decay. Therefore, it is unlikely that the A and E soil horizons would be depleted of calcium through acid rain in the time periods indicated. There are also large reserves of calcium in the B and C soil horizons and in the biomass, which will influence calcium flux in the ecosystem. In reality, it is the leaf litter (O horizon) that is the source of calcium leached by acid rain.

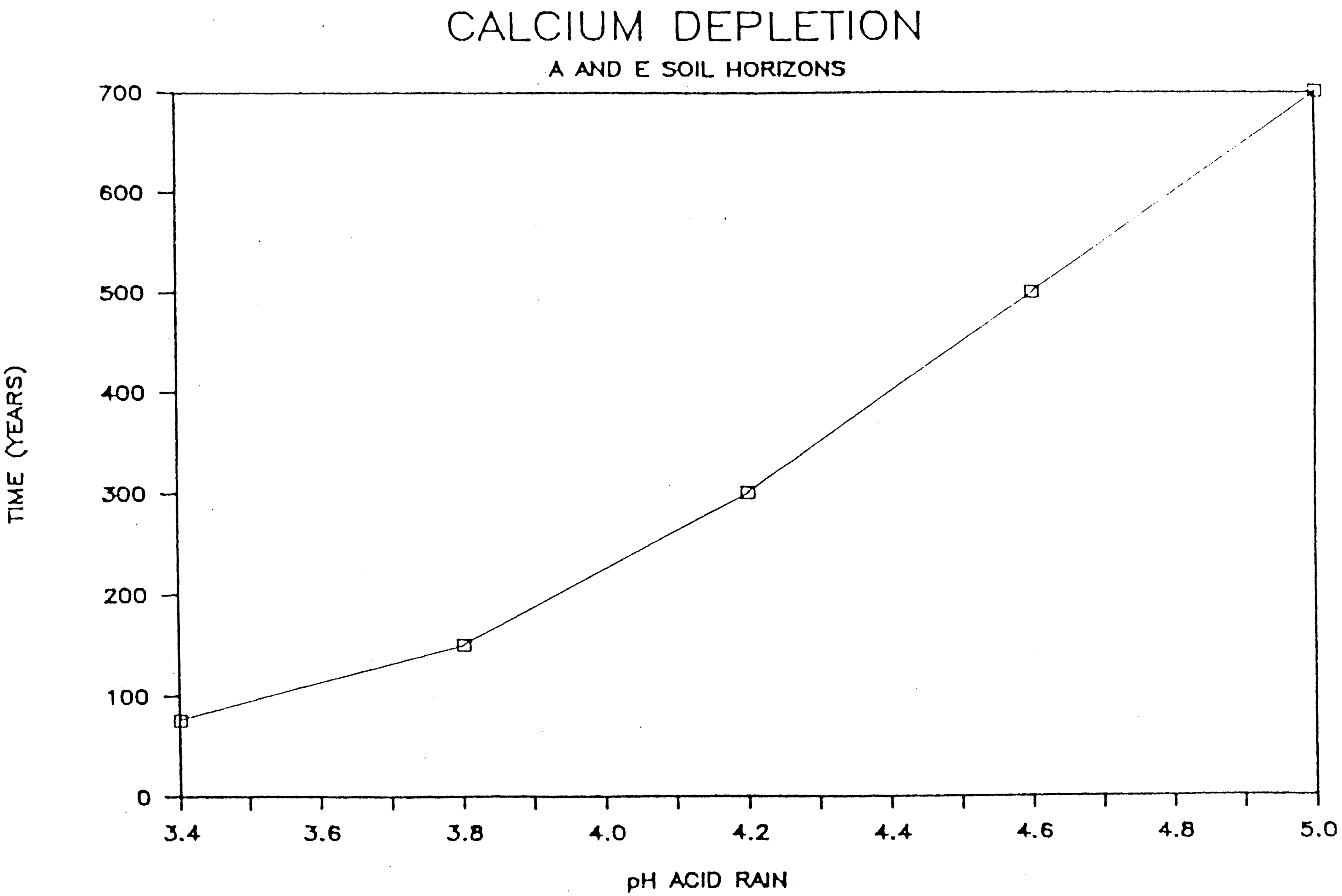

Figure 34. Calcium Depletion of the A and E Soil Horizons.

A restatement of the assumptions used in these calculations is important for emphasis. The amount of calcium removed each year remains constant. This may not occur, in fact, when there is less exchangeable calcium resulting from acid rain leaching of the forest soil over a long period of time. What may occur is, when soil exchangeable calcium is reduced, forest vegetation will eventually become deficient in calcium, resulting in less calcium in the leaf litter. Since the leaf litter contains a high percentage of the total calcium, and is very susceptible to leaching by acid rain, less calcium may be leached the following year. In other words, a first order reaction may occur rather than a zero order reaction.

Cation - Anion Balance

The meq/l of cations and anions were compared. A cation - anion balance was approximated for leachate of the O, A, E, B, and C horizons for the acid and control treatments for the deciduous and conifer sites (Table V).

Theoretically a balance in the meq/l of cations and anions in leachate should exist. The meq/l of cations were found to be greater than the meq/l of anions (Table V). This is probably due to bicarbonate and organic acids in solution which were not measured and contribute to the total ion concentration.

The amount of carbonate in the form of bicarbonate in

TABLE V

CATION ANION BALANCE MEQ/L

	SOIL HORIZONS				
HARDWOOD - ACID	O	A	E	B	C
ANIONS	0.27	0.30	0.31	0.32	0.20
CATIONS	0.27	0.38	0.39	0.40	0.26
% DIFFERENCE	0	0.12	0.12	0.11	0.13

	SOIL HORIZONS				
CONIFER - ACID	O	A	E	B	C
ANIONS	0.27	0.30	0.31	0.24	0.21
CATIONS	0.29	0.33	0.29	0.31	0.28
% DIFFERENCE	0.04	0.05	0.03	0.13	0.14

	SOIL HORIZONS				
CONTROL	O	A	E	B	C
ANIONS	0.11	0.15	0.16	0.21	0.21
CATIONS	0.18	0.23	0.31	0.32	0.27
% DIFFERENCE	0.24	0.21	0.32	0.21	0.13

solution is highly dependant on pH. At low pH levels (<4.5) most carbonate is in the form of carbonic acid, while at near nuetral pH all carbonate is in the form bicarbonate.

The control has a much greater percent difference between meq/l cations and anions in the upper horizons than the acid rain. This may be due to a higher rain water pH (5.6). At pH 5.6 there is approximately 15% more bicarbonate in solution than at pH 3.8. In lower soil horizons the leachate pH of the control and acid rainfall treatments were similar resulting in a close cation - anion balance.

Soil Chemistry after Leaching

Soil pH increased in all soil horizons by a .05 pH unit following both the acid and control rainfall treatments. This is most likely due to the leaching of bases from the litter layer, which were consequently exchanged for hydrogen ions in the lower soil horizons. There was no significant difference detected in the exchangeable acidity before and after leaching. The test for pH is more sensitive and, therefore, the detection of small changes in soil acidity were possible, while the exchangeable acidity test is not as sensitive, and small changes in in exchangeable acidity were not apparent.

CHAPTER V

SUMMARY AND CONCLUSIONS

The major objective of this study was to determine if sulfuric acidity contributes to additional leaching of base cations of an ultisol forest soil in a laboratory environment. Secondary objectives were to determine the ability of the soil to adsorb sulfate and thus restrict base cation leaching, and to characterize the chemical and physical properties of soil horizons under hardwood and conifer forest stands, and to determine changes in leachate chemistry resulting from acidic and nonacidic rainfall. With this information, predictions were made on possible environmental impacts due to acid rain in the forest ecosystem.

The soils studied were found to be low in cation exchange capacity, base saturation, nutrients, and are very acidic. The soils have parent materials composed of sandstone and shale which are low in alkalinity and release only small amounts of base cations through weathering. Calcium is the most abundant cation nutrient in the upper soil horizons, while magnesium is most abundant in the lower soil horizons. These soils have little ability to adsorb sulfate in the upper soil horizons. The B and C soil horizons have a high ability to adsorb sulfate, as they have a high percentage of clay.

Forest soils of the Ouachita Mountains of Arkansas and Oklahoma are susceptible to calcium and magnesium leaching due to acid rainfall. Calcium and magnesium are displaced from soil cation exchange sites in the O soil horizon by excess hydrogen ions. The excess hydrogen ions are produced through the reaction of sulfer dioxide with precipitation to form sulfuric acid. Once calcium and magnesium are displaced into solution they move in association with sulfate, which becomes available through the dissociation of sulfuric acid. If sulfate is not adsorbed on the soil exchange complex, calcium and magnesium are leached by acid rain and exported through stormflow.

The soils of the Ouachita Mountains in Arkansas and Oklahoma are susceptible to acid rain as they are low in calcium, magnesium and alkalinity, have little ability to adsorb sulfates in the upper soil horizons and limited amounts of total rainfall inputs percolate through the dense clays of the B and C soil horizons, which are high in sulfate adsorption capacity.

Calcium is most susceptible to leaching by acid rain. This is due to a high percentage of the total available calcium being located in the O, A, and E soil horizons. The horizons have little ability to adsorb sulfate and are subject to leaching because a large percentage of water entering the forest environment interacts with these soil horizons.

The amount of magnesium lost through acid rain leaching is much smaller than calcium because a much larger percentage of the total exchangeable magnesium is located in the B and C soil horizons. These soil horizons are in contact with a much smaller percentage of the total precipitation and have a much higher ability to adsorb sulfate.

Even at rainfall acidities as low as pH (3.8), it would take hundreds to thousands of years to deplete the soil of calcium and magnesium. There could possibly be much greater losses of these base cations through erosion and timber harvesting. However, plant calcium deficiancies may occur prior to soil calcium depletion. Therefore additional calcium loses due to acid rain may warrant concern by forest managers in the Ouachita Mountains. At the current rainfall pH of (4.6) the losses of calcium and magnesium due to increasingly acid rain through leaching is most likely insignificant.

At a rainfall pH of 3.8, surface runoff and interflow pH is lowered 0.5 pH units when compared to the leachate of natural rainfall pH (5.6). The average pH of the acid rain leachate of the O, A and E soil horizons is near a pH of 5.0. Since a large contribution of stream discharge is produced by stormflow, a low rainfall pH may have a significant negative impact on the pH values of streams and could possibly affect the aquatic ecosystems of streams in the Ouachita Mountains of Arkansas and Oklahoma.

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APPENDIX A

STATISTICS

Table VI

SOIL CHEMISTRY ANALYSIS OF VARIANCE
PR>F

FACTOR	pH	ACID	O.M.	CEC	B.S.	Na	K	Mg	Ca
UNLEACHED SOIL FOR ALL DATA									
SITE	.50	.012	.27	.057	.52	.96	.40	.73	.22
SOIL HOR	.0001	.0001	.0001	.0001	.0001	.011	.0001	.0001	.001
SITE*HOR	.0003	.0045	.187	.013	.67	.72	.75	.003	.13
AOV FOR CONIFER SITE									
PIT	.057	.086	.69	.058	.075	.89	.02	.04	.15
HORIZON	.0001	.0007	.0008	.003	.004	.03	.0005	.012	.009
AOV FOR HARDWOOD SITE									
PIT	.53	.24	.16	.19	.15	.10	.27	.10	.32
HORIZON	.0001	.0008	.003	.002	.007	.36	.008	.002	.024
AOV FOR EACH HORIZON									
A SITE	.014	.019	.23	.08	.44	.59	.71	.40	.20
E SITE	.28	.38	.34	.45	.43	.13	.54	.76	.57
B SITE	.59	.009	.44	.009	.85	.84	.16	.05	.18
C SITE	.25	.023	.34	.29	.87	.69	.59	.06	.67
LEACHED SOIL FOR ALL DATA									
TIME	.0001	.11							

Table VII

SOIL LEACHATE ANALYSIS OF VARIANCE FOR ALL DATA
PR>F

	pH	Cl	SO_4	NO_3	Na	K	Ca	Mg
SITE	.61	.92	.27	.71	.82	.93	.27	.15
ACID RAIN	.004	.97	.0001	.0001	.52	.038	.0001	.0001
SITE*RAIN	.44	.25	.99	.47	.83	.059	.92	.025
SOIL HORIZON	.001	.0001	.0001	.0001	.0001	.0001	.014	.15
SITE*HORIZON	.67	.35	.18	.77	.16	.33	.27	.19
RAIN*HORIZON	.007	.86	.0001	.0001	.61	.51	.0001	.0001
RAIN*HOR*SITE	.55	.25	.0001	.84	.35	.34	.58	.47

Table VIII

SOIL LEACHATE ANALYSIS OF VARIANCE BY HORIZON
PR>F

	pH	Cl	SO_4	NO_3	NA	K	CA	MG
O HORIZON								
SITE	.99	.21	.58	.42	.74	.22	.87	.99
ACID RAIN	.007	.78	.0001	.0001	.12	.26	.001	.002
SITE*RAIN	.50	.59	.99	.66	.12	.68	.93	.37
A HORIZON								
SITE	.57	.55	.80	.49	.83	.39	.78	.72
ACID RAIN	.028	.33	.0001	.002	.70	.19	.002	.0001
SITE*RAIN	.79	.33	.0001	.49	.99	.18	.58	.37
E HORIZON								
SITE	.99	.45	.51	.47	.96	.20	.43	.64
ACID RAIN	.02	.90	.0001	.0001	.20	.87	.005	.001
SITE*RAIN	.24	.12	.99	.31	.20	.71	.56	.64
B HORIZON								
SITE	.16	.75	.02	.94	.21	.63	.069	.28
ACID RAIN	.15	.62	.0001	.0003	.71	.16	.71	.016
SITE*RAIN	.45	.94	.99	.83	.78	.17	.049	.68
C HORIZON								
SITE	.85	.45	.03	.60	.32	.27	.07	.13
ACID RAIN	.90	.90	.0001	.023	.59	.54	.91	.12
SITE*RAIN	.30	.12	.99	.84	.22	.29	.75	.016

Table IX

SOIL CHEMISTRY MEANS AND STANDARD DEVIATIONS

						MEQ/G SOIL			
HZN	pH	%OM	EXACID	%BS	CEC	Ca	Mg	K	Na
HARDWOOD - MEANS 9 SAMPLES									
A	3.51	6.86	.136	37.4	.22	.040	.021	.016	.005
E	3.75	3.00	.083	26.2	.11	.011	.008	.007	.004
B	3.82	1.54	.083	23.9	.11	.004	.011	.005	.005
C	3.83	1.00	.150	27.5	.20	.005	.038	.005	.006
HARDWOOD - STANDARD DEVIATION									
A	.02	2.25	.009	13.3	.04	.020	.006	.005	.001
E	.02	.44	.018	5.2	.02	.002	.002	.001	.001
B	.04	.32	.009	3.0	.01	.001	.005	.001	.001
C	.02	.19	.012	3.7	.02	.003	.008	.001	.001
CONIFER - MEANS 9 SAMPLES									
A	3.32	9.58	.220	38.2	.36	.085	.029	.018	.005
E	3.78	3.71	.099	27.4	.14	.016	.009	.008	.004
B	3.84	1.26	.169	24.8	.22	.013	.024	.008	.005
C	3.87	0.77	.178	18.4	.22	.006	.023	.006	.006
CONIFER - STANDARD DEVIATION									
A	.07	3.59	.033	10.3	.08	.038	.011	.003	.001
E	.04	2.89	.016	14.5	.04	.013	.004	.002	.001
B	.07	0.72	.027	8.6	.03	.008	.005	.003	.001
C	.06	0.45	.007	4.0	.01	.002	.003	.001	.001

Table X

LEACHATE CHEMISTRY MEANS AND STANDARD DEVIATIONS

*C-A = CONIFER ACID 3 SAMPLES except (SO4, C-C, 2 samples)
C-C = CONIFER CONTROL (SO4, H-C, 1 sample)
H-A = HARDWOOD ACID
H-C = HARDWOOD CONTROL

			MEQ/L					
	pH	SO_4	NO_3	Cl	Mg	Ca	Na	K
O HORIZON MEAN								
C-A	5.50	.184	.052	.031	.036	.115	.094	.040
C-C	5.27	.057	.008	.036	.014	.043	.094	.032
H-A	5.37	.191	.054	.062	.033	.118	.084	.026
H-C	6.40	.058	.009	.047	.016	.048	.097	.022
STANDARD DEVIATION								
C-A	.44	.035	.003	.022	.005	.026	.010	.006
C-C	.35	.004	.001	.015	.005	.015	.018	.015
H-A	.75	.035	.003	.046	.008	.050	.013	.013
H-C	.20	.	.001	.004	0	.023	.010	.010

(CONTINUED)

	pH	SO_4	NO_3	Cl	Mg	Ca	Na	K
A HORIZON MEAN								
C-A	4.90	.189	.054	.053	.038	.093	.115	.073
C-C	5.47	.067	.008	.066	.014	.042	.110	.074
H-A	4.93	.175	.049	.074	.036	.095	.113	.117
H-C	5.60	.070	.008	.074	.014	.033	.110	.056
STANDARD DEVIATION								
C-A	.20	.034	.004	.006	.005	.019	.007	.008
C-C	.25	.001	.001	.020	.005	.010	.009	.041
H-A	.38	.023	.012	.035	.005	.026	.026	.035
H-C	.26	.	.001	.038	.005	.003	.009	.022
E HORIZON MEAN								
C-A	5.53	.179	.055	.078	.036	.093	.161	.075
C-C	5.87	.085	.006	.078	.014	.060	.161	.090
H-A	5.33	.194	.052	.054	.038	.088	.148	.097
H-C	6.07	.084	.007	.084	.014	.047	.172	.091
STANDARD DEVIATION								
C-A	.31	.010	.005	.014	.005	.018	.019	.021
C-C	.23	.018	.001	.025	.005	.015	.012	.009
H-A	.31	.029	.004	.013	.005	.010	.016	.040
H-C	.25	.	.001	.030	.005	.016	.032	.046

(CONTINUED)

	pH	SO_4	NO_3	Cl	Mg	Ca	Na	K
B HORIZON MEAN								
C-A	6.17	.092	.037	.123	.036	.045	.117	.093
C-C	6.30	.084	.007	.112	.022	.032	.128	.092
H-A	5.67	.171	.038	.114	.047	.067	.149	.132
H-C	6.03	.114	.006	.100	.036	.077	.151	.082
STANDARD DEVIATION								
C-A	.15	.022	.003	.055	.005	.005	.017	.034
C-C	.30	.011	.002	.056	.005	.008	.039	.050
H-A	.50	.012	.009	.035	.013	.025	.016	.042
H-C	.23	.	.001	.043	.021	.026	.035	.007
C HORIZON MEAN								
C-A	5.93	.071	.017	.156	.022	.033	.103	.107
C-C	6.10	.058	.007	.106	.037	.035	.113	.095
H-A	6.13	.100	.019	.084	.033	.053	.099	.056
H-C	6.00	.110	.008	.128	.036	.050	.094	.097
STANDARD DEVIATION								
C-A	.55	.003	.005	.058	.010	.010	.018	.029
C-C	.26	.003	.001	.024	.010	.010	.004	.034
H-A	.06	.022	.007	.023	.014	.020	.011	.016
H-C	.35	.	.002	.068	.009	.005	.018	.052

APPENDIX B

SOIL CHEMISTRY DATA

TABLE XI

POTASSIUM MG/GRAM OF SOIL

	HARDWOOD				CONIFER			
	SOIL HORIZONS							
PITS	A	E	B	C	A	E	B	C
1								
	5.97	2.86	2.24	1.98	8.14	4.16	4.22	3.09
	6.00	2.59	2.25	1.84	7.72	4.03	4.36	2.86
	5.72	2.65	2.09	2.47	8.40	4.58	4.20	2.87
2								
	3.79	2.56	1.50	2.08	6.95	2.48	1.90	1.86
	4.64	2.62	1.57	1.99	6.81	2.42	1.95	1.80
	4.18	3.09	1.49	1.90	6.95	2.49	2.04	2.00
3								
	8.93	2.99	2.47	1.99	5.59	2.73	3.68	1.90
	8.20	2.80	2.31	2.03	5.47	2.86	3.46	1.85
	8.88	2.70	2.17	2.05	5.63	2.73	3.51	1.94

TABLE XII

MAGNESIUM MG/GRAM OF SOIL

	HARDWOOD				CONIFER			
	SOIL HORIZONS							
PITS	A	E	B	C	A	E	B	C
1								
	2.06	0.77	0.57	3.56	5.01	1.82	3.38	3.56
	2.23	0.74	0.62	3.61	5.00	1.76	3.30	3.25
	2.15	0.72	0.61	3.59	4.82	1.76	3.25	2.97
2								
	1.86	1.13	2.11	4.42	3.53	0.85	2.77	2.73
	1.98	1.10	1.96	4.49	3.55	0.80	3.42	2.53
	1.91	1.10	2.30	4.43	3.35	0.86	3.24	2.52
3								
	3.37	1.10	1.44	5.97	1.95	0.72	3.30	2.75
	3.66	1.12	1.36	5.77	1.93	0.70	2.10	2.59
	3.58	1.12	1.42	5.84	2.03	0.70	2.40	2.61

TABLE XIII

SODIUM MG/GRAM OF SOIL

	HARDWOOD				CONIFER			
	SOIL HORIZONS							
PITS	A	E	B	C	A	E	B	C
1								
	1.52	.94	1.74	1.77	1.61	.83	1.19	1.32
	1.37	.89	1.69	1.68	1.59	.84	1.19	1.28
	1.32	.93	1.65	1.56	1.48	.84	1.15	1.22
2								
	1.05	.16	.93	1.12	1.04	.83	1.17	1.54
	0.92	1.00	.98	1.15	1.12	.81	1.22	1.55
	0.84	1.05	.94	1.11	0.97	.84	1.26	1.57
3								
	1.35	.83	.98	1.11	1.20	.83	1.07	1.26
	1.43	.84	.93	1.14	1.53	.85	1.04	1.30
	1.20	.89	.94	1.12	1.56	.75	1.00	1.49

TABLE XIV

CALCIUM MG/GRAM OF SOIL

	HARDWOOD				CONIFER			
	SOIL HORIZONS							
PITS	A	E	B	C	A	E	B	C
1								
	8.04	2.21	0.87	1.02	24.31	6.89	4.48	1.65
	8.75	2.07	1.03	1.55	24.87	6.22	4.57	1.56
	8.29	1.95	0.99	1.96	25.11	6.55	4.08	1.67
2								
	3.08	1.77	0.62	0.59	18.34	1.57	0.69	1.27
	3.27	1.57	0.55	0.61	17.89	1.51	0.83	1.02
	3.03	1.70	0.52	0.88	18.42	2.55	0.79	1.14
3								
	2.10	2.57	1.02	0.49	7.91	1.08	2.42	0.64
	12.32	2.59	0.96	0.48	7.81	1.12	2.44	0.41
	12.22	2.66	0.90	0.54	8.20	1.12	2.55	0.57

TABLE XV

SOIL pH

	SOIL pH BEFORE LEACHING					
	CONIFER			HARDWOOD		
	SOIL PITS					
SOIL HORIZONS	1	2	3	1	2	3
A	3.40	3.29	3.28	3.51	3.54	3.49
	3.43	3.28	3.30	3.49	3.54	3.51
	3.39	3.27	3.23	3.49	3.53	3.49
E	3.83	3.74	3.80	3.76	3.74	3.77
	3.76	3.73	3.83	3.76	3.73	3.75
	3.77	3.75	3.81	3.77	3.73	3.75
B	3.87	3.78	3.83	3.82	3.78	3.88
	3.87	3.78	3.90	3.79	3.78	3.87
	3.86	3.77	3.84	3.83	3.77	3.85
C	3.91	3.83	3.95	3.86	3.84	3.83
	3.91	3.81	3.97	3.85	3.78	3.83
	3.90	3.79	3.91	3.82	3.83	3.86
	SOIL pH AFTER BEING LEACHED WITH ACID RAIN					
A	3.47	3.52	3.59	3.63	3.63	3.74
E	3.85	3.80	3.92	3.79	3.81	3.89
B	3.87	3.92	3.89	3.88	3.85	3.89
C	3.85	3.86	3.98	3.89	3.93	3.93

	.01M CaCl	DISTILLED
HARDWOOD - PIT 2 - E SOIL HORIZON pH =	3.89	4.76
CONIFER - PIT 3 - B SOIL HORIZON pH =	3.89	4.81
CONIFER - PIT 1 - C SOIL HORIZON pH =	3.85	4.77

TABLE XVI

PERCENT ORGANIC MATTER

	CONIFER			HARDWOOD		
	SOIL PITS					
SOIL HORIZONS	1	2	3	1	2	3
A	10.6	10.1	11.6	7.8	3.8	8.3
	10.5	10.1	11.2	8.0	3.6	8.6
	11.2	10.9	11.0	7.8	4.3	8.7
E	3.9	1.9	2.3	3.2	2.4	3.5
	3.9	1.9	2.7	3.2	2.4	3.3
	4.1	2.0	2.7	3.1	2.5	3.4
B	1.6	0.9	0.7	1.8	1.2	1.7
	1.5	0.8	0.8	1.9	1.1	1.7
	1.5	0.8	0.7	1.8	1.1	1.6
C	0.9	0.6	0.6	1.3	0.9	0.9
	0.9	0.5	0.5	1.2	0.8	1.0
	0.8	0.6	0.5	1.3	0.9	1.0

TABLE XV11

EXCHANGEABLE ACIDITY

	EXCHANGABLE ACIDITY BEFORE LEACHING MEQ/G					
	CONIFER			HARDWOOD		
	SOIL PITS					
SOIL HORIZONS	1	2	3	1	2	3
A	0.24	0.25	0.18	0.13	0.13	0.14
	0.24	0.24	0.17	0.15	0.13	0.14
	0.24	0.24	0.18	0.14	0.12	0.14
E	0.12	0.08	0.09	0.06	0.10	0.09
	0.12	0.09	0.09	0.06	0.10	0.09
	0.12	0.09	0.09	0.06	0.10	0.09
B	0.19	0.18	0.14	0.07	0.07	0.09
	0.19	0.19	0.13	0.08	0.09	0.09
	0.19	0.18	0.13	0.08	0.09	0.09
C	0.18	0.17	0.18	0.14	0.13	0.17
	0.19	0.17	0.18	0.15	0.15	0.16
	0.18	0.17	0.18	0.14	0.15	0.16
	EXCHANGABLE ACIDITY AFTER LEACHING MEQ/G					
A	0.16	0.19	0.21	0.16	0.10	0.14
	0.16	0.20	0.21	0.15	0.08	0.15
E	0.08	0.07	0.06	0.10	0.10	0.08
	0.08	0.09	0.08	0.10	0.08	0.08
B	0.20	0.20	0.12	0.08	0.09	0.08
	0.18	0.15	0.14	0.09	0.08	0.07
C	0.18	0.17	0.18	0.13	0.14	0.15
	0.16	0.17	0.17	0.14	0.14	0.14

TABLE XVIII

SOLUBLE SULFATE

	SOIL HORIZONS				
PITS	O	A	E	B	C
HARDWOOD					
1	30.0	26.5	27.0	30.0	28.3
2	27.0	26.5	25.5	31.0	25.0
3	31.5	30.0	24.5	22.8	31.5
CONIFER					
1	28.2	33.0	33.0	31.5	28.5
2	25.0	29.5	25.0	30.0	27.0
3	28.5	30.0	25.5	25.0	30.0

TABLE XIX

SULFATE ADSORPTION ISOTHERMS FOR HARDWOOD SITE

HARDWOODS	ORIGINAL SO4 CONCENTRATION uM	SOLUTION SO4 CONCENTRATION MEQ/L	SOIL SO4 ADSORBED MEQ/G
A SOIL HORIZON			
	200	0.506	-0.021
	400	0.590	0.042
	800	1.210	0.078
	1600	2.666	0.106
	3200	5.766	0.126
	6400	9.474	0.665
E SOIL HORIZON			
	200	0.50	-0.020
	400	0.52	0.055
	800	1.57	0.080
	1600	2.59	0.121
	3200	5.58	0.162
	6400	9.73	0.613
B SOIL HORIZON			
	200	0.10	0.058
	400	0.49	0.060
	800	1.07	0.106
	1600	2.834	0.074
	3200	4.926	0.294
	6400	9.266	0.706
C SOIL HORIZON			
	200	0.116	0.056
	400	0.088	0.142
	800	0.600	0.200
	1600	1.552	0.329
	3200	4.154	0.449
	6400	7.600	1.040

TABLE XX

SULFATE ADSORPTION ISOTHERMS FOR CONIFER SITE

CONIFER	ORIGINAL SO4 CONCENTRATION uM	SOLUTION SO4 CONCENTRATION MEQ/L	SOIL SO4 ADSORBED MEQ/G
A SOIL HORIZON			
	200	0.514	-0.022
	400	0.8	0
	800	1.09	0.102
	1600	2.77	0.086
	3200	5.51	0.178
	6400	9.5	0.66
E SOIL HORIZON			
	200	0.45	-0.01
	400	0.704	0.02
	800	1.338	0.054
	1600	2.84	0.072
	3200	5.19	0.242
	6400	8.97	0.766
B SOIL HORIZON			
	200	0.406	0.002
	400	0.188	0.122
	800	0.31	0.258
	1600	1.64	0.312
	3200	4.08	0.464
	6400	6.97	1.166
C SOIL HORIZON			
	200	0.17	0.046
	400	0.108	0.138
	800	0.316	0.256
	1600	0.996	0.44
	3200	3.888	0.502
	6400	6.4	1.28

APPENDIX C

SOIL PHYSICAL PROPERTIES DATA

TABLE XX1

SOIL PHYSICAL PARAMETERS

	CONIFER		HARDWOOD	
SOIL HORIZON	DEPTH/CM	% MOISTURE	DEPTH/CM	% MOISTURE
A	3	22	7	19
E	14	17	9	18
B	27	24	24	19
C	20	22	20	22

TABLE XXII

TEXTURE

	CONIFER			HARDWOOD		
HORIZON	% SILT	% SAND	% CLAY	% SILT	% SAND	% CLAY
A	42	38	20	31	46	23
E	26	46	28	18	67	15
B	18	28	54	26	56	18
C	20	18	6	23	21	56

TABLE XXIII

VOLUME OF RAINFALL AND SOIL USED IN SOIL LEACHATE STUDY

	SIMULATED RAIN VOLUME		SOIL WEIGHT/G	
	VOLUME ADDED		USED IN COLUMNS	
SOIL HORIZON	LITERS	DEPTH/CM	CONIFER	HARDWOOD
O	4.5	97	375	375
A	4.0	86	123	287
E	3.5	76	711	492
B	2.0	43	1450	1315
C	0.75	15	1100	1100

APPENDIX D

SOIL LEACHATE DATA

TABLE XXIV

LEACHATE pH

		HARDWOOD		CONIFER	
	PITS	ACID	CONTROL	ACID	CONTROL
O HORIZON					
	1	5.8	6.6	5.8	6.3
	2	4.5	6.2	5.0	5.9
	3	5.8	6.4	5.7	6.6
A HORIZON					
	1	5.1	5.7	5.1	5.5
	2	4.5	5.8	4.7	5.2
	3	5.2	5.3	4.9	5.7
E HORIZON					
	1	5.6	6.3	5.2	6.0
	2	5.4	6.1	5.8	5.6
	3	5.0	5.8	5.6	6.0
B HORIZON					
	1	5.2	5.9	6	6.3
	2	6.2	6.3	6.3	6.0
	3	5.6	5.9	6.2	6.6
C HORIZON					
	1	6.1	5.6	5.3	5.8
	2	6.2	6.2	6.3	6.2
	3	6.1	6.2	6.2	6.3

TABLE XXV

LEACHATE CALCIUM MG/L

		HARDWOOD		CONIFER	
SOIL HORIZON		ACID	CONTROL	ACID	CONTROL
LITTER					
	1	2.0	0.7	2.9	1.2
	2	1.6	0.7	2.0	0.8
	3	3.5	1.5	2.0	0.6
A	1	1.6	0.7	2.3	1.0
	2	1.6	0.6	1.6	0.9
	3	2.5	0.7	1.7	0.6
E	1	1.7	1.3	2.2	1.5
	2	2.0	0.7	1.9	1.2
	3	1.6	0.8	1.5	0.9
B	1	1.0	1.1	0.8	0.8
	2	1.9	2.0	0.9	0.5
	3	1.1	1.5	1.0	0.6
C	1	1.3	0.9	0.5	0.7
	2	1.3	1.0	0.9	0.9
	3	0.6	1.1	0.6	0.5

TABLE XXVI

LEACHATE MAGNESIUM MG/L

		HARDWOOD		CONIFER	
SOIL HORIZON		ACID	CONTROL	ACID	CONTROL
LITTER					
	1	0.5	0.2	0.5	0.2
	2	0.4	0.2	0.4	0.2
	3	0.3	0.2	0.4	0.1
A	1	0.4	0.1	0.5	0.2
	2	0.4	0.2	0.5	0.2
	3	0.5	0.2	0.4	0.1
E	1	0.4	0.2	0.4	0.2
	2	0.5	0.1	0.5	0.2
	3	0.5	0.2	0.4	0.1
B	1	0.4	0.2	0.5	0.3
	2	0.7	0.7	0.4	0.2
	3	0.6	0.4	0.4	0.3
C	1	0.5	0.5	0.4	0.3
	2	0.5	0.5	0.2	0.1
	3	0.2	0.3	0.2	0.1

TABLE XXVII

LEACHATE SODIUM MG/L

		HARDWOOD		CONIFER	
SOIL HORIZON		ACID	CONTROL	ACID	CONTROL
LITTER					
	1	2.2	2.5	2.3	2.4
	2	1.6	2.1	1.9	1.7
	3	2.0	2.1	2.3	2.4
A	1	3.3	2.3	2.8	2.6
	2	2.2	2.7	2.6	2.3
	3	2.3	2.5	2.5	2.7
E	1	3.8	4.8	3.9	4.0
	2	3.1	3.7	4.0	3.5
	3	3.3	3.4	3.2	3.6
B	1	3.6	3.1	2.6	3.4
	2	3.7	4.4	2.7	1.9
	3	3.0	2.9	2.3	3.5
C	1	2.5	2.5	2.5	2.7
	2	2.3	2.3	2.7	2.6
	3	2.0	1.7	1.9	2.5

TABLE XXVIII

LEACHATE POTASSIUM MG/L

		HARDWOOD		CONIFER	
SOIL HORIZON		ACID	CONTROL	ACID	CONTROL
LITTER					
	1	1.6	1.3	1.6	1.9
	2	0.8	0.7	1.3	1.0
	3	0.7	0.6	1.8	0.8
A	1	4.6	2.3	3.2	4.5
	2	5.9	1.3	2.6	2.8
	3	3.2	3.0	2.7	1.3
E	1	4.6	3.5	3.2	3.8
	2	2.0	5.4	2.0	3.6
	3	4.8	1.8	3.6	3.1
B	1	6.5	3.0	2.1	1.5
	2	5.6	3.5	4.6	3.9
	3	3.3	3.1	4.2	5.4
C	1	2.5	5.6	4.2	3.5
	2	2.6	4.1	5.3	2.5
	3	1.5	1.6	4.3	5.1

TABLE XXIX

LEACHATE SULFATE uM/L

	HARDWOOD		CONIFER	
LEACHATE	ACID	CONTROL	ACID	CONTROL
		SOIL PIT 1		
RAINFALL	70	12	70	12
O	76	29	91	281
A	79	35	92	113
E	81	42	95	110
B	79	57	58	112
C	47	53	37	76
		SOIL PIT 2		
RAINFALL	70	12	70	12
O	109	345	75	30
A	101	242	79	34
E	101	169	86	36
B	90	162	37	38
C	62	79	35	28
		SOIL PIT 3		
RAINFALL	70	12	70	12
O	102	247	1035	27
A	83	255	113	33
E	109	132	87	49
B	88	88	43	46
C	41	57	34	100

TABLE XXX

LEACHATE NITRATE uM/L

	HARDWOOD		CONIFER	
LEACHATE	ACID	CONTROL	ACID	CONTROL
		SOIL PIT 1		
RAINFALL	45.8	7.4	45.8	7.4
O	55.8	8.1	48.0	8.3
A	56.3	8.3	51.2	7.5
E	53.7	7.0	50.0	5.8
B	44.7	6.5	40.8	9.0
C	10.6	9.5	22.3	7.5
		SOIL PIT 2		
RAINFALL	45.8	7.4	45.8	7.4
O	55.0	10.5	53.2	8.5
A	54.7	7.7	52.7	8.3
E	53.8	6.4	59.0	6.6
B	28.0	6.7	35.3	6.2
C	24.2	7	17.5	6.3
		SOIL PIT 3		
RAINFALL	45.8	7.4	45.8	7.4
O	50.2	8.2	54.2	8.0
A	35.2	7.3	58.4	8.2
E	47.1	7.5	55.8	6.6
B	40.2	5.6	35.7	6.0
C	22.3	6.3	11.4	7.0

TABLE XXXI

LEACHATE CHLORIDE uM/L

	HARDWOOD		CONIFER	
LEACHATE	ACID	CONTROL	ACID	CONTROL
		SOIL PIT 1		
RAINFALL	3	3	3	3
O	22	47	14	38
A	64	68	59	55
E	62	101	91	56
B	154	100	72	53
C	98	167	122	92
		SOIL PIT 2		
RAINFALL	3	3	3	3
O	112	51	23	49
A	113	115	54	89
E	39	102	80	105
B	88	143	115	165
C	96	168	223	92
		SOIL PIT 3		
RAINFALL	3	3	3	3
O	51	44	56	20
A	45	39	47	55
E	61	50	63	73
B	101	57	182	118
C	58	50	124	134

Vita 2

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