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I am submitting herewith a thesis written by David V. Peterson entitled "Soil Acidification and Sawdust Amendment Effects on Rabbiteye Blueberry Growth, and the Effects of Acidification on Soil Properties." I have read this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Science.

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SOIL ACIDIFICATION AND SAWDUST AMENDMENT EFFECTS ON RABBITEYE BLUEBERRY GROWTH, AND THE EFFECTS OF ACIDIFICATION ON SOIL PROPERTIES

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

David V. Peterson

Winter 1982

3058008

ACKNOWLEDGMENTS

The author expresses gratitude and appreciation to the following persons:

Dr. David A. Lietzke, my major professor, for his guidance and encouragement throughout the court of this study;

Dr. J. D. Wolt, Dr. D. E. Deyton, and Dr. C. A. Mullins for their advice and suggestions, and for serving as members of the graduate committee;

Dr. V. H. Reich and Dr. W. L. Sanders for their assistance in the statistical analysis of the experiment;

Mr. Richard Hammer and Ms. Sandy Robertson for assistance in laboratory analysis;

Ms. Betty Gorman and Mrs. Lonnie Nordmeyer for typing of the original manuscript;

The University of Tennessee, Knoxville, Agricultural Experiment Station for financial assistance in the form of an assistantship;

My parents for their encouragement and financial support during the course of my graduate work.

ABSTRACT

Aluminum sulfate ($Al_2(SO_4)_3$) and elemental sulfur (elemental S) at four rates each were used to acidify a sandy loam soil to various levels of soil acidity. Aluminum sulfate was applied at rates of 7.5, 15.0, 30.0, and 60.0 grams per pot (3000, 6000, 12,000, and 24,000 kg/ha, respectively), while elemental S was added at rates of 1.9, 3.8, 7.5, and 15.0 grams per pot (750, 1500, 3000, and 6000 kg/ha, respectively). Sawdust was incorporated into the soil at rates of 0, 20, 40, and 60% by volume.

In the first part of this investigation, the two soil acidulents were evaluated for their potential to produce optimal growth in rabbiteye blueberries (Vaccinium ashei) through lowering of soil pH. The greatest plant weight gain was achieved using elemental S at 7.5 grams per pot, and 60% sawdust, which acidified the soil to pH 4.4. At the highest rates of application of both acidulents, plant weight gain decreased considerably from the optimum, suggesting that a toxicity may have existed. Growth was severely reduced where no sawdust was amended into the soil, regardless of the source or rate of acidulent.

In the second part of this investigation, the acidulents were compared for their effects on several soil properties. These soil properties included silver-thiourea extractable Ca, Mg, K, Na, Al, and H, plus CEC, pH, and mineralogy. Magnesium and Ca levels in the most acid treatments were approximately double those of the controls and appeared to be the result of the amount of decrease of pH, rather than

the source of acidulent. Potassium levels were substantially higher in the high elemental S treatments than in the controls, apparently as a result of destruction of hydroxy interlayered vermiculite (HIV) and a subsequent release of K in this treatment. Sodium levels differed from the controls only in the $Al_2(SO_4)_3$ treatments, where they increased with increasing rate of application. Aluminum and H levels increased sharply only at the highest rates of application of both acidulents. Much of this effect was pH related.

In addition to being more favorable for plant growth, 1 unit weight of elemental S was found to cause the same pH decrease as approximately 8 times as much $Al_2(SO_3)_4$. Sawdust levels had no significant effect on the amount of decrease in pH.

Destruction of clay minerals was evident in DSC patterns at the highest rate of elemental S application. Clay minerals that showed alteration were gibbsite, kaolinite, and HIV. This destruction of clay minerals, however, led to increases in Ca/Mg and K/NH_4 CEC values, when compared to the controls. These increases are thought to be a result of creation of more edges or exposure of interlayer of HIV.

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CHAPTER I

GENERAL INTRODUCTION

There are large acreages of naturally acid sandy soils on the Cumberland Plateau in Tennessee. Blueberries are an abundant natural understory plant in many of the areas that have not been cleared for cultivation. Much of the cleared land has been limed to provide conditions conducive to the growth of agronomic crops. Many agronomic crops, however, do not perform well under conditions of mid and late summer drought, which frequently occurs on the Cumberland Plateau. There has been an increased interest in converting some of this limed cropland into a higher income producing crop suited to the conditions of the area. Rabbiteye blueberries (Vaccinium ashei) are a recent introduction of cultivated blueberries which are adapted to warmer southern climates. Members of the Ericaceae family, which includes blueberries, are known to perform best under acid soil conditions. Consequently, in order to obtain conditions desirable for blueberry growth, it is necessary for growers to acidify previously limed soils. Since little is known of the effects of acidifying previously limed soils on blueberry plant growth or on soil properties themselves, a study was conducted to examine these effects.

CHAPTER II

LITERATURE REVIEW

I. Soil Conditions for Blueberry Production

Most members of the Ericaceae family, including azalea, rhododendron, winterberry, huckleberry, cranberry, and blueberry, are acid loving plants. Optimum soil pH ranges for blueberries have been studied by a number of researchers (13, 14, 15, 30, 41, 63, 64) with somewhat variable results. Most studies have indicated that a soil pH range of 4.0 to 5.2 is generally the most acceptable for blueberry production. Townsend (64) using nutrient solutions as a growth medium, found growth to be best at pH 4.0, but only slightly better than that at 5.0. Growth was restricted at pH levels 3.0 and 6.0, and nonexistant at 2.5. Plants grown in a pH 3.0 nutrient solution had relatively coarse root systems, while those grown at higher pH values had considerably finer root systems. Plants grown in pH 5.0 and 6.0 nutrient solutions had abnormally dark root systems. It is not known if the darker root color observed at higher pH values was due to disease or other physiological disorders, which resulted in reduced growth, or due to secondary injuries resulting from the high pH. Townsend (64) observed abnormally high levels of Fe and Mn at pH 6.0 and above, suggesting that precipitation of these elements occurred on or within the root. His explanation of the darker root color was the presence of insoluble hydrated manganese oxide, which resulted from the oxidation

of soluble manganous hydroxide. The combined effects of high pH and air exposure could readily lead to the oxidation of manganese.

Plants grown on soils having higher than optimal pH values have also been characterized by weak plant growth and poor production (30). Poor plant growth and production associated with high soil pH values has been shown to be coincident with leaf chlorosis, which was attributed to iron deficiency (5). Oertli (42) observed that chlorotic leaves contained less iron than healthy ones, but found no evidence that the chlorosis was a result of iron deficiency. As opposed to Oertli, Cain (14) found that plants growing on high pH soils often contained as much or more iron in their foliage as those growing at a lower pH. Herath and Eaton (32) concluded that soil acidity influences growth indirectly, and is not a result of the direct effect of soil pH on the nutrient composition of the foliage. They suggested that the role of soil pH is related to the form of soil nitrogen. This conclusion is in agreement with the findings of several other researchers (14, 42). Cain (14) suggested that one of the major reasons for the failure of blueberries on high pH soils is a lack of ammonium nitrogen. In a later study (15), he found that chlorotic foliage associated with plants grown on high pH soils contained higher concentrations of bases than healthy green leaves of plants grown on low pH soils. High leaf base concentration was generally concomitant with high leaf pH. Clark (19) showed that the presence of ammonium ions in the soil resulted in decreased base uptake in strawberries (Fragaria chiloensis x virginiana). Near neutral pH values in soils provide conditions favorable for

nitrification of ammonium to nitrate, which in turn would lead to increased uptake of bases.

Cain (15) considered leaf chlorosis to be the result of the failure of iron to perform its function in the leaf, rather than a lack of iron in the leaf. He suggested that in order for iron to perform its roles in the synthesis of chlorophyll and protein, it must exist at least part of the time as the ferric ion. Since the solubility of the ferric ion decreases 1000 fold for each unit rise in pH, it is relatively insoluble under near neutral conditions. The major differences between green and chlorotic leaves were that leaf base concentrations and pH were significantly higher in those that were chlorotic. Cain postulated that the conversion of soil ammonium to nitrate at high soil pH levels resulted in an increase in leaf base concentration. This in turn would raise the leaf pH, causing iron precipitation and a decrease in protein synthesis and chlorophyll production. This conclusion is in agreement with the findings of Oertli (42) who showed that significantly greater yields could be attained at higher soil pH values using ammonium nitrogen as opposed to nitrate nitrogen.

As previously pointed out, most studies have indicated that a soil pH range of 4.0 to 5.2 is best for the growth of blueberries. Harmer (30) studied blueberry wood growth and fruit production over a two year period on muck soils in Michigan. The optimum soil pH for wood growth was in agreement with that found by the researchers previously mentioned, but he suggested that the optimum for fruit production may be slightly higher. In the first year the blueberries produced, a soil of pH 4.6 resulted in the most blossoms and fruit.

However, the following year, those plants grown on soils of pH 5.5 to 5.7 resulted in significantly larger amounts of blossoms and fruit than at any other soil pH level sampled. The findings of Hall et al. (28) also suggested that slightly higher soil pH values than those previously mentioned may be optimal. Their study, which was based on growth using a compost medium, showed that plant growth was best on soils in the pH range of 4.9 to 5.5. They suggested, however, that this optimum range may have been related to the type of medium used in the study. Since Harmer (30) used a muck soil, and Hall et al. (28) used a composted medium, there is a possibility that optimum soil pH levels are somewhat dependent on organic matter levels and on the type of medium used.

Organic matter amendments, usually in the form of sawdust, were found to improve blueberry growth and production (10, 11). Sawdust incorporated into the soil was found to be superior to surface mulching, and a combination of the two gave the best results. Kender and Eggert (36) found that surface mulching was superior to incorporation. However, since their study used lowbush blueberries, incorporation resulted in destruction of and inhibition of rhizome development, causing decreased growth. Since highbush and rabbiteye blueberries are not dependent on rhizome development for increased growth, this study may not be relevant, except for lowbush blueberries. Townsend (65) found that sawdust was beneficial to blueberry growth only if it was at least partially decomposed, and that incorporation of raw sawdust was detrimental to plant growth. An additional benefit of incorporating sawdust for blueberry growth may be the improvement of soil aeration (7).

Decomposing organic matter was found to improve the solubility

of iron in acid soils (9). The use of sawdust was shown to result in increased levels of extractable iron and decreased pH in the foliage (10). Larger applications of sawdust were correlated with increased buffer action to a point where fertilizer applications had no significant effect on soil pH (11).

Optimum soil conditions for blueberry production were summarized by Ballinger and Goldston (6) in one of the most comprehensive studies on the subject. Their study used two varieties of highbush blueberries, 'Murphy' and 'Wolcott'. Yields of both varieties were negatively correlated with soil pH and the calcium percentage of the cation exchange capacity. Yields of 'Murphy' were also positively correlated with soil magnesium, potassium, manganese, total bases, cation exchange capacity, and organic matter.

II. Soil Acidulents

Since soil pH values are often higher than those considered optimal for the growth of blueberries and other acid loving plants, many researchers (21, 43, 57) have investigated the use of a number of acidifying materials to decrease soil pH. These acidulents include elemental sulfur, sulfuric acid, aluminum sulfate, iron sulfate, ammonium nitrate, and ammonium sulfate. Sulfuric acid, iron sulfate, ammonium nitrate, and ammonium sulfate have been found to be much less effective in lowering soil pH, when compared to elemental sulfur and aluminum sulfate (33, 41, 43, 62).

Elemental sulfur is the most widely used soil acidulent, also being used to provide sulfur necessary for plant growth (12). Since

elemental sulfur is insoluble in water, it must first be oxidized before it can be utilized by plants or cause changes in soil pH. Its oxidation to produce increased soil acidity is summarized by the following general reaction: $2S + 3O_2 + 2H_2O \rightarrow 4H^+ + 2SO_4^=$. The processes by which sulfur is oxidized includes biological and organic chemical oxidation, the former being far more important (39). Autotrophic bacteria of the genus Thiobacillus have been studied in more detail than any of the other sulfur oxidizing organisms, and are considered to be the most important (12). Three species of Thiobacillus account for most of the sulfur oxidation in arable soils (58). These species include T. thiooxidans, T. thioparus, and T. denitrificans. T. thiooxidans is tolerant of a wide pH range, developing best at pH 2.0 to 3.0. T. thioparus grows best at reactions close to neutrality. T. denitrificans is unique in that it can grow either aerobically or anaerobically.

Optimum temperatures for biological sulfur oxidation are in the range of 30 to 40°C. (44). Since the oxidation of elemental sulfur requires both oxygen and water, it is evident that an adequate supply of water is necessary but not so much that it causes air to be limiting. Moser and Olson (40) found that sulfur oxidation was most rapid at moisture contents slightly above field capacity. They also found oxidation to be more rapid in heavier textured soils. Sulfur oxidation rates also appear to increase with increasing soil pH, although pH may not be critical in most soils since oxidation is fairly rapid over a range of pH 4.0 to 9.6 (52, 67, 68). Ratsek (51) found that the rate of oxidation increased with decreasing particle size. Elemental sulfur of size 325 mesh oxidized faster than 32, 16, or 8 mesh, but was too

expensive and was also difficult to apply. Since 16 mesh gave about the same rate of oxidation as 32 mesh, Ratsek recommended its use because it was less expensive. The 8 mesh elemental sulfur oxidized far too slowly to be practical for use in most situations.

Aluminum sulfate, although not widely used in agriculture, has been used as an acidulent to some extent, particularly by floriculturalists for acid loving ornamentals. It reacts with water by the following general hydrolysis reaction:

$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^=$ (61). It also causes a lowering of pH by replacing exchangeable cations on the soil colloid by the following reaction:

$$Al_2(SO_4)_3 + \left[\text{clay}\right]^{4H}_{Ca} \rightarrow {}^{Al}_{Al}\left[\text{clay}\right] + CaSO_4 + 4H^+ + 3SO_4^= \text{ again}$$

resulting in the production of hydrogen ions (61).

A number of researchers have attempted to establish relationships between amounts of elemental sulfur and aluminum sulfate required to bring about a unit change in soil pH (16, 41, 51, 59). There is extreme variability in their findings, probably due at least in part to differences in soil texture and chemical properties. Mullin (41) found that 1680 kg/ha (1500 lb/A) of elemental sulfur resulted in a two unit decrease in pH on a sandy loam soil. Chadwick (16) and Stoeckeler and Arnemann (59) in spearate studies, found that an application of 2464 kg/ha (2200 lb/A) of elemental sulfur gave a decrease in pH of two units on silt loam soils. Stoeckeler and Arnemann (59) reported that 3024 kg/ha (2700 lb/A) of aluminum sulfate gave a two unit decrease, while

Chadwick (16) reported an application nearly twice that was necessary to get the same decrease in pH. Ratsek (51) found an even greater difference in the acidifying potential of elemental sulfur and aluminum sulfate. Aluminum sulfate acidified the soil more quickly than elemental sulfur. However, after only three weeks, one pound of elemental sulfur resulted in the same soil pH decrease as one pound of aluminum sulfate, and after three months, one pound of sulfur was approximately equal to seven pounds or more of aluminum sulfate. Reported rates of acidification by elemental sulfur are variable ranging from two weeks (33), to four months (55), to more than a year (43). Since the amount of decrease in soil pH is highly correlated with the amount of sulfur oxidized (44), differences in rates of acidification are probably due to those factors which regulate oxidation rates. Overley and Allmendinger (43) found that gradual decreases in soil pH continued for up to three years at a depth of four feet.

The acidity produced from applications of aluminum sulfate has been reported to persist in the soil for one year, while the acidity produced from the oxidation of elemental sulfur has been found to persist for up to three years, with little increase in pH. Trevett and Durgin (66) reported that the soil pH on plots where elemental sulfur had been applied at 616 kg/ha (550 lb/A) was still considerably lower than the control after nine years.

Excessive applications of aluminum sulfate and elemental sulfur have been found to result in damage to blueberries (56, 66). Trevett and Durgin (66) recommended that no more than 1120 kg/ha (1000 lb/A) of elemental sulfur be applied within a two year period. Spurway and

Wildon (57) recommended that only 196 kg/ha (175 lb/A) elemental sulfur and 1288 kg (1150 lb/A) of aluminum sulfate be applied at one time without danger of crop injury. Collison (21) suggested that continued applications of aluminum sulfate over time may leave soluble aluminum salts which may prove toxic. Audus and Quastel (3) showed that $S_2O_3^{=}$, an intermediate formed in the oxidation of sulfur, inhibited root growth in a number of plants.

III. Soil Chemistry

The effect of pH on the cation exchange capacity (CEC) of soils has been demonstrated by a number of researchers (20, 22, 48). Cation exchange capacity is the result of negative charges on the colloidal clay and humus particles of the soil. This negative charge can be divided into two components, a constant or permanent charge, and a variable or pH-dependent charge. The permanent charge is generated by isomorphous substitution of Al^{+++} for Si^{++++} in the tetrahedral sheet, and of Mg^{++} or Fe^{++} for aluminum in the octahedral sheet of a clay lattice (54). The variable, or pH-dependent charge is the consequence of pH-dependent dissociation of hydroxyl groups, which may be located at the edges of silicate clays, in phenolic or carboxyl groups, or at the edges of alumino-silicate gels. A blocking of negative charge by strongly adsorbed hydroxy-aluminum cations may also contribute. As the pH rises, these cations precipitate as aluminum hydroxide leaving a negatively charged site free (4). The amount of pH-dependent charge appears to be positively correlated with the amount of clay and organic matter in the soil (29, 35, 48). There is extreme variability in the

reported ranges where the greatest increases in CEC occurs with increasing pH. Pratt (48), working with acid soils in California, found that some soils exhibited a constant increase in CEC from pH 3.0 to 8.0, while others showed little or no increase between pH 3.0 and 4.5, with a constant increase from pH 4.5 to 8.0. Helling et al. (31) working with a variety of soils in Wisconsin having an average organic matter content of 3.4 percent and an average clay content of 13.3 percent, observed a constant increase in CEC between pH 2.5 and 5.0. The increase was somewhat smaller between pH 5.0 and 6.0, with a particularly marked rise between 7.0 and 8.0. Between pH 2.5 and 8.0, the CEC of the organic matter was found to increase by a factor of 6, while the CEC of the clay increased by a factor of 1.7. Kalisz and Stone (34) working with forest soils in New York and New England, observed that the CEC doubled over the pH range 3.5 to 5.5. They found that the CEC values of these acid, humus dominated soils were only 1/4 to 1/2 that estimated at pH 7.0. Base saturation, accordingly, was two to four times as great at pH 7.0 as at 3.5 to 5.5.

A large amount of variability exists among the findings of researchers concerning pH-dependent and total CEC of organic matter and clay fractions. Incorporated organic matter has been shown to have a higher CEC per unit mass than surface litter (34). The degree of decomposition of organic materials greatly increases the CEC of the organic matter fraction (38, 45, 50). The amount of colloidal acids has been found to increase with the degree of decomposition of the organic matter (50). Since these colloidal acids are the most active part of the organic matter, presumably they are highly significant in

increasing the CEC. McGeorge (38) observed that the lignin content of organic matter is a linear function of the base exchange capacity. The lignin content was thought to be related to the degree of destruction of simple carbohydrates and proteins.

The amount of pH-dependent charge in the clay fraction appears to be related, at least in part to the mineralogy of the clays, with amorphous materials having one of the largest pH-dependent CEC values of those clay minerals studied (8, 22, 49, 53). The development of a positive charge under acidic conditions by allophane is thought to be responsible for the presence of a low permanent charge and the large increase in CEC as the pH is raised (31). Coleman et al. (20) observed that the degree of pH-dependency was related to the amount of hydroxy-aluminum present in the soil system. Aluminous chlorite (hydroxy interlayered vermiculite) has been shown to have a large pH-dependent component and its presence appears to be a common property of soil clays exhibiting a pH-dependent CEC (22). Since the amount of clay edge surface area is related to the pH-dependent CEC, kaolinite has a large pH-dependent component (25). However in 2:1 type clay minerals, clay edges represent only about 1 percent of the total surface area (23). Hence, pH-dependent charge is far less important in these clay minerals. Pratt (48) working with a mixture of soil clays dominated by montmorillonite and illite, with somewhat smaller amounts of kaolinite, quartz, and amorphous materials, observed a range of pH-dependent CEC from 11.2 to 24.2 meq per 100 grams soil.

Traditional methods of measuring CEC, which include NH_4OAc displacement at pH 7.0 (17), and the sum of cations using $BaCl_2$

buffered at pH 8.2 for the exchange acidity and NH_4OAc for exchangeable bases (46), have been found to overestimate the CEC of acid soils in reference to the actual field conditions (26). This would be particularly important in those soils containing materials with large pH dependent CEC values, as discussed previously. The commonly used procedure for measurement of the effective cation exchange capacity (ECEC) involves measuring exchange acidity by leaching with unbuffered KCl and measuring the extractable bases with neutral NH_4OAc (20). Chhabra et al. (18) showed that the Ag-thiourea cation has a stronger affinity for soil colloids than for those cations occurring in the soil, and that it was highly effective in displacing exchangeable cations in soils. When compared to ECEC values obtained from the KCl-NH_4OAc method, Ag-thiourea CEC values had multiple coefficient of determination (R^2) values ranging from a low of .65 for K to a high of .93 for Mg. The R^2 value for total CEC was exceptionally good (.92).

CHAPTER III

A COMPARISON OF SOIL ACIDULENTS FOR THEIR EFFECT ON THE GROWTH OF BLUEBERRIES

I. Abstract

Aluminum sulfate [$Al_2(SO_4)_3$] and elemental sulfur (elemental S) at four rates each were used to acidify a sandy loam soil to various levels of soil acidity, and to compare their effects on the growth of rabbiteye blueberries (Vaccinium ashei). In addition, sawdust was incorporated into the soil at rates of 0, 20, 40, and 60% by volume. The soil used for this experiment had been previously limed and had an initial pH of 6.2 to 6.5. The effects of the acidulents and sawdust and their interaction effects were related to plant weight gain. The greatest plant weight gain was achieved using elemental S at 7.5 grams per pot, and 60% sawdust, which acidified the soil to pH 4.4. At the highest rates of application of both acidulents, plant weight gain decreased significantly from the optimum, suggesting that a toxicity may have existed. Growth was severely reduced where no sawdust was amended into the soil, regardless of the source or rate of acidulent. In addition to being more favorable for plant growth, 1 kg of elemental S was found to cause approximately the same decrease in soil pH as 8 times that amount of $Al_2(SO_4)_3$.

II. Introduction

Most studies concerning the importance of pH to the growth of blueberries indicate that a pH between 4.0 and 5.2 is optimal (13, 15, 30, 64). Blueberries grown on high pH soils have been characterized by weak plant growth and iron chlorosis (5, 30). This chlorosis is thought to result from high calcium levels in the leaf, causing a high leaf pH. This results in inactivation of enzyme systems involving iron (15).

Since many agricultural soils have initially high pH values from past lime applications, it is often necessary to acidify these soils before planting blueberries. Elemental S and $Al_2(SO_4)_3$ have been found to be the most effective acidulents in reducing soil pH (41, 43, 62). Excessive applications of elemental S may cause plant injury (57, 66) and continued applications of $Al_2(SO_4)_3$ may leave soluble aluminum salts, which could prove toxic.

While most soil studies relating to blueberries have focused on pH, several researchers have suggested the importance of organic matter amendments, specifically sawdust (7, 9). Boller (7) emphasized the importance of sawdust in increasing soil aeration, while Bradley and Smittle (9) found that the use of sawdust resulted in increased levels of soluble iron and decreased leaf pH.

It is noteworthy to point out that in all the previously mentioned studies, lowbush (Vaccinium augustifolium) or highbush (Vaccinium corymbosum) blueberries were used. The increased interest in and planting of rabbiteye (Vaccinium ashei) blueberries in the southern United States has led to a need for further study on the soil

conditions necessary for optimal plant growth and production. The objectives of this study were:

1) to compare the effects of $Al_2(SO_4)_3$ and elemental S acidulents and sawdust amendments in a controlled study for their effects on the growth of rabbiteye blueberries (Vaccinium ashei) in pots, when starting with a previously limed agricultural soil,
2) to relate soil pH, extractable soil magnesium, potassium, aluminum, and calcium levels, to the growth of rabbiteye blueberries.

III. Materials and Methods

This experiment was conducted as a greenhouse study at The University of Tennessee, Knoxville. The soil used was a Hartsells (Typic Hapludult, fine-loamy, thermic) sandy loam Ap horizon collected from an old orchard site at the Plateau Experiment Station located near Crossville, Tennessee. The soil had been previously limed with dolomitic limestone and had an original pH between 6.2 and 6.5. The soil was not altered in any way that would change the soil biota and was also not allowed to become air-dry.

The experiment was established as two 4 x 4 factorials using four levels of sawdust (0, 20, 40, and 60% by volume), and four rates each of $Al_2(SO_4)_3$ and elemental S, and a control, all replicated four times. It should be pointed out that although the formula $(Al_2(SO_4)_3$ is used to refer to aluminum sulfate, aluminum sulfate available as an acidulent has a number of H_2O molecules present. In this experiment,

the aluminum sulfate used had a chemical formula of $Al_2(SO_4)_3 \cdot 18H_2O$. However, for convenience it will be referred to as $Al_2(SO_4)_3$ throughout this paper. The well mixed soil-sawdust combinations were placed in 22.9 cm (9 in.) diameter plastic pots. Aluminum sulfate was incorporated into the top 15 to 20 cm of soil at rates of 2.5, 5.0, 10.0, and 20.0 grams per pot (1000, 2000, 4000, and 8000 kg/ha, respectively). Elemental S was incorporated at rates of 1.3, 2.5, 5.0, and 10.0 grams per pot (500, 1000, 2000, and 4000 kg/ha, respectively). Pots were watered with two 500 ml increments of distilled water per week starting July 1980, to aid in oxidation of the elemental S and reaction of the $Al_2(SO_4)_3$, and to approximate a winter rain leaching environment typical of the Cumberland Plateau of Tennessee. Due to unexpected rises in pH during the course of the study, it was necessary to add more $Al_2(SO_4)_3$ in October and January at rates equal to those originally used, giving final application rates of 7.5, 15.0, 30.0, and 60.0 grams per pot (3000, 6000, 12,000, and 24,000 kg/ha, respectively). It was also necessary to add more elemental S in January at rates of 0.6, 1.2, 2.5, and 5.0 grams per pot (250, 500, 1000, and 2000 kg/ha, respectively) giving final application rates of 1.9, 3.8, 7.5, and 15.0 grams per pot (750, 1500, 3000, and 6000 kg/ha, respectively). Ammonium nitrate was added at a rate of 1.2 grams per pot (500 kg/ha) in August and October to aid in sulfur oxidation and to increase the rate of sawdust decomposition.

The blueberry plants were set in the previously treated pots in February 1981, and were allowed to grow through the end of May 1981. Plants were washed free of soil and weighed before planting and again

after four months of growth. Rabbiteye blueberries (Vaccinium ashei c.v. 'Tifblue') were used since they are best adapted to the climatic conditions in Tennessee. Growth was evaluated by percent weight gain on a whole plant basis.

Soil determinations were made for pH, and for extractable K, Al, Ca, and Mg. Soil pH was measured monthly in a 1:1 soil to water solution. Unbuffered silver-thiourea was used as an extractant for K, Al, Ca, and Mg (47). Potassium was determined by flame emission spectrophotometry, while Al, Ca, and Mg were measured by atomic absorption spectrophotometry.

Regression analysis was used to show relationships between the interactions of the acidulents and sawdust amendments, and their effect on plant weight gain. Regression was also used to determine any relationships between soil pH and silver-thiourea extractable cations as they affected plant weight gain. Orthogonal contrasts were used to make specific comparisons of treatment effects on plant weight gain. Significant differences were determined at $\alpha = .05$, except where regression was used to construct surface response curves, in which case $\alpha = .10$.

IV. Results

Within the elemental S treatments, plant weight gain increased to a maximum with increasing rates of application, and then decreased at the highest rates (Figure 1 and Table 1). When compared to the controls, elemental S at 1.9 and 3.8 grams per pot (750 and 1500 kg/ha, respectively) resulted in slight increases in plant weight gain at all

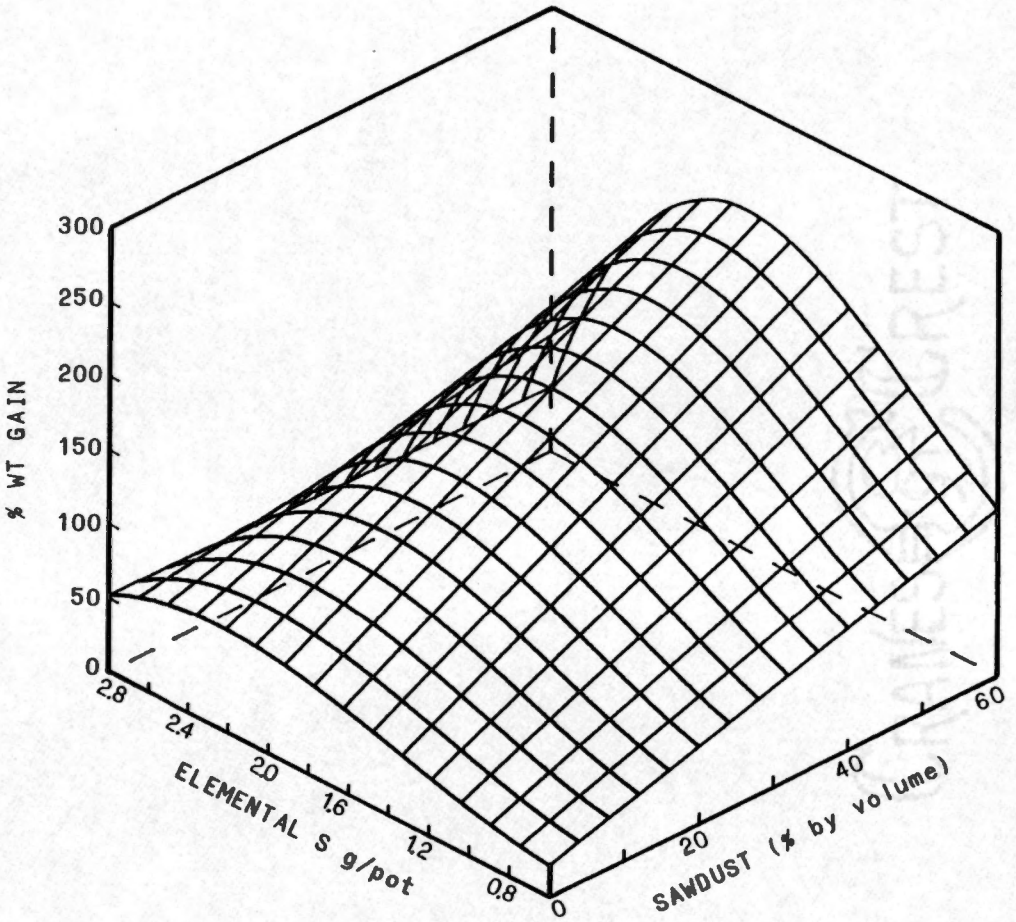


Figure 1. The effects of sawdust and elemental S application rate on blueberry plant growth (elemental S application rates of 1.9, 3.8, 7.5, and 15.0 g/pot are plotted as their corresponding logs of 0.6, 1.3, 2.0, and 2.7).

Table 1. Effects of elemental sulfur and aluminum sulfate and their interactions with sawdust on blueberry plant growth, soil pH, and aluminum levels.

Soil Acidulent Source	Rate	Average pH†	Extractable Al‡	Weight Gain
	g/pot		ug/g	%
		0% Sawdust		
Elemental S	0.0	6.2	2	25
	1.9	5.6	2	2
	3.8	5.2	2	42
	7.5	4.5	3	71
	15.0	3.8	60	54
		20% Sawdust		
	0.0	6.6	3	47
	1.9	5.8	2	99
	3.8	5.3	3	94
	7.5	4.4	10	120
	15.0	3.6	216	62
		40% Sawdust		
	0.0	6.8	4	54
	1.9	5.8	4	99
	3.8	5.5	3	101
	7.5	4.4	11	190
	15.0	3.6	112	85
		60% Sawdust		
	0.0	6.5	3	94
	1.9	5.8	4	140
	3.8	5.3	5	141
	7.5	4.4	12	274
	15.0	3.3	144	52
		0% Sawdust		
$Al_2(SO_4)_3$	0.0	6.2	2	25
	7.5	5.9	3	15
	15.0	5.5	2	19
	30.0	5.1	14	26
	60.0	4.4	171	33
		20% Sawdust		
	0.0	6.6	3	47
	7.5	6.1	4	109
	15.0	5.7	4	116
	30.0	4.9	18	150
	60.0	4.3	290	84
		40% Sawdust		
	0.0	6.8	5	54
	7.5	6.0	5	95
	15.0	5.5	5	119
	30.0	4.8	40	94
	60.0	4.2	235	69
		60% Sawdust		
	0.0	6.5	3	94
	7.5	6.0	4	106
	15.0	5.5	4	100
	30.0	4.8	40	199
	60.0	4.2	203	102

†pH taken as a mean of the months February through June, 1981.

‡Al determined at time of planting of blueberries (February 1981).

sawdust levels, but the gain was not significant when tested at $\alpha = .05$ (Table 2).

Plant weight gain also increased with increasing levels of sawdust with all elemental S treatments (Table 1). Where no sawdust was added, plant growth was severely restricted at all rates of elemental S application. When rate of sawdust was compared across all sulfur rates, growth was most favorable at the 60% level. Sawdust added at rates of 20 and 40% were generally not significantly different from each other across the same level of acidulent (Table 2). Both rates gave better results than no sawdust, but were generally not as good as 60% sawdust with any of the elemental S treatments.

In the $Al_2(SO_4)_3$ treatments, plant weight gain increased to a maximum with increasing rate of application, and then decreased at the highest rates (Figure 2 and Table 1), as was the case with elemental S. Aluminum sulfate at 7.5 and 15.0 grams per pot (3000 and 6000 kg/ha, respectively), resulted in slightly better plant weight gains than the controls at all sawdust levels, but the differences were not significant (Table 2). Aluminum sulfate at 30.0 grams per pot (12,000 kg/ha) was the most effective rate of application at three of the four sawdust levels. Plant growth at this rate was significantly greater than the controls, at all sawdust levels but 0%. As was the case with elemental S, growth increased with increasing rate of sawdust. However, while increases in plant growth were relatively linear as sawdust levels were increased in the elemental S treatments (Figure 1), growth in $Al_2(SO_4)_3$ treated soils showed an initial increase from 0 to 20%

Table 2. Orthogonal contrasts used to compare the effects of soil treatments on blueberry plant growth.

Contrast	Sig.
0 g. S - 0% sawdust vs. 1.9 g. S - 0% sawdust	NS
0 g. S - 20% sawdust vs. 1.9 g. S - 20% sawdust	NS
0 g. S - 40% sawdust vs. 1.9 g. S - 40% sawdust	NS
0 g. S - 60% sawdust vs. 1.9 g. S - 60% sawdust	NS
0 g. S - 0% sawdust vs. 3.8 g. S - 0% sawdust	NS
0 g. S - 20% sawdust vs. 3.8 g. S - 20% sawdust	NS
0 g. S - 40% sawdust vs. 3.8 g. S - 40% sawdust	NS
0 g. S - 60% sawdust vs. 3.8 g. S - 60% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 0% sawdust vs. 7.5 g. $Al_2(SO_4)_3$ - 0% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 20% sawdust vs. 7.5 g. $Al_2(SO_4)_3$ - 20% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 40% sawdust vs. 7.5 g. $Al_2(SO_4)_3$ - 40% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 60% sawdust vs. 7.5 g. $Al_2(SO_4)_3$ - 60% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 0% sawdust vs. 15.0 g. $Al_2(SO_4)_3$ - 0% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 20% sawdust vs. 15.0 g. $Al_2(SO_4)_3$ - 20% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 40% sawdust vs. 15.0 g. $Al_2(SO_4)_3$ - 40% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 60% sawdust vs. 15.0 g. $Al_2(SO_4)_3$ - 60% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 0% sawdust vs. 30.0 g. $Al_2(SO_4)_3$ - 0% sawdust	NS
0 g. $Al_2(SO_4)_3$ - 20% sawdust vs. 30.0 g. $Al_2(SO_4)_3$ - 20% sawdust	*
0 g. $Al_2(SO_4)_3$ - 40% sawdust vs. 30.0 g. $Al_2(SO_4)_3$ - 40% sawdust	*
0 g. $Al_2(SO_4)_3$ - 60% sawdust vs. 30.0 g. $Al_2(SO_4)_3$ - 60% sawdust	*
7.5 g. S - 60% sawdust vs. 30 g. $Al_2(SO_4)_3$ - 60% sawdust	*

*Significant at the 0.05 level.

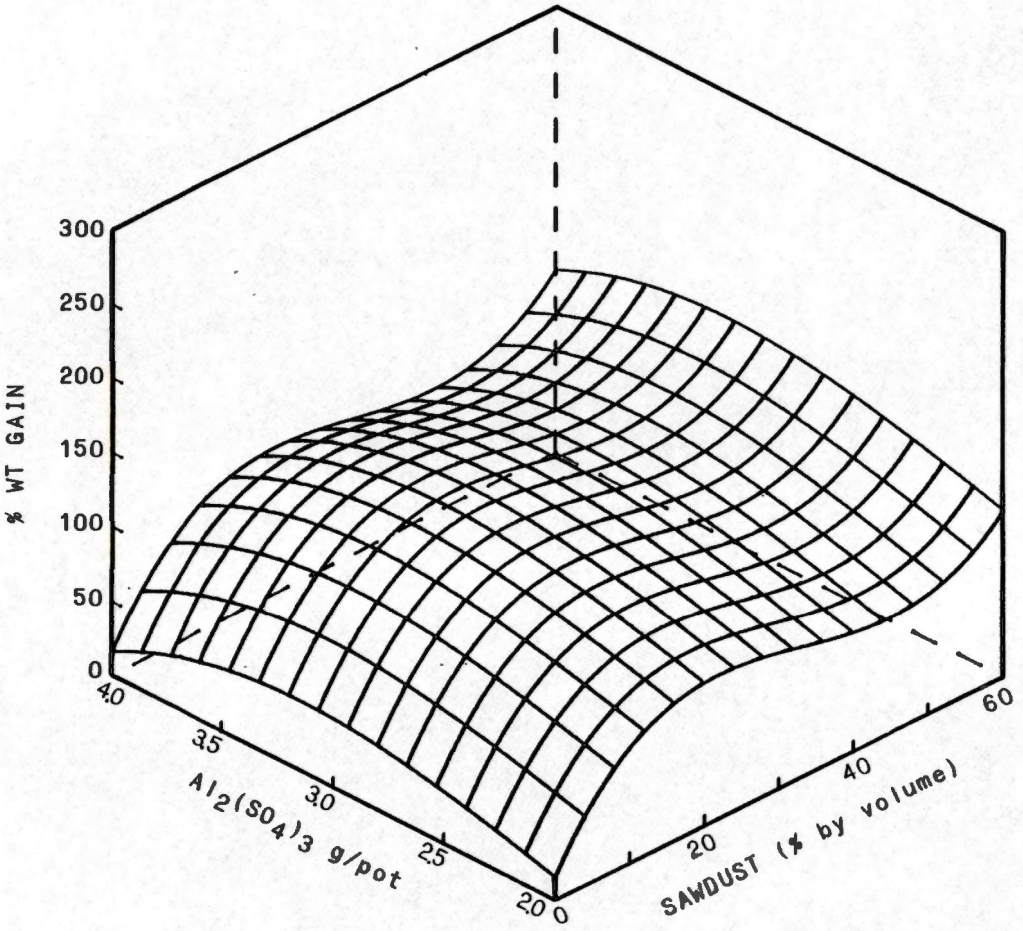


Figure 2. The effects of sawdust and $Al_2(SO_4)_3$ application rate on blueberry plant growth ($Al_2(SO_4)_3$ application rates of 7.5, 15.0, 30.0, and 60.0 g/pot are plotted as their corresponding logs of 2.0, 2.7, 3.4, and 4.1).

sawdust, leveling off between the 20 and 40% rates, and again increasing at the 60% rate (Figure 2).

Sawdust-elemental sulfur interactions did not product significant effects on plant growth when tested at $\alpha = .05$, but they were significant at $\alpha = .10$. Aluminum sulfate-sawdust interactions did not significantly effect plant growth when tested at $\alpha = .05$ or $\alpha = .10$.

The best overall treatment combination was elemental S at 7.5 grams per pot (3000 kg/ha) combined with 60% sawdust. This treatment resulted in significantly greater plant weight gain than all other treatments (Table 2). The next best treatment combination was $Al_2(SO_4)_3$ at 30.0 grams per pot (12,000 kg/ha) and 60% sawdust. Elemental S at 7.5 grams per pot (3000 kg/ha) and $Al_2(SO_4)_3$ at 30.0 grams per pot (12,000 kg/ha) were generally the best acidulent treatments within each sawdust level.

The effects of elemental S and $Al_2(SO_4)_3$ on soil pH values and extractable aluminum levels, and the concomitant plant weight gains are shown in Table 1. Approximately eight times as much $Al_2(SO_4)_3$ as elemental S by weight was required to give a two unit decrease in pH. It was necessary to make three separate applications of $Al_2(SO_4)_3$ during the course of the study to achieve the desired levels of soil acidity. The pH had begun to rise by the time it was measured the second month after application. The acidity produced by elemental S was longer lived, although the pH also began to rise a few months after application.

Aluminum levels were low at the two lowest rates of application of both acidulents, and increased markedly at the two highest rates

(Table 1, page 20). A comparison of the regression of soil Al levels on soil pH in June 1981 (at the end of the study) indicated that Al buildups may occur more readily with applications of $Al_2(SO_4)_3$ than with elemental S below pH 4.5 (Figure 3).

Regression analysis was performed to determine the effects of soil pH, and silver-thiourea extractable K, Al, Ca, and Mg on plant weight gain. Potassium (R^2 = .23) was more effective as a predictor of plant growth than any other single soil factor. The combination of K, Al, and soil pH accounted for approximately 40% of the variability in plant weight gain. Extractable Ca and Mg levels had little effect on improving R^2 values.

In addition to the measurable characteristics previously described, there are several observations that should be pointed out. Iron chlorosis (Figure 4) was evident in practically all plants grown on soils with pH values greater than 5.0. The severity of chlorosis generally increased with increasing soil pH. Chlorotic leaves were evident in all acidulent treatments regardless of pH where no sawdust was added. It was also observed that much of the difference in plant weight gain between sawdust levels may have been due to poor root growth where no sawdust was amended (Figure 5). The highest rate of elemental S (15.0 grams per pot) not only resulted in poor plant growth (Figure 6), but also a scorching of the leaves (Figure 7).

V. Discussion

At least part of the effect of elemental S and $Al_2(SO_4)_3$ on plant weight gain may be attributable to the soil pH values produced

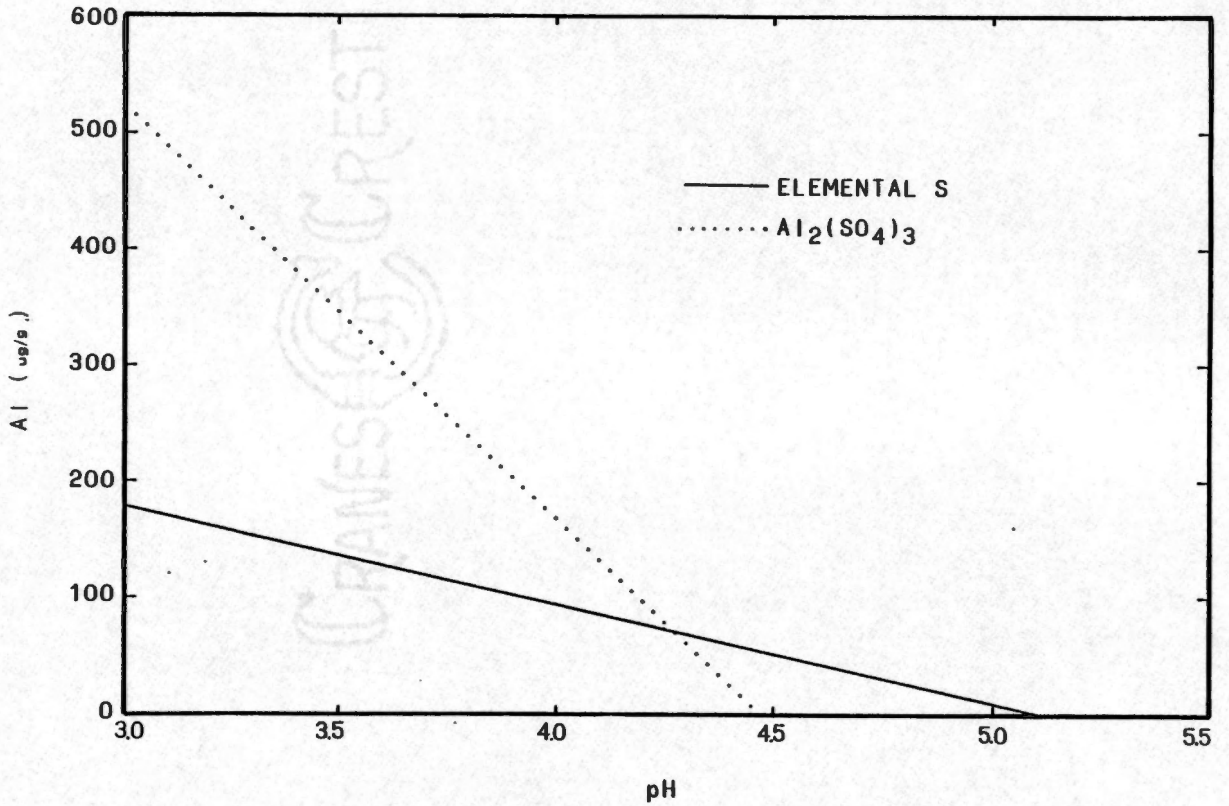


Figure 3. The regression of extractable soil Al levels on soil pH in June 1981 as influenced by elemental S and $Al_2(SO_4)_3$ applications.



Figure 4. Chlorosis of a blueberry plant grown on an elemental S treated soil with a pH of 5.2 which received no sawdust amendment.



Figure 5. A comparison of blueberry root growth of plants grown on soils receiving 7.5 g elemental S per pot with 0% sawdust (left) and 60% sawdust (right).



Figure 6. Poor plant growth at the highest rate of elemental S (15.0 g/pot) when compared to the best rate (7.5 g/pot).



Figure 7. Leaf scorch and curl observed as toxic effects of high rates of elemental S application.

by these acidulents. The best overall treatment combination of elemental S at 7.5 grams per pot (3000 kg/ha) and sawdust amended at 60%, resulted in a soil of pH 4.4. This is within the optimum range of pH 4.0-5.2 described by most researchers (13, 42, 64) for the growth of blueberries. However, it does not agree with the findings of Harmer (30) and Hall et al. (28), who suggested that pH values as high as 5.7 may be optimal on high organic matter soils.

The treatment combination of $Al_2(SO_4)_3$ applied at 30.0 grams per pot (12,000 kg/ha) and 60% sawdust resulted in a pH of 4.8 and gave the second best growth of any soil treatment used in this experiment. However, an application of 60.0 grams per pot (24,000 kg/ha) at the same sawdust level gave a pH of 4.2 and resulted in plant growth that was only about half that of the 30.0 gram (12,000 kg/ha) treatment. Since the pH of 4.2 falls within the optimum range previously described, it is probable that there is some other reason for the decrease in growth. High levels of silver-thiourea extractable Al may be a cause of the decreased plant growth in the 60.0 gram (24,000 kg/ha) $Al_2(SO_4)_3$ treatment (Table 1, page 20). Aluminum sulfate at 60.0 grams per pot (24,000 kg/ha) and 60% sawdust resulted in a silver-thiourea extractable Al concentration in the soil of 203 ug/g while at 30.0 grams per pot (12,000 kg/ha) and the same sawdust level, it was only 40 ug/g. Elemental S at 7.5 grams per pot (3000 kg/ha) and 60% sawdust had only 12 ug/g Al (Table 1, page 20), but when elemental S was increased to 15.0 grams per pot (6000 kg/ha), Al increased to 144 ug/g. It should also be pointed out, however, that the 15.0 gram (6000 kg) elemental S treatment was pH 3.3, far outside the optimum pH range previously

discussed. Although there are no known reports of toxic levels of Al for blueberries, it has been suggested that $Al_2(SO_4)_3$ applications over time may leave toxic levels of Al salts (21). The sharp reduction in plant growth at the highest acidulent applications, and the coincident rise in Al levels, particularly in the high $Al_2(SO_4)_3$ treatment, may lend support to this suggestion.

The importance of sawdust amendments to blueberry production has been suggested by several researchers (10, 11), and is consistent with the results of this experiment. Ballinger and Goldston (6) found that soils low in organic matter permitted only poor plant growth, as in this experiment.

Cain (15) had found that plants grown on high organic matter soils were able to tolerate higher base levels in the foliage, without the occurrence of chlorosis. He suggested that creation of an acid root environment in these high organic matter soils resulted in the stimulation of organic acid production in the plant, which lowered leaf pH. Therefore, leaf chlorosis, which was shown to be coincident with high leaf pH, was avoided. In this experiment, leaf chlorosis was evident throughout all acidulent treatments where no sawdust was added, and was less severe or absent in those receiving sawdust additions. Cain's findings are consistent with and may provide a logical explanation for the results obtained here.

The effects of the acidulents on soil pH values appeared to be counteracted by previous lime applications to the soil used in this experiment. Soil pH values had begun to rise after only one month in $Al_2(SO_4)_3$ treated soils and after only a few months in elemental S

treated soils. Acidity produced from elemental S has been reported to persist for up to three years without noticeable increases in soil pH (43). Tobia and Pollard (62) found that the acidity produced from $Al_2(SO_4)_3$ applied on calcareous soils persisted for up to one year. Their findings are not consistent with those found in this study. Ratsek (51) showed that 1 pound of elemental S was able to cause the same decrease in soil pH as 7 pounds or more of $Al_2(SO_4)_3$. In this experiment, approximately 8 times as much $Al_2(SO_4)_3$ as elemental S by weight was required to give a two unit decrease in pH. Theoretically, on an equivalent weight basis, elemental S and $Al_2(SO_4)_3$ would be expected to produce approximately equal amounts of acidity. On a gram for gram basis, elemental S would be expected to produce about seven times the acidity produced by $Al_2(SO_4)_3$. Therefore, the eight fold difference in amounts of acidulent required is very near the expected value.

It should be pointed out that none of the researchers who studied the effects of $Al_2(SO_4)_3$ on soil pH values noted the number of H_2O molecules attached to the $Al_2(SO_4)_3$ they used. The $Al_2(SO_4)_3$ used in this experiment had 18 attached H_2O molecules. However, $Al_2(SO_4)_3$ is available with a number of different amounts of attached H_2O molecules. Such differences alter the formula weight, hence, changing the acidifying potential of the $Al_2(SO_4)_3$. This provides a possible explanation of some of the variability in reported pH decreases with a given application rate of $Al_2(SO_4)_3$.

Conclusions

Elemental S appeared to be superior to $Al_2(SO_4)_3$ both in its acidifying potential and in its effect on blueberry growth. It was necessary to add more acidulent to limed soils to cause desired decreases in soil pH than on other soils. While rate and source of acidulent were important, only poor growth resulted where no sawdust was added. Hence, a combination of acidulent and sawdust amendment appeared to be necessary for acceptable growth on a previously limed soil, such as the one used in this experiment.

CHAPTER IV

THE EFFECTS OF SOIL ACIDIFICATION ON SELECTED SOIL CHEMICAL AND MINERALOGICAL PROPERTIES

I. Abstract

Two soil acidulents were compared for their effects on several soil chemical and mineralogical properties. Aluminum sulfate [$Al_2(SO_4)_3$] was applied at rates of 7.5, 15.0, 30.0, and 60.0 grams per pot (3000, 6000, 12,000, and 24,000 kg/ha, respectively), while elemental sulfur (elemental S) was added at rates of 1.9, 3.8, 7.5, and 15.0 grams per pot (750, 1500, 3000, and 6000 kg/ha, respectively). Sawdust was incorporated into the soil at rates of 0, 20, 40, and 60% by volume. The soil used in this experiment was a previously limed sandy loam surface soil having an initial pH of 6.2 to 6.5. On a gram for gram basis, approximately 8 times as much $Al_2(SO_4)_3$ as elemental S was needed to cause the same decrease in soil pH. Extractable Ca and Mg levels in the highest elemental S and $Al_2(SO_4)_3$ treatments were approximately double those of the controls and appeared to be a result of the amount of decrease in soil pH, rather than the source of acidulent. Potassium levels were substantially higher in the high elemental S treatments than in the controls, apparently as a result of destruction of hydroxy interlayered vermiculite (HIV) and a subsequent release of K in this treatment. Sodium levels differed from the controls only in the $Al_2(SO_4)_3$ treatments, where they

increased with increasing rate of application. Aluminum and H levels were greater than the controls only at the higher rates of application of both acidulents. This effect was due at least in part to the pH values in these treatments. Destruction of clay minerals (including gibbsite, kaolinite, and HIV) was evident in the high elemental S treatments. Aluminum sulfate had little effect on clay mineralogy when compared to the controls. Increases in Ca/Mg and K/NH_4 CEC values were observed where soils were treated with high rates of elemental S.

II. Introduction

Studies on the effects of soil acidulents on soil properties generally focus almost entirely on soil pH. Soil pH has been shown to have a significant effect on the solubility of many soil constituents and on levels of extractable and exchangeable cations (31, 48, 54). Exchangeable bases increase with increasing pH due to a higher saturation of exchange sites. The increase in exchangeable bases has also been related to organic matter levels, clay content, and clay mineralogy (31). The degree of humification and the composition of organic matter account for differences in pH-dependent charges of the organic fraction of the soil (34, 38, 50). Variation in pH-dependent charge of the clay fraction can be attributed to differences in mineralogy (22, 48).

While the effects discussed above resulted from increasing the soil pH, little attention has been paid to the effects of deliberately decreasing pH. deVilliers and Jackson (22) found that the pH-dependent charge of clay fractions was not reversible by simply decreasing the

pH of the saturating solution. Ammonium sulfate, which has soil acidifying properties, has been shown to render soluble some of the K of muscovite and orthoclase (24). Ames (2) found that applications of ammonium sulfate resulted in slightly increased levels of extractable K, Mg, and Ca, while elemental S greatly increased extractable K, Mg, Ca, and Al. The combination of calcium carbonate added with elemental S decreased the solubility of Al and K, when compared with elemental S alone. Magnesium levels were unaffected, while Ca increased (2).

The purpose of this study was to compare the effects of $Al_2(SO_4)_3$ and elemental S and their interactions with sawdust, on several soil chemical and mineralogical properties. Soils were analyzed for extractable levels of Ca, Mg, K, Na, Al, and H, and for CEC and pH. Clay fractions were analyzed for mineralogy.

III. Materials and Methods

The experimental design and description of treatments is the same as that discussed in Chapter III, Section III.

Soil determinations were made for pH, extractable K, Ca, Mg, Na, Al, and H, CEC, and clay mineralogy. The pH was measured monthly in a 1:1 soil to water solution on an Orion 701 digital pH meter. Extractable cations were measured initially before acidification in July 1980, in February 1981, and at the end of the experiment in June 1981.

Extractable cations were determined at field pH using unbuffered silver-thiourea as an extractant, as described by Pleysier and Juo (47). Calcium, Mg, and Al were measured in the silver-thiourea

extracts by atomic absorption spectrophotometry on a Perkin Elmer 5000 atomic absorption spectrophotometer. Lanthanum was added to the extracts to prevent interferences. Sodium and K were determined by flame emission spectrophotometry on the same instrument. Extractable Al plus H was measured by titrating the silver-thiourea extracts with 0.02 N NaOH to the phenolthalein endpoint. Hydrogen was calculated by subtracting Al from the Al plus H values obtained from the titration described above.

Soils of selected treatments were treated for separation of clay fractions, as described by Kunze (37). The treatments from which clay fractions were separated included the control, 15.0 grams per pot (6000 kg/ha) of elemental S, and the 60.0 grams per pot (24,000 kg/ha) treatment of $Al_2(SO_4)_3$, from those soils which had no sawdust amended. Clay fractions were analyzed for mineralogy by X-ray diffraction following pretreatments of Mg saturation, K saturation, and heat treatments of 110, 300, and 550°C, respectively. The silt fraction was also analyzed by X-ray diffraction to determine the mineralogical composition. Quantitative determinations were made for gibbsite, quartz, and kaolinite on a differential scanning calorimeter (DSC).

Additional analyses were performed to determine the effects of the acidulents on soil CEC values. Ca/Mg and K/NH_4 CEC values were determined as described by Alexiades and Jackson (1), on a whole soil basis, using soils from the treatments analyzed for clay mineralogy.

A comparison of regression lines using analysis of covariance, as described by Snedecor and Cochran (56), was used to determine significant differences between the effects of elemental S and $Al_2(SO_4)_3$ on extractable cation levels.

IV. Results

The effects of $Al_2(SO_4)_3$ and elemental S on soil pH values are shown in Figures 8 and 9. Sawdust had little effect on the degree to which the pH was lowered, so the graph represents mean values across all sawdust levels. Soil pH values decreased to a maximum one month after application with the $Al_2(SO_4)_3$. However, the pH had begun to rise by the second month after application. Additional applications of $Al_2(SO_4)_3$ were made in October and January. In each case, the lowest readings were generally obtained the first month after application, with a concomitant rise in the months following.

The lowest pH values from applications of elemental S were attained one to four months after application, depending on the rate used (Figure 9). Again, sawdust had little effect on the lowering of soil pH, so mean values of pH across all sawdust levels were used. The decrease in pH was longer lived in the elemental S than $Al_2(SO_4)_3$ treatments, but the pH also began to rise after several months. One month after application, 10 grams of elemental S per pot had caused an average decrease in pH of 0.8 units, while the same amount of $Al_2(SO_4)_3$ had caused a decrease of 0.6 units. Three months after application of the above rates of acidulents, elemental S had resulted in a net decrease of 2.0 pH units, while $Al_2(SO_4)_3$ had resulted in only a 0.3 unit net decrease.

Additions of $Al_2(SO_4)_3$ resulted in increased amounts of silver-thiourea extractable Ca at all levels of sawdust when compared to the controls (Figure 10). Calcium levels also increased with increasing rate of application of $Al_2(SO_4)_3$. There was no apparent increase in

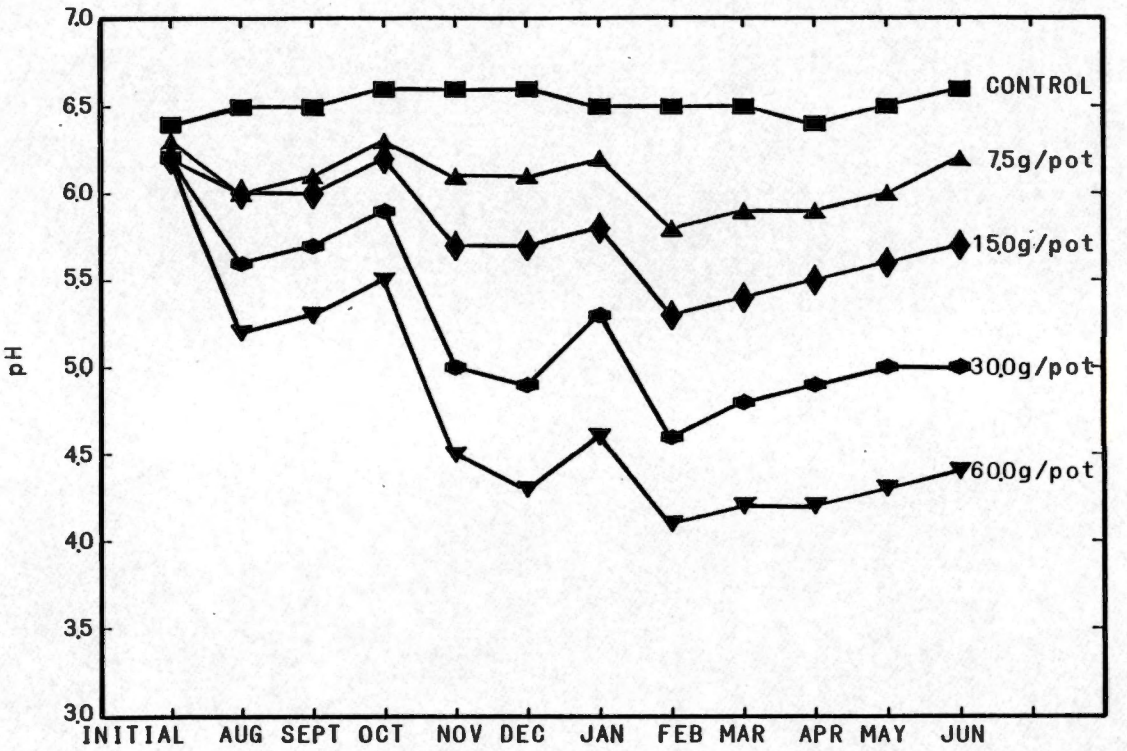


Figure 8. The effect of $Al_2(SO_4)_3$ application rate on monthly soil pH values. Aluminum sulfate was applied after sampling in July 1980 (Initial), October 1980, and January 1981.

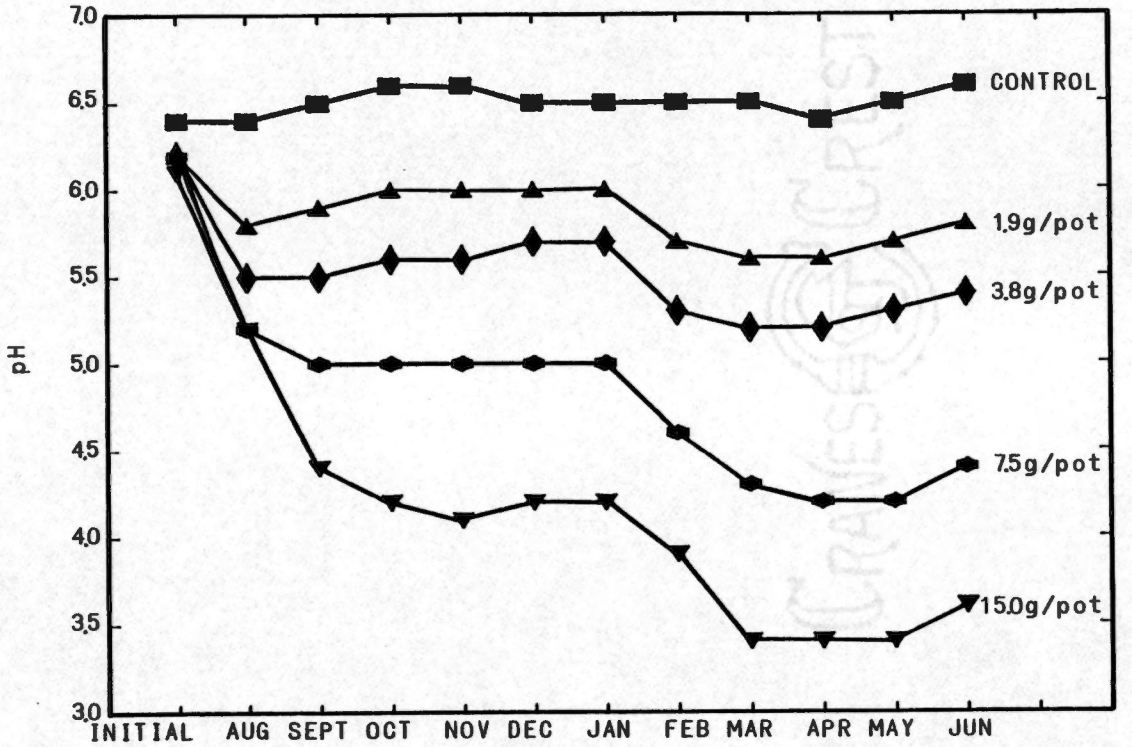


Figure 9. The effect of elemental S application rate on monthly soil pH values. Elemental S was applied after sampling in July 1980 (Initial) and in January 1981.

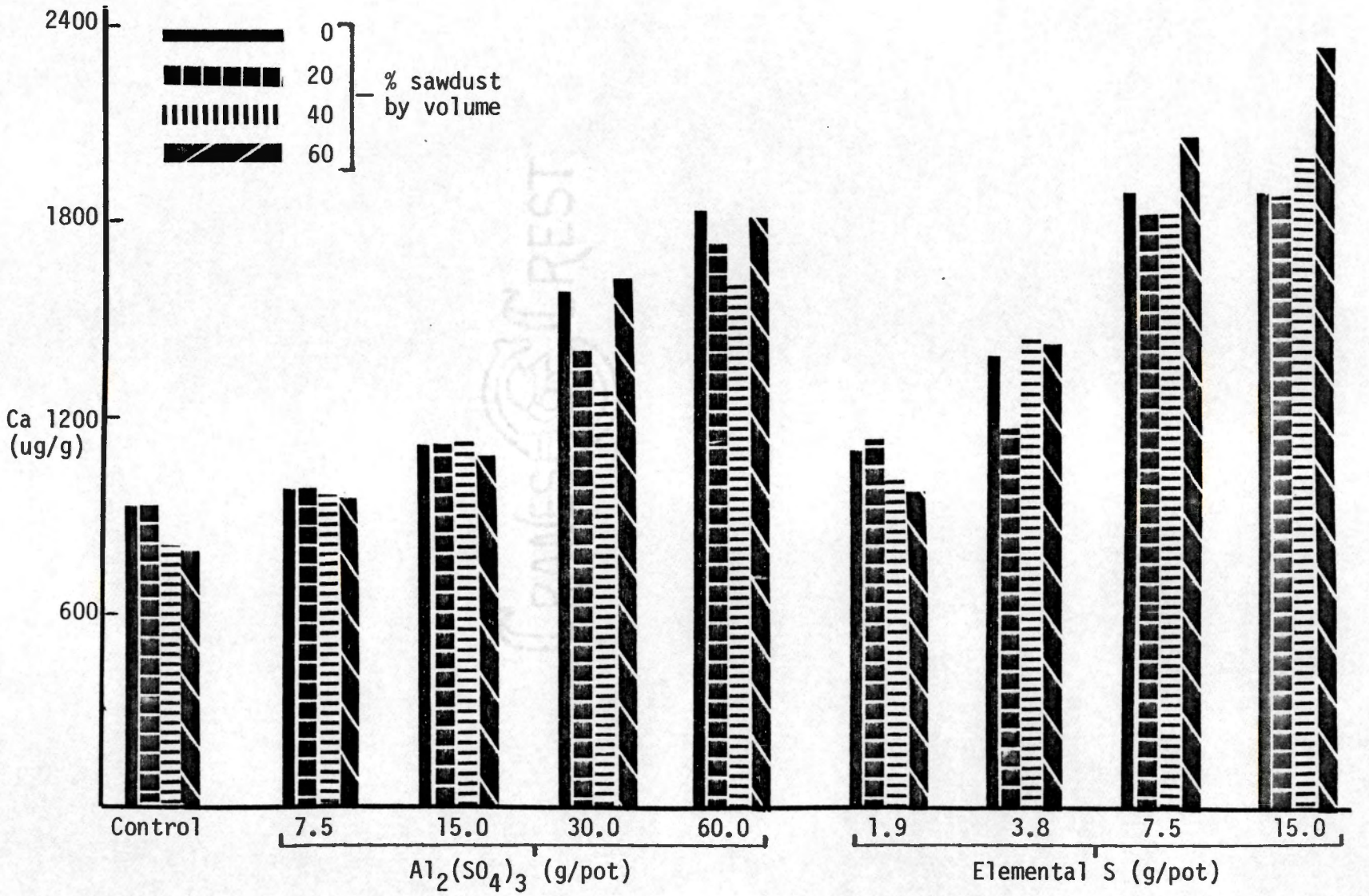


Figure 10. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S on extractable soil Ca levels.

levels of extractable Ca with increasing rates of sawdust. There was also little change in Ca levels between February 1981 and June 1981 at any of the levels of sawdust (Table 3). Calcium levels increased in all treatments from the beginning of the experiment to the end, with the exception of the controls containing 40% and 60% sawdust, which showed a slight decrease.

Elemental S also increased levels of extractable Ca with increased rates of application (Figure 10). Again, sawdust levels had little effect on the amount of Ca extracted, although at the highest rates of elemental S application, Ca levels were slightly greater in the 60% sawdust treatments. In contrast to the $Al_2(SO_4)_3$ treatments, elemental S treated soils continued to increase in extractable Ca levels between February and June 1981. These increases, however, were generally smaller than those between July 1980 and February 1981 (Table 3). Elemental S at the highest rates of application resulted in higher levels of extractable Ca than $Al_2(SO_4)_3$ at its highest application rates (Figure 10). However, if corresponding pH values are compared, there is no significant differences in Ca levels between elemental S and $Al_2(SO_4)_3$ treated soils (Figure 11).

Silver-thiourea extractable Mg levels behaved similarly to Ca in both the $Al_2(SO_4)_3$ and elemental S treatments. Extractable Mg levels increased with increasing rate of acidulent (Figure 12) and there was no apparent relation between sawdust level and Mg content when considered over all rates of acidulents. Magnesium levels showed little change between February 1981 and June 1981 in the $Al_2(SO_4)_3$ treated soils, while Mg levels in elemental S treated soils tended to increase

Table 3. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S treatments on soil pH and Ca levels.

Sawdust % by Vol	$Al_2(SO_4)_3$ g/pot	July 1980 pH	July 1980 Ca ug/g	Feb. 1981 pH	Feb. 1981 Ca ug/g	June 1981 pH	June 1981 Ca ug/g	Elemental S g/pot	July 1980 pH	July 1980 Ca ug/g	Feb. 1981 pH	Feb. 1981 Ca ug/g	June 1981 pH	June 1981 Ca ug/g
0	0.0	6.2	829	6.2	946	6.3	921	0.0	6.2	829	6.2	946	6.3	921
0	7.5	6.2	763	5.6	1077	6.1	952	1.9	6.1	792	5.6	1060	5.7	1076
0	15.0	6.1	791	5.2	1124	5.7	1088	3.8	6.1	788	5.3	1159	5.2	1393
0	30.0	6.2	782	4.6	1486	5.2	1586	7.5	6.1	794	4.7	1346	4.4	1913
0	60.0	6.2	796	4.1	1638	4.5	1849	15.0	6.2	791	4.1	1783	3.7	1920
20	0.0	6.4	777	6.6	781	6.6	961	0.0	6.4	777	6.6	781	6.6	961
20	7.5	6.3	785	5.9	942	6.2	963	1.9	6.3	782	5.7	903	5.8	1135
20	15.0	6.4	777	5.4	1143	5.8	1091	3.8	6.3	765	5.3	1046	5.4	1160
20	30.0	6.4	778	4.7	1342	5.1	1398	7.5	6.1	738	4.6	1381	4.5	1843
20	60.0	6.2	774	4.1	1657	4.4	1723	15.0	6.3	746	3.8	1857	3.6	1919
40	0.0	6.4	899	6.8	902	6.8	803	0.0	6.4	899	6.8	902	6.8	803
40	7.5	6.2	872	5.7	1065	6.1	956	1.9	6.2	874	5.8	974	5.9	1043
40	15.0	6.1	888	5.2	1280	5.7	1105	3.8	6.2	880	5.6	1223	5.5	1422
40	30.0	6.2	905	4.6	1561	4.9	1309	7.5	6.2	868	4.6	1286	4.5	1848
40	60.0	6.2	849	4.1	1320	4.3	1642	15.0	6.3	856	3.9	1800	3.7	1983
60	0.0	6.4	853	6.6	815	6.5	789	0.0	6.4	853	6.6	815	6.5	789
60	7.5	6.2	964	5.8	1170	6.2	944	1.9	6.2	864	5.8	1044	5.9	987
60	15.0	6.4	835	5.4	1467	5.7	1057	3.8	6.3	835	5.4	1351	5.4	1419
60	30.0	6.3	825	4.7	1889	4.9	1654	7.5	6.2	825	4.6	1908	4.4	2024
60	60.0	6.3	855	4.1	1745	4.3	1813	15.0	6.4	855	3.6	2689	3.3	2316

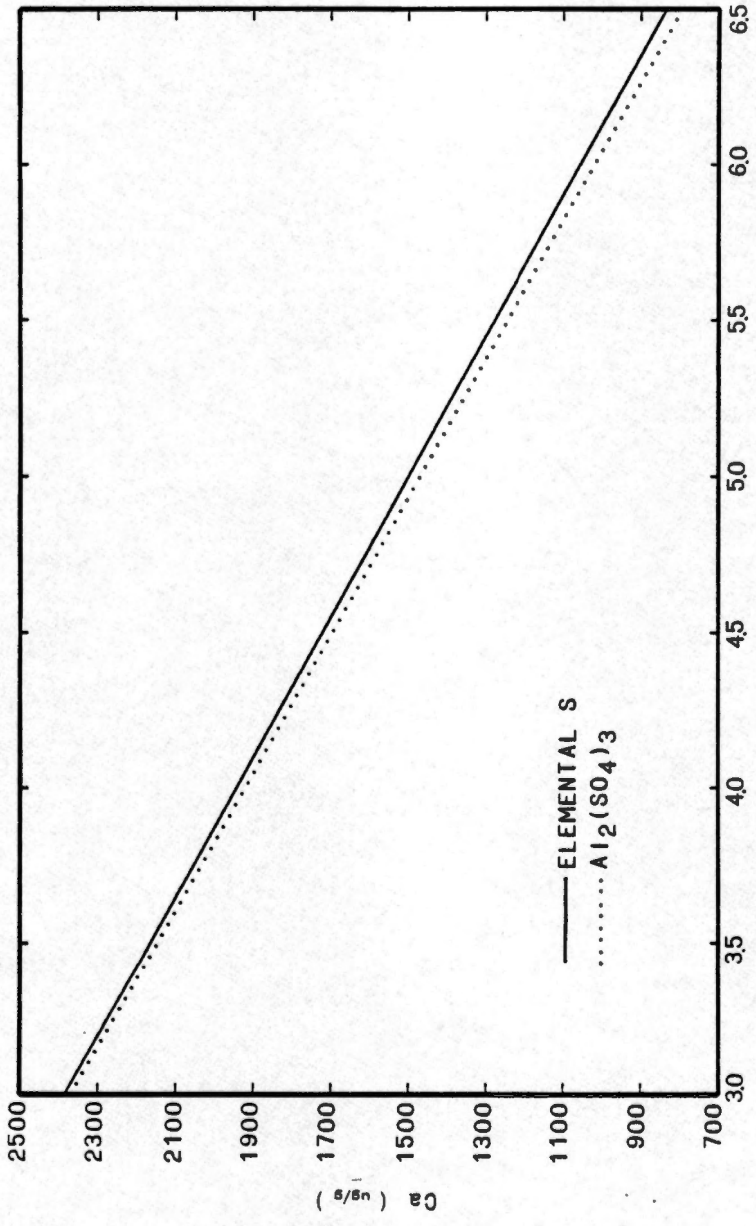


Figure 11. The regression of extractable soil Ca levels on soil pH as influenced by elemental S and $Al_2(SO_4)_3$ applications.

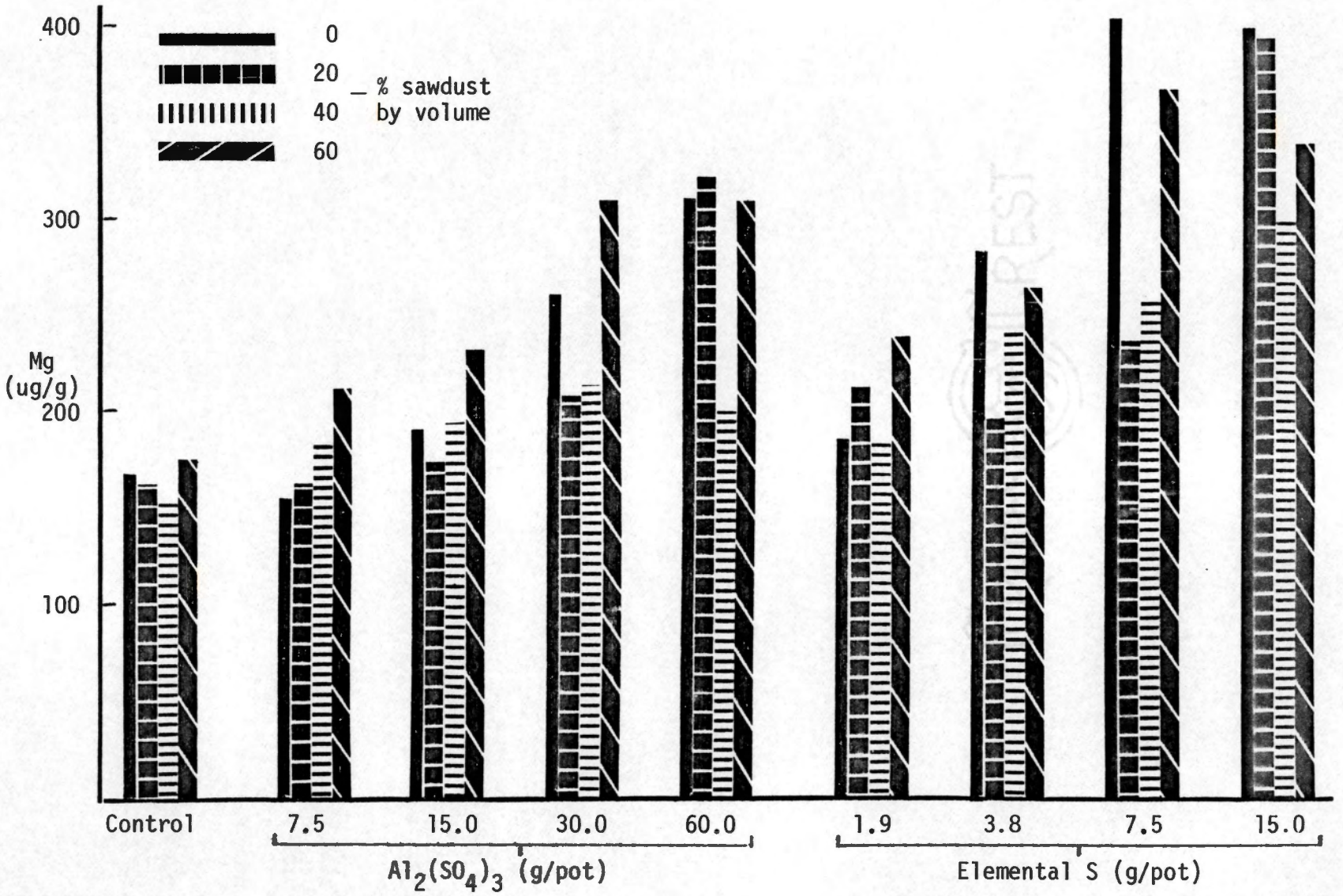


Figure 12. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S on extractable soil Mg levels.

slightly (Table 4). When corresponding pH values were compared for the acidulents, there was no significant difference in extractable Mg levels, although they were slightly higher in the elemental S treatments (Figure 13).

Extractable K levels, like Ca and Mg, increased with increasing rate of elemental S application (Figure 14). However, while $Al_2(SO_4)_3$ treatments increased extractable K levels slightly in February 1981, there was little change in the June 1981 K levels when compared to the controls (Table 5). Unlike Ca and Mg, K levels appear to be partially related to the level of sawdust applied (Figure 14), increasing with higher levels of sawdust within each acidulent treatment. Applications of high rates of elemental S significantly increased extractable K levels (Figure 15). The $Al_2(SO_4)_3$ had little effect on increasing extractable K levels.

June 1981 extractable Na levels increased with increasing rate of $Al_2(SO_4)_3$ application and showed little change with any of the rates of elemental S (Figure 16). Sodium levels generally increased with increasing levels of sawdust within each level of acidulent. There was little difference in February 1981 and June 1981 Na levels at all sawdust levels, except at 60% sawdust (Table 6). Sodium levels in the 60% sawdust treatments were higher in February 1981 than in June 1981. February 1981 Na levels in elemental S treated soils had increased from their initial values, but by June 1980, they had decreased to levels approaching the controls.

There was little difference in February 1981 silver-thiourea extractable Al levels between the controls and the two lowest rates of

Table 4. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S treatments on soil pH and Mg levels.

Sawdust % by Vol	$Al_2(SO_4)_3$ g/pot	July 1980		Feb. 1981		June 1981		Elemental S g/pot	July 1980		Feb. 1981		June 1981	
		pH	Mg ug/g	pH	Mg ug/g	pH	Mg ug/g		pH	Mg ug/g	pH	Mg ug/g	pH	Mg ug/g
0	0.0	6.2	107	6.2	135	6.3	167	0.0	6.2	107	6.2	135	6.3	167
0	7.5	6.2	78	5.6	140	6.1	156	1.9	6.1	91	5.6	155	5.7	185
0	15.0	6.1	83	5.2	161	5.7	190	3.8	6.1	90	5.3	191	5.2	286
0	30.0	6.2	83	4.6	187	5.2	260	7.5	6.1	87	4.7	203	4.4	405
0	60.0	6.2	90	4.1	224	4.5	311	15.0	6.2	85	4.1	240	3.7	404
20	0.0	6.4	105	6.6	137	6.6	161	0.0	6.4	105	6.6	137	6.6	161
20	7.5	6.3	101	5.9	160	6.2	162	1.9	6.3	84	5.7	155	5.8	212
20	15.0	6.4	98	5.4	180	5.8	175	3.8	6.3	82	5.3	172	5.4	197
20	30.0	6.4	99	4.7	230	5.1	209	7.5	6.1	88	4.6	238	4.5	238
20	60.0	6.2	87	4.1	272	4.4	321	15.0	6.3	92	3.8	317	3.6	398
40	0.0	6.4	113	6.8	159	6.8	153	0.0	6.4	113	6.8	159	6.8	153
40	7.5	6.2	98	5.7	173	6.1	185	1.9	6.2	117	5.8	169	5.9	184
40	15.0	6.1	100	5.2	183	5.7	194	3.8	6.2	117	5.6	225	5.5	244
40	30.0	6.2	100	4.6	216	4.9	215	7.5	6.2	106	4.6	255	4.5	261
40	60.0	6.2	111	4.1	242	4.3	200	15.0	6.3	108	3.9	320	3.7	302
60	0.0	6.4	132	6.6	169	6.5	176	0.0	6.4	132	6.6	169	6.5	176
60	7.5	6.2	136	5.8	224	6.2	211	1.9	6.2	127	5.8	218	5.9	239
60	15.0	6.4	131	5.4	264	5.7	233	3.8	6.3	133	5.4	250	5.4	266
60	30.0	6.3	128	4.7	300	4.9	310	7.5	6.2	145	4.6	338	4.4	369
60	60.0	6.3	133	4.1	339	4.3	310	15.0	6.2	138	3.6	373	3.3	340

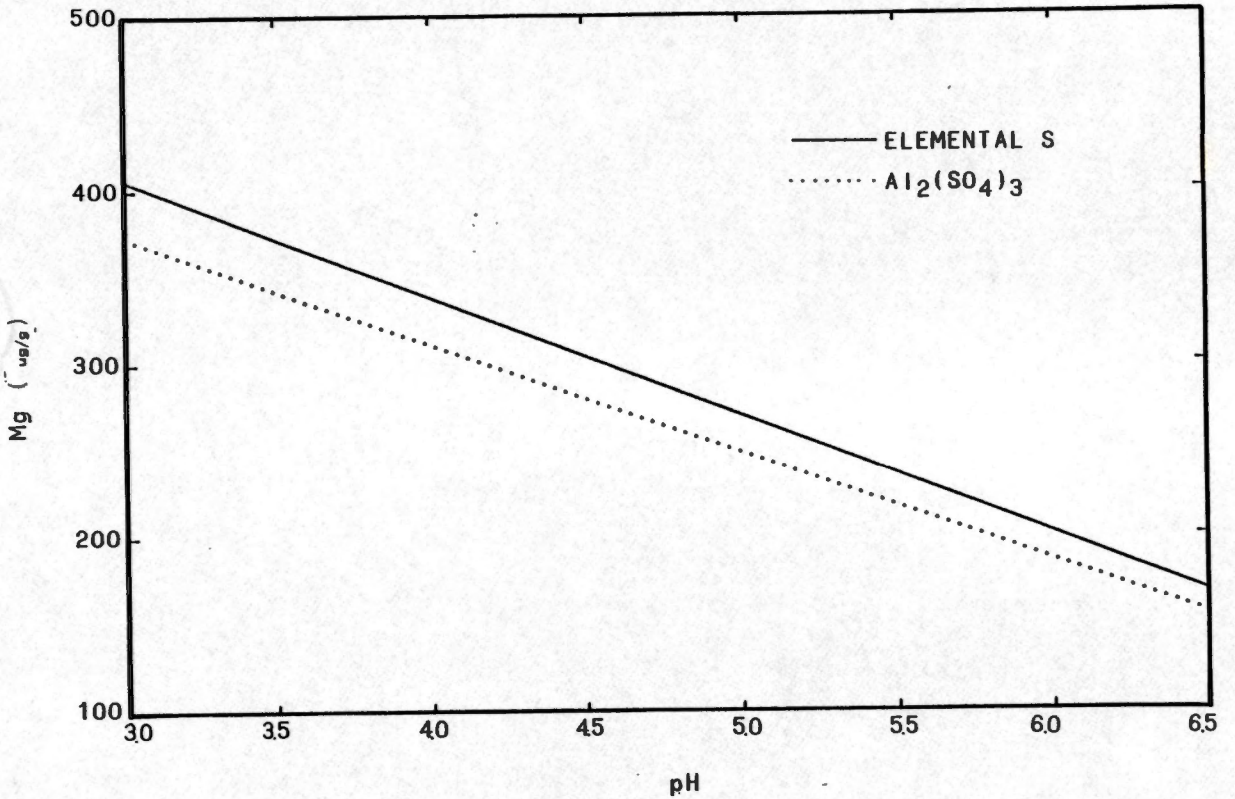


Figure 13. The regression of extractable soil Mg levels on soil pH as influenced by elemental S and $Al_2(SO_4)_3$ applications.

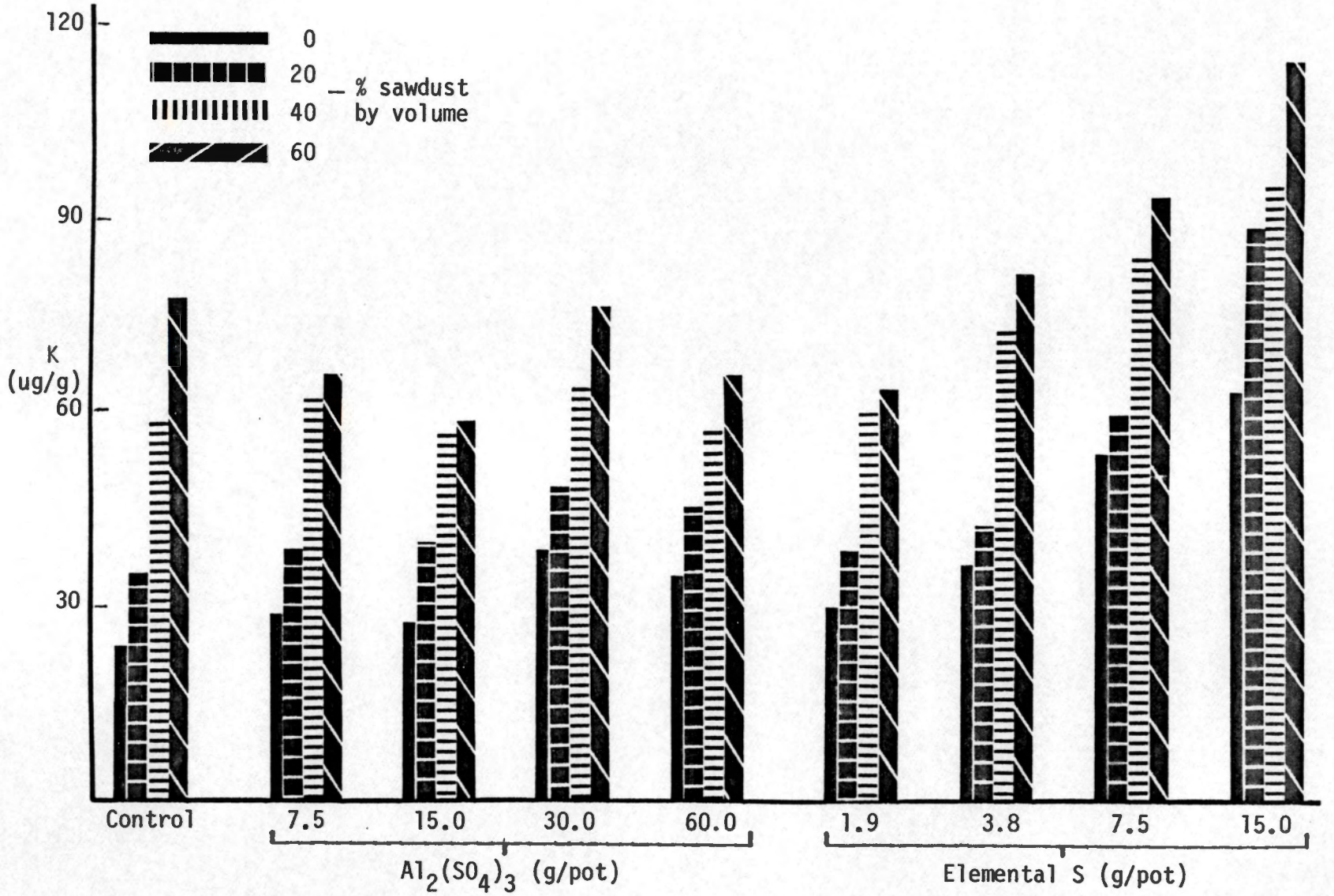


Figure 14. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S on extractable soil K levels.

Table 5. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S treatments on soil pH and K levels.

Sawdust % by Vol	$Al_2(SO_4)_3$ g/pot	July 1980 pH	July 1980 K ug/g	Feb. 1981 pH	Feb. 1981 K ug/g	June 1981 pH	June 1981 K ug/g	Elemental S	July 1980 pH	July 1980 K ug/g	Feb. 1981 pH	Feb. 1981 K ug/g	June 1981 pH	June 1981 K ug/g
0	0.0	6.2	37	6.2	31	6.3	24	0.0	6.2	37	6.2	31	6.3	24
0	7.5	6.2	40	5.6	38	6.1	29	1.9	6.1	34	5.6	35	5.7	27
0	15.0	6.1	37	5.2	43	5.7	28	3.8	6.1	35	5.3	39	5.2	37
0	30.0	6.2	35	4.6	51	5.2	39	7.5	6.1	35	4.7	46	4.4	54
0	60.0	6.2	32	4.1	54	4.5	35	15.0	6.2	37	4.1	61	3.7	64
20	0.0	6.4	42	6.6	39	6.6	35	0.0	6.4	42	6.6	39	6.6	35
20	7.5	6.3	55	5.9	47	6.2	39	1.9	6.3	55	5.7	45	5.8	39
20	15.0	6.4	56	5.4	54	5.8	40	3.8	6.3	55	5.3	51	5.4	43
20	30.0	6.4	58	4.7	75	5.1	49	7.5	6.1	52	4.6	62	4.5	60
20	60.0	6.2	53	4.1	63	4.4	46	15.0	6.3	54	3.8	77	3.6	89
40	0.0	6.4	60	6.8	59	6.8	59	0.0	6.4	60	6.8	59	6.8	59
40	7.5	6.2	75	5.7	72	6.1	62	1.9	6.2	70	5.8	62	5.9	61
40	15.0	6.1	68	5.2	64	5.7	58	3.8	6.2	67	5.6	69	5.5	73
40	30.0	6.2	60	4.6	76	4.9	65	7.5	6.2	63	4.6	76	4.5	85
40	60.0	6.2	64	4.1	72	4.3	58	15.0	6.3	68	3.9	90	3.7	96
60	0.0	6.4	98	6.6	88	6.5	78	0.0	6.4	98	6.6	88	6.5	78
60	7.5	6.2	79	5.8	83	6.2	66	1.9	6.2	85	5.8	86	5.9	64
60	15.0	6.4	75	5.4	78	5.7	59	3.8	6.3	93	5.4	95	5.4	82
60	30.0	6.3	83	4.7	81	4.9	77	7.5	6.2	85	4.6	97	4.4	94
60	60.0	6.3	97	4.1	75	4.3	66	15.0	6.4	90	3.6	116	3.3	112

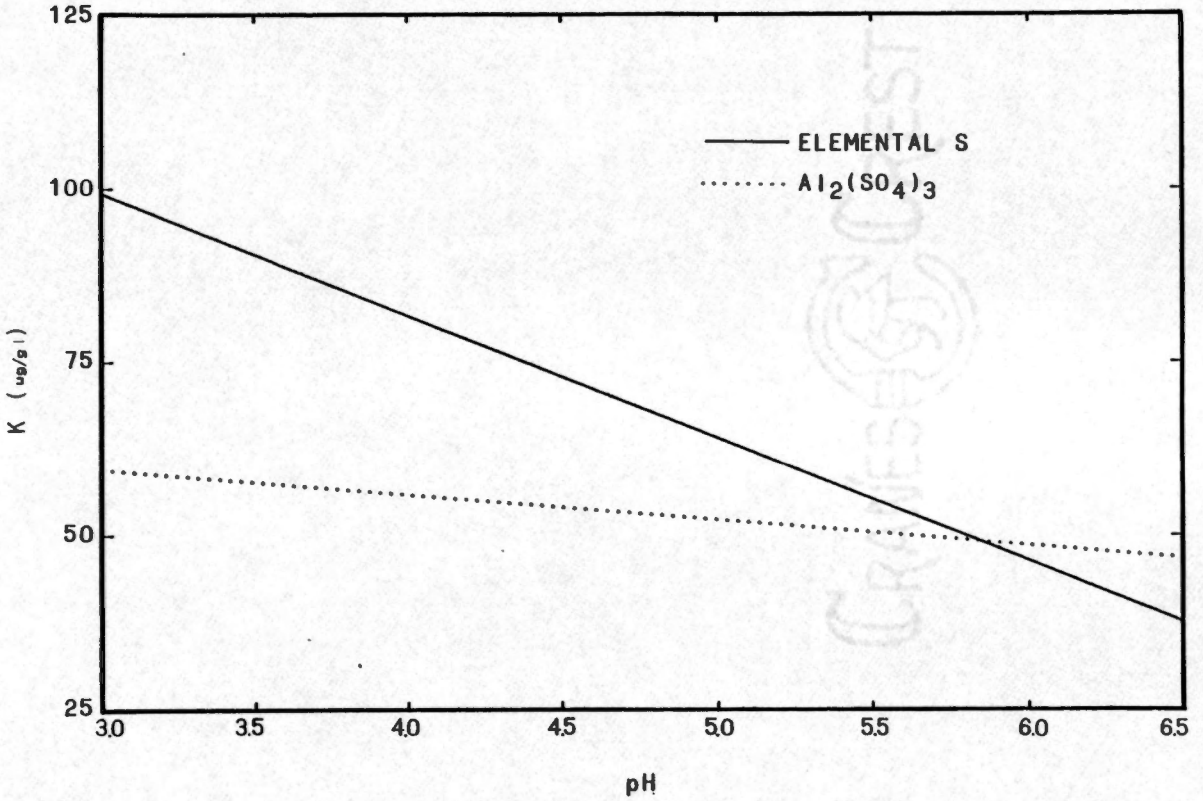


Figure 15. The regression of extractable soil K levels on soil pH as influenced by elemental S and $Al_2(SO_4)_3$ applications.

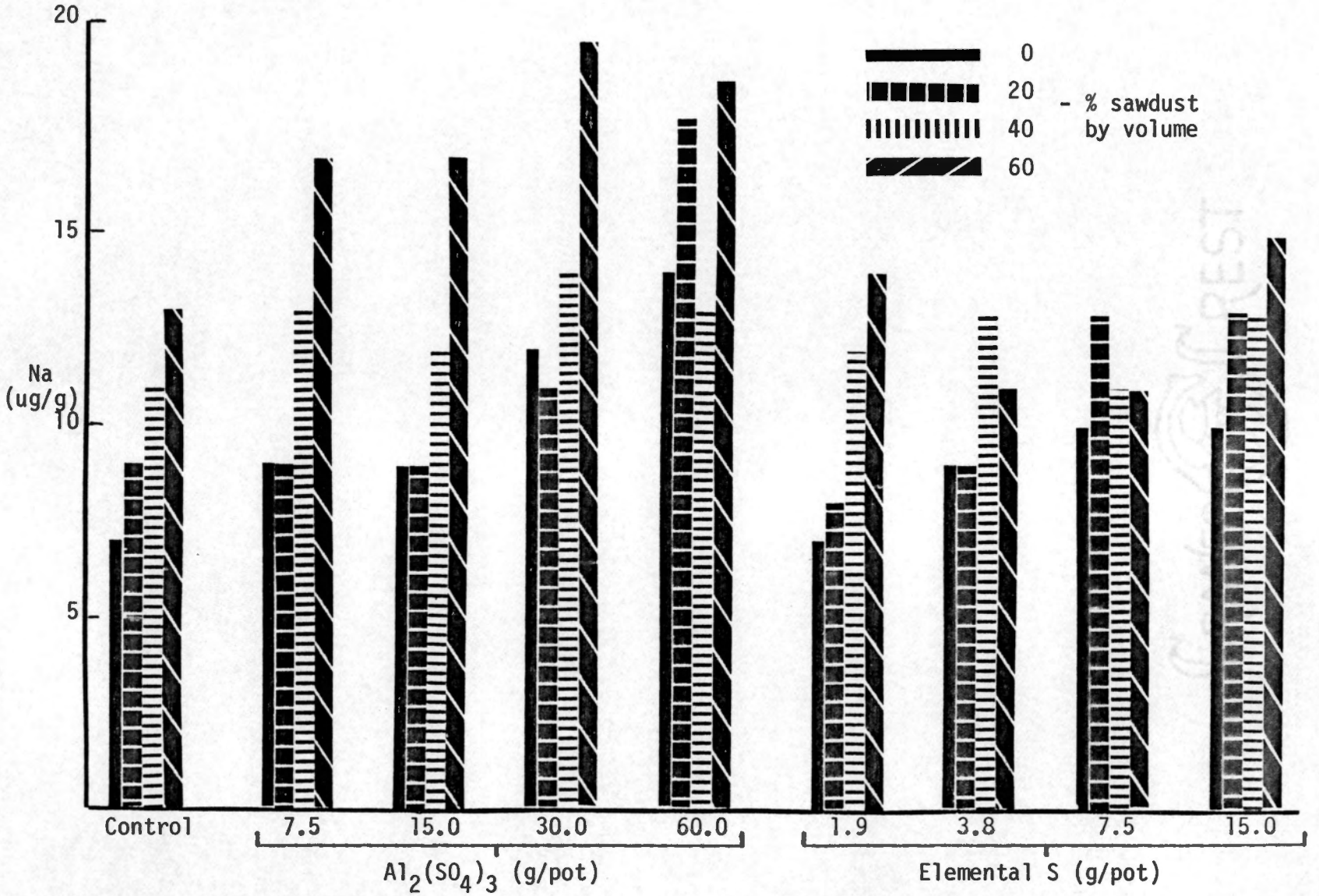


Figure 16. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S on extractable soil Na levels.

Table 6. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S treatments on soil pH and Na levels.

Sawdust % by Vol	$Al_2(SO_4)_3$ g/pot	July 1980 pH	July 1980 Na ug/g	Feb. 1981 pH	Feb. 1981 Na ug/g	June 1981 pH	June 1981 Na ug/g	Elemental S g/pot	July 1980 pH	July 1980 Na ug/g	Feb. 1981 pH	Feb. 1981 Na ug/g	June 1981 pH	June 1981 Na ug/g
0	0.0	6.2	11	6.2	6	6.4	7	0.0	6.2	11	6.2	6	6.3	7
0	7.5	6.2	10	5.6	7	6.1	9	1.9	6.1	11	5.6	7	5.7	7
0	15.0	6.1	10	5.2	11	5.7	9	3.8	6.1	8	5.3	11	5.2	9
0	30.0	6.2	7	4.6	10	5.2	12	7.5	6.1	8	4.7	10	4.4	10
0	60.0	6.2	7	4.1	16	4.5	14	15.0	6.2	8	4.1	14	3.7	10
20	0.0	6.4	12	6.6	7	6.6	9	0.0	6.4	12	6.6	7	6.6	9
20	7.5	6.3	8	5.9	7	6.2	9	1.9	6.3	10	5.7	8	5.8	8
20	15.0	6.4	10	5.4	9	5.8	9	3.8	6.3	9	5.3	9	5.4	9
20	30.0	6.4	9	4.7	11	5.1	11	7.5	6.1	9	4.6	9	4.5	13
20	60.0	6.2	9	4.1	14	4.4	18	15.0	6.3	9	3.6	9	3.6	13
40	0.0	6.4	11	6.8	9	6.8	11	0.0	6.4	11	6.8	9	6.8	11
40	7.5	6.2	12	5.7	9	6.1	13	1.9	6.2	13	5.8	9	5.9	12
40	15.0	6.1	11	5.2	13	5.7	12	3.8	6.2	10	5.6	13	5.5	13
40	30.0	6.2	7	4.6	14	4.9	14	7.5	6.2	9	4.6	14	4.5	11
40	60.0	6.2	11	4.1	13	4.3	13	15.0	6.3	16	3.9	15	3.7	13
60	0.0	6.4	15	6.6	20	6.5	13	0.0	6.4	15	6.6	20	6.5	13
60	7.5	6.2	11	5.8	22	6.2	17	1.9	6.2	17	5.8	18	5.9	14
60	15.0	6.4	11	5.4	25	5.7	17	3.8	6.3	11	5.4	18	5.4	12
60	30.0	6.3	12	4.7	29	4.9	21	7.5	6.2	9	4.6	23	4.4	12
60	60.0	6.3	8	4.1	36	4.3	22	15.0	6.4	7	3.6	24	3.3	15

application of both acidulents at all levels of sawdust (Figure 17). Aluminum sulfate at 30.0 grams per pot (12,000 kg/ha) and elemental S at 7.5 grams per pot (3000 kg/ha) increased extractable Al levels, but these increases were much smaller than those increases with the highest rates of acidulents. There was no apparent relationship between sawdust level and the amount of extractable Al when considered over all rates of application of both acidulents (Figure 17). Aluminum levels at the highest rates of $Al_2(SO_4)_3$ application decreased between February and June 1981, which parallelled an increase in pH (Table 7). In the elemental S treatments, Al levels increased between February and June 1981, parallelling a decrease in pH. The regression of Al levels on soil pH indicated that Al levels were higher in the elemental S treatments than in the $Al_2(SO_4)_3$ treatments in February 1981, when corresponding pH values were compared (Figure 18). However, this trend was reversed by June 1981 (Figure 19).

The lowest two rates of application of both acidulents did not increase silver-thiourea extractable H values to any great extent (Figure 20). Elemental S at 7.5 grams per pot (3000 kg/ha) and $Al_2(SO_4)_3$ at 30.0 grams per pot (12,000 kg/ha) resulted in slight increases in extractable H levels, with the sharpest increases occurring at the highest rates of application of both acidulents. At the highest rate of $Al_2(SO_4)_3$ application, February 1981, H levels were higher than in the highest elemental S treatments (Table 8). However, H levels decreased between February 1981 and June 1981 in the $Al_2(SO_4)_3$ treatments parallelling an increase in pH, while H levels increased between February and June in the elemental S treated

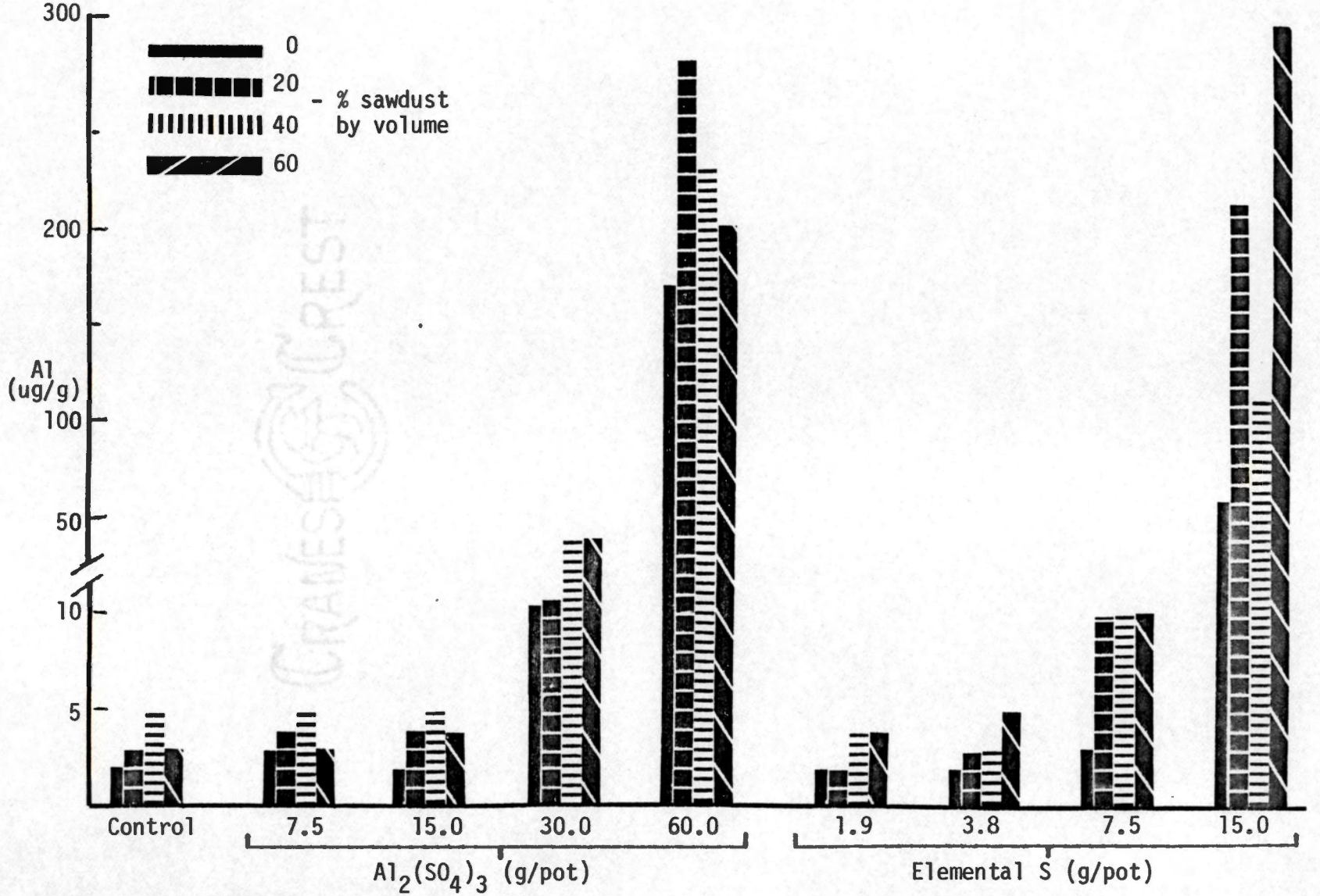


Figure 17. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S on extractable soil Al levels.

Table 7. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S treatments on soil pH and Al levels.

Sawdust % by Vol.	$Al_2(SO_4)_3$ g/pot	July 1980		Feb. 1981		June 1981		Elemental S g/pot	July 1980		Feb. 1981		June 1981	
		pH	Al ug/g	pH	Al ug/g	pH	Al ug/g		pH	Al ug/g	pH	Al ug/g	pH	Al ug/g
0	0.0	6.2	2	6.2	2	6.3	3	0.0	6.2	2	6.2	2	6.3	3
0	7.5	6.2	3	5.6	3	6.1	3	1.9	6.1	4	5.6	2	5.7	2
0	15.0	6.1	3	5.2	2	5.7	4	3.8	6.1	2	5.3	2	5.2	4
0	30.0	6.2	2	4.6	14	5.2	3	7.5	6.1	2	4.7	3	4.4	17
0	60.0	6.2	3	4.1	171	4.5	35	15.0	6.2	2	4.1	60	3.7	207
20	0.0	6.4	2	6.6	3	6.6	3	0.0	6.4	3	6.6	3	6.6	3
20	7.5	6.3	4	5.9	4	6.2	4	1.9	6.3	3	5.7	2	5.8	3
20	15.0	6.4	4	5.4	4	5.8	3	3.8	6.3	3	5.3	3	5.4	4
20	30.0	6.4	3	4.7	18	5.1	7	7.5	6.1	3	4.6	10	4.5	15
20	60.0	6.2	3	4.1	290	4.4	61	15.0	6.3	3	3.8	216	3.6	279
40	0.0	6.4	3	6.8	5	6.8	4	0.0	6.4	3	6.8	5	6.8	4
40	7.5	6.2	4	5.7	5	6.1	3	1.9	6.2	2	5.8	4	5.9	3
40	15.0	6.1	4	5.2	5	5.7	2	3.8	6.2	3	5.6	3	5.5	6
40	30.0	6.2	3	4.6	40	4.9	8	7.5	6.2	3	4.6	11	4.5	16
40	60.0	6.2	3	4.1	235	4.3	59	15.0	6.3	2	3.9	112	3.7	281
60	0.0	6.4	2	6.6	3	6.5	3	0.0	6.4	4	6.6	3	6.5	3
60	7.5	6.2	3	5.8	3	6.2	2	1.9	6.2	2	5.8	4	5.9	2
60	15.0	6.4	4	5.4	4	5.7	3	3.8	6.3	3	5.4	5	5.4	4
60	30.0	6.3	2	4.7	40	4.9	9	7.5	6.2	2	4.6	12	4.4	25
60	60.0	6.3	3	4.1	203	4.3	92	15.0	6.4	2	3.6	144	3.3	490

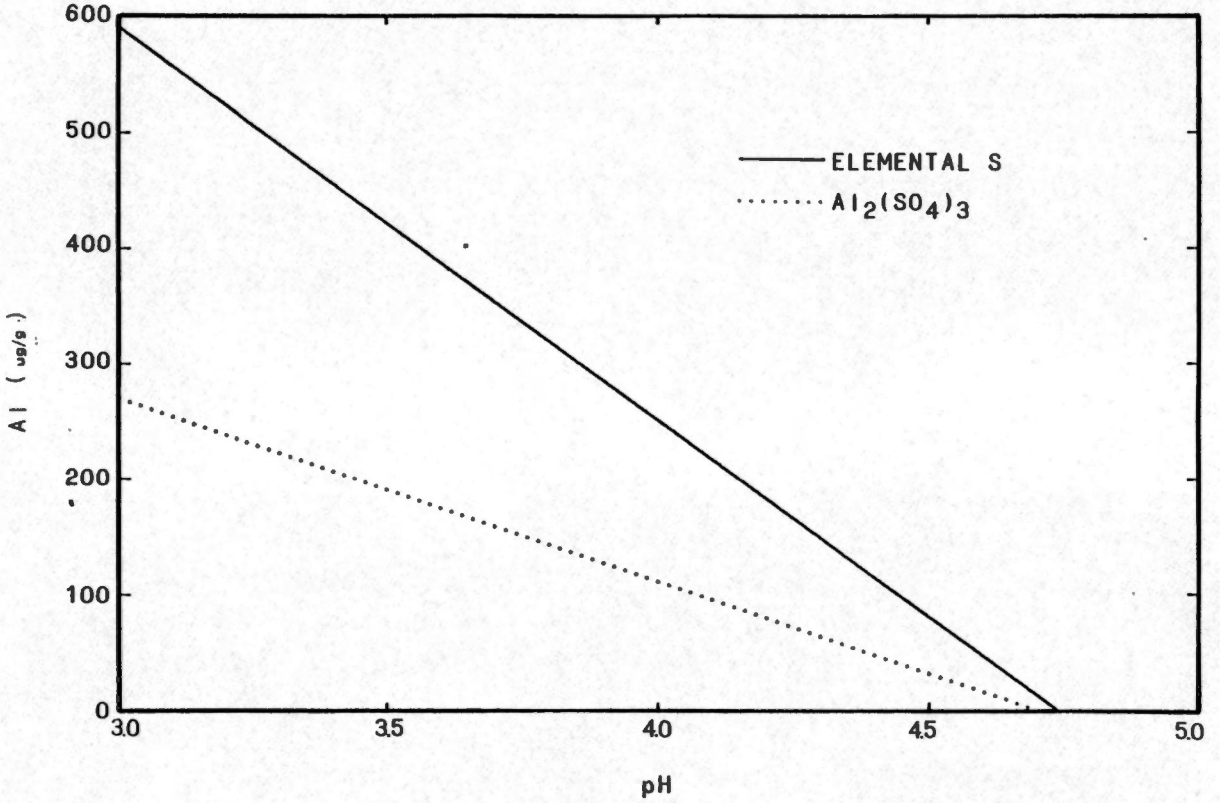


Figure 18. The regression of extractable soil Al levels on pH in February 1981 as influenced by elemental S and $Al_2(SO_4)_3$ applications.

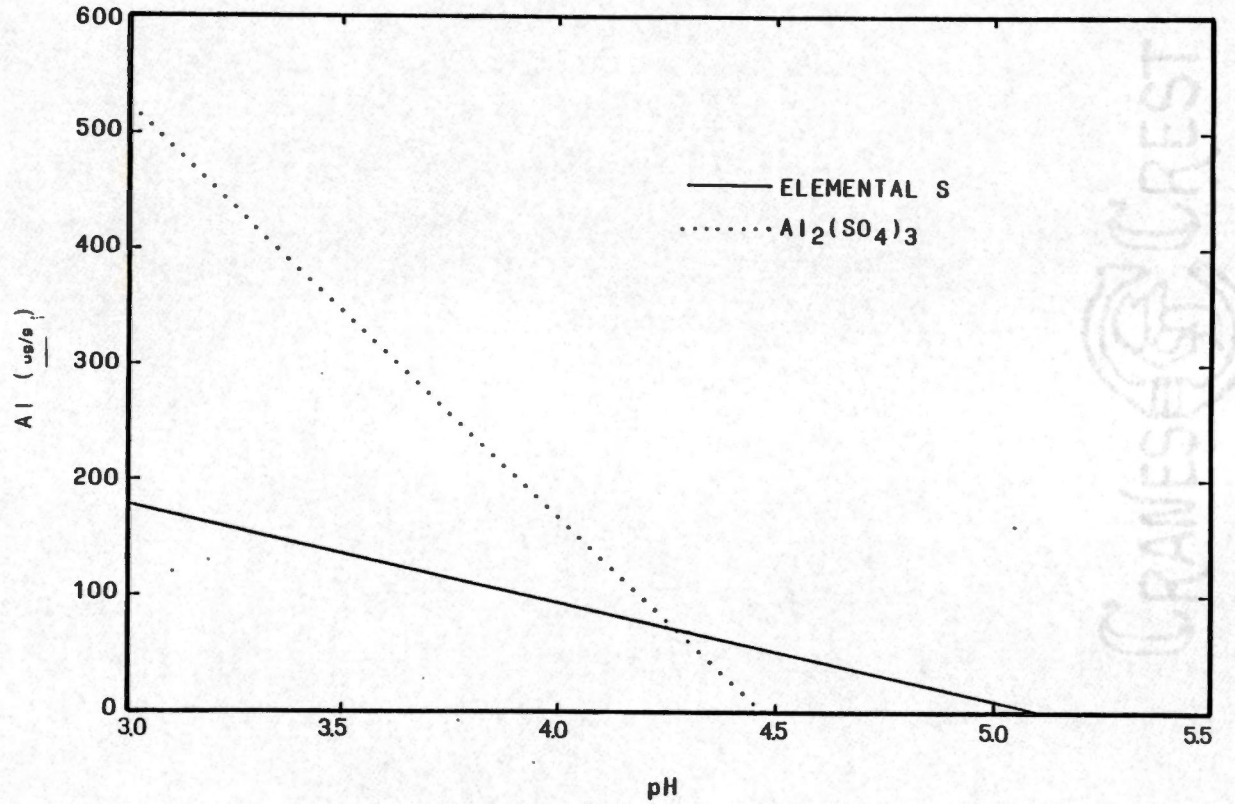


Figure 19. The regression of extractable soil Al levels on soil pH in June 1981 as influenced by elemental S and $Al_2(SO_4)_3$ applications.

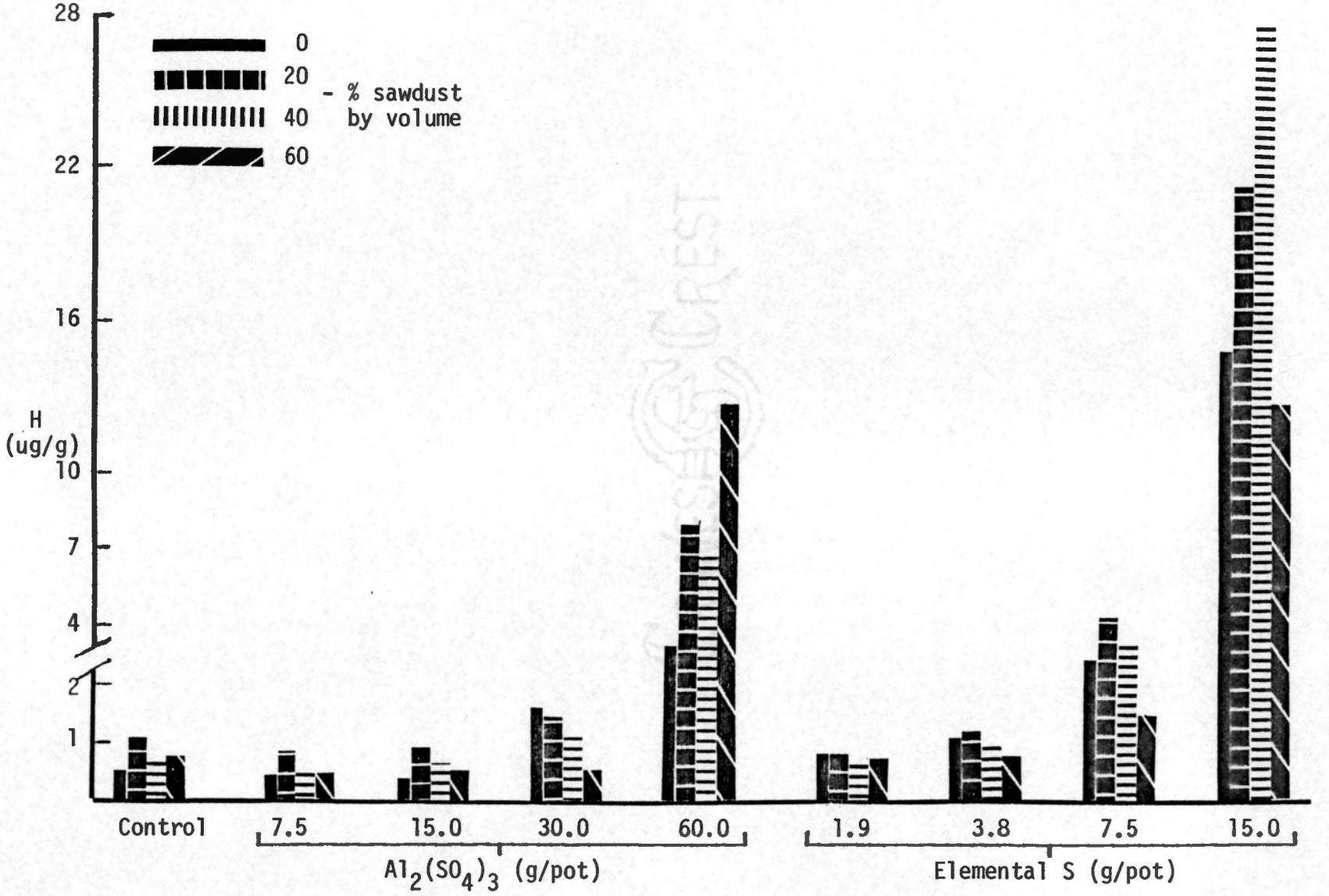


Figure 20. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S on extractable soil H levels.

Table 8. The effects of sawdust, $Al_2(SO_4)_3$, and elemental S treatments on soil pH and H levels.

Sawdust % by Vol	$Al_2(SO_4)_3$ g/pot	July 1980 pH	July 1980 H ug/g	Feb. 1981 pH	Feb. 1981 H ug/g	June 1981 pH	June 1981 H ug/g	Elemental S g/pot	July 1980 pH	July 1980 H ug/g	Feb. 1981 pH	Feb. 1981 H ug/g	June 1981 pH	June 1981 H ug/g
0	0.0	6.2	0.8	6.2	0.8	6.3	0.5	0.0	6.2	0.8	6.2	0.8	6.3	0.5
0	7.5	6.2	0.6	5.6	1.1	6.1	0.5	1.9	6.1	0.6	5.6	1.1	5.7	0.8
0	15.0	6.1	0.6	5.2	1.5	5.7	0.4	3.8	6.1	0.8	5.3	1.1	5.2	1.1
0	30.0	6.2	0.6	4.6	1.3	5.2	1.6	7.5	6.1	0.8	4.7	1.5	4.4	2.4
0	60.0	6.2	0.5	4.1	3.6	4.5	2.9	15.0	6.2	0.9	4.1	4.4	3.7	14.9
20	0.0	6.4	0.7	6.6	1.2	6.6	1.1	0.0	6.4	0.7	6.6	1.2	6.6	1.1
20	7.5	6.3	0.6	5.9	0.8	6.2	0.8	1.9	6.3	0.6	5.7	1.4	5.8	0.8
20	15.0	6.4	0.5	5.4	1.0	5.8	0.9	3.8	6.3	0.6	5.3	1.2	5.4	1.2
20	30.0	6.4	0.6	4.7	1.7	5.1	1.4	7.5	6.1	0.7	4.6	2.2	4.5	4.4
20	60.0	6.2	0.5	4.1	9.1	4.4	8.0	15.0	6.3	0.7	3.8	4.4	3.6	21.4
40	0.0	6.4	0.8	6.8	0.8	6.8	0.7	0.0	6.4	0.8	6.8	0.8	6.8	0.7
40	7.5	6.2	0.7	5.7	0.5	6.1	0.5	1.9	6.2	0.9	5.8	1.1	5.9	0.7
40	15.0	6.1	0.5	5.2	0.5	5.7	0.6	3.8	6.2	0.7	5.6	1.1	5.5	0.9
40	30.0	6.2	0.4	4.6	1.9	4.9	1.2	7.5	6.2	0.7	4.6	2.0	4.5	3.3
40	60.0	6.2	0.7	4.1	38.2	4.3	6.8	15.0	6.3	0.8	3.9	16.5	3.7	28.9
60	0.0	6.4	0.8	6.6	0.8	6.5	0.7	0.0	0.8	0.8	6.6	0.8	6.5	0.7
60	7.5	6.2	0.8	5.8	0.8	6.2	0.5	1.9	0.5	0.5	5.8	1.1	5.9	0.7
60	15.0	6.4	0.7	5.4	1.1	5.7	0.5	3.8	0.9	0.9	5.4	1.7	5.4	0.7
60	30.0	6.3	0.8	4.7	2.0	4.9	0.5	7.5	0.9	0.9	4.6	2.9	4.4	1.5
60	60.0	6.3	0.7	4.1	35.4	4.3	12.8	15.0	0.8	0.8	3.6	25.8	4.4	12.9

soils at three of the four sawdust levels, parallelling a decrease in pH. The regression of soil H levels on soil pH in June 1981 showed that extractable H levels were higher above pH 4.0 in the elemental S treatments than in the $Al_2(SO_4)_3$ treatments (Figure 21). The opposite effect was observed below pH 4.0.

The highest elemental S application of 15.0 grams per pot (6000 kg/ha) resulted in the destruction of gibbsite and kaolinite, when compared to the control in the DSC patterns (Figure 22). Gibbsite is identified by an endotherm at 270°C. The controls had about 1% gibbsite in the clay fraction. The endotherm at 475° identifies the presence of kaolinite and HIV. Both gibbsite and kaolinite were reduced by approximately one half when compared to the corresponding control taken before acidification (1% to 0.5% gibbsite, and 20% to 10% kaolinite). Aluminum sulfate at 60.0 grams per pot (24,000 kg/ha) resulted in no apparent change in clay minerals when compared against its corresponding control. A flattening of the curve between 370 and 450°C in all samples indicates the presence of vermiculite (HIV). It should be pointed out, however, that this effect is particularly pronounced in the 15.0 gram per pot (6000 kg/ha) elemental S treatment.

The X-ray diffraction patterns for the elemental S and $Al_2(SO_4)_3$ treatments are shown in Figures 23, 24, and 25. The identifiable clay minerals include hydroxy interlayered vermiculite (HIV) at 14.2A°. Only the K saturated air dry and 550°C heat treatments are shown for clarity since there were few differences in the intermediate heat treatments. The 4.8A° gibbsite peak shown in the K saturated air dry treatments disappeared at 300°C. Other changes generally did not show

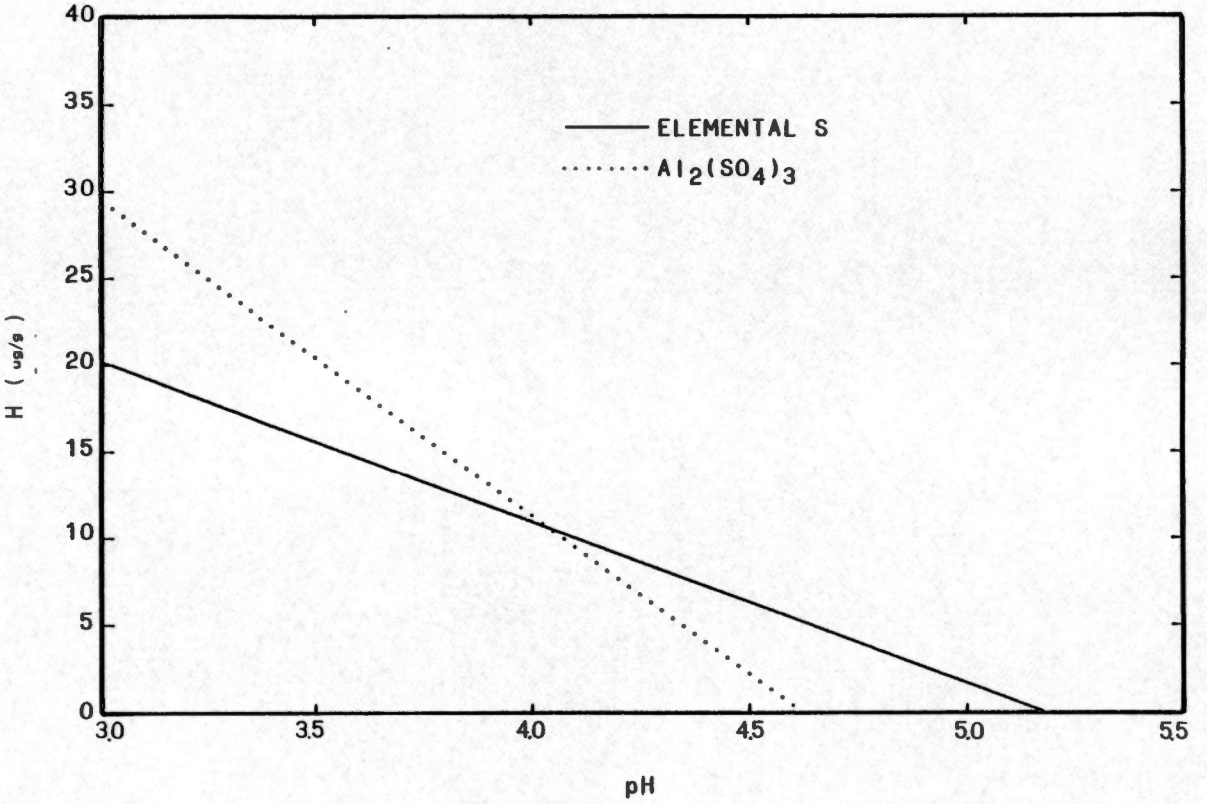


Figure 21. The regression of extractable soil H on soil pH as influenced by elemental S and $Al_2(SO_4)_3$ applications.

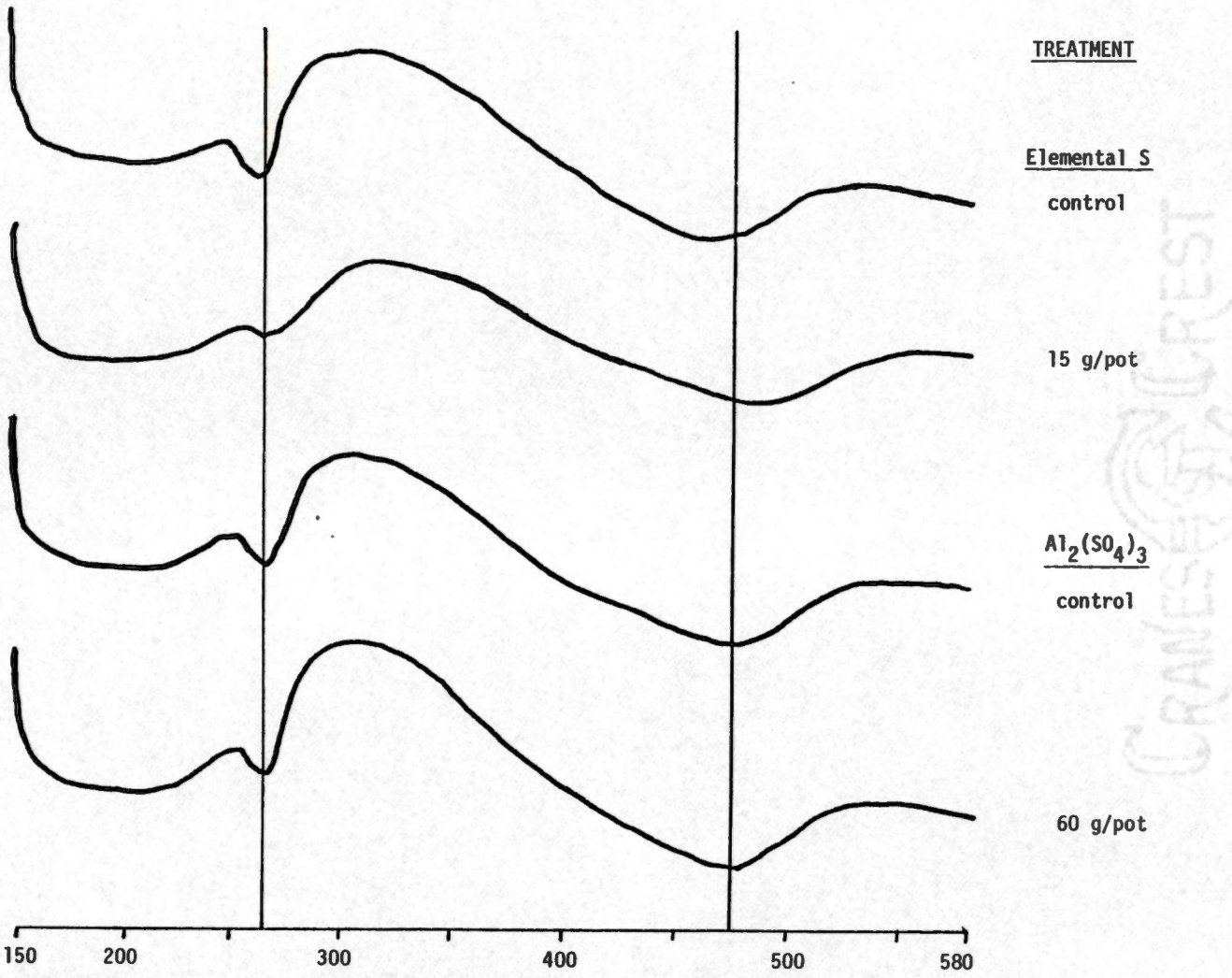


Figure 22. DSC scans for elemental S and $Al_2(SO_4)_3$ treatments and their corresponding controls.

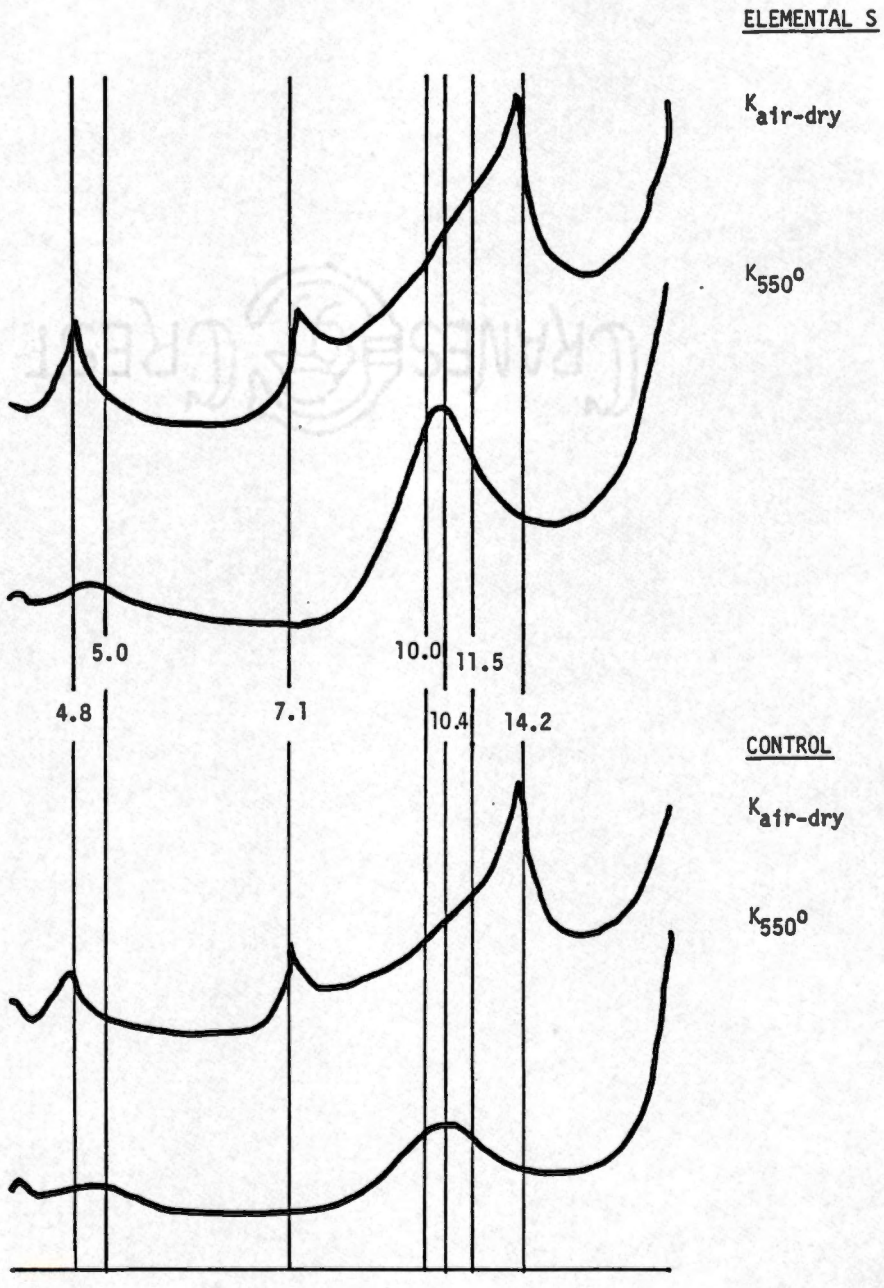


Figure 23. X-ray diffraction patterns for elemental S at 15.0 g/pot and its corresponding control.

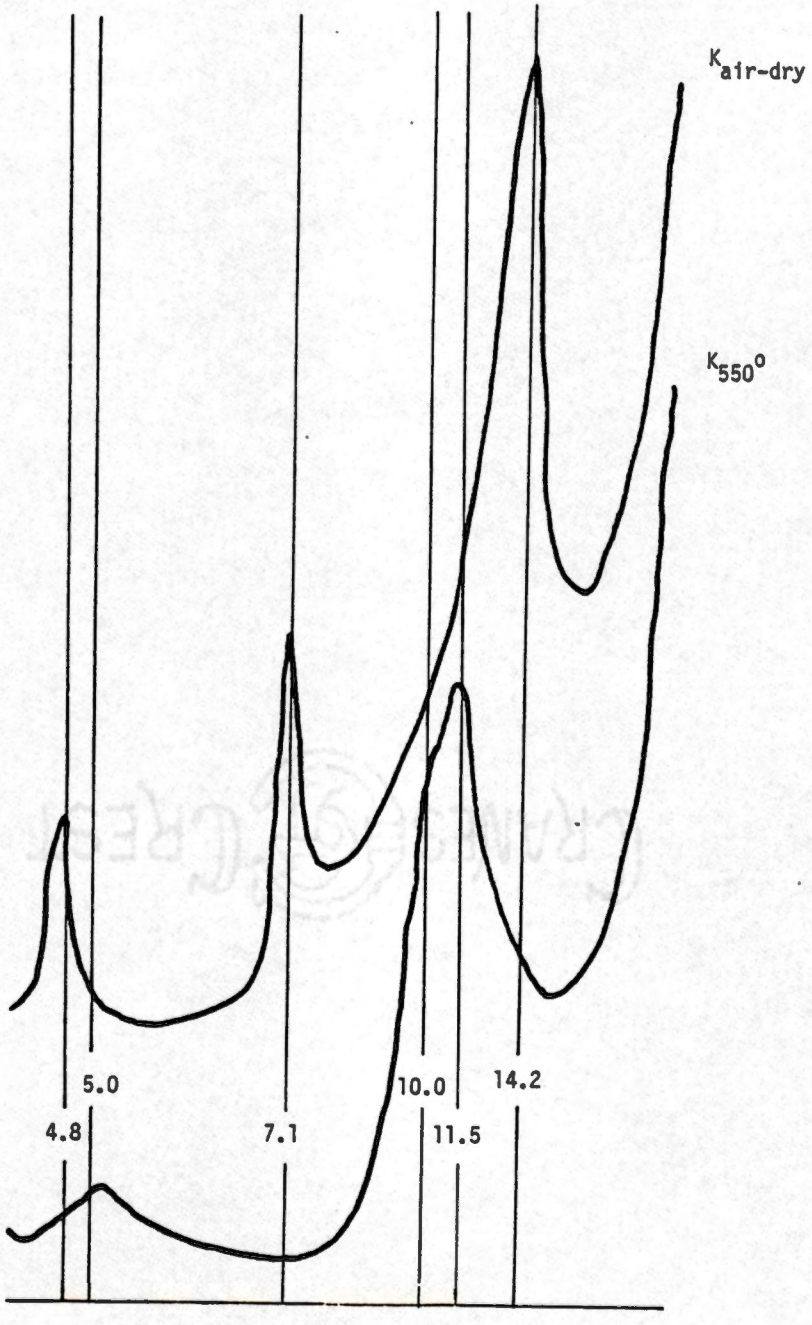


Figure 24. X-ray diffraction patterns for $Al_2(SO_4)_3$ at 60.0 g/pot.

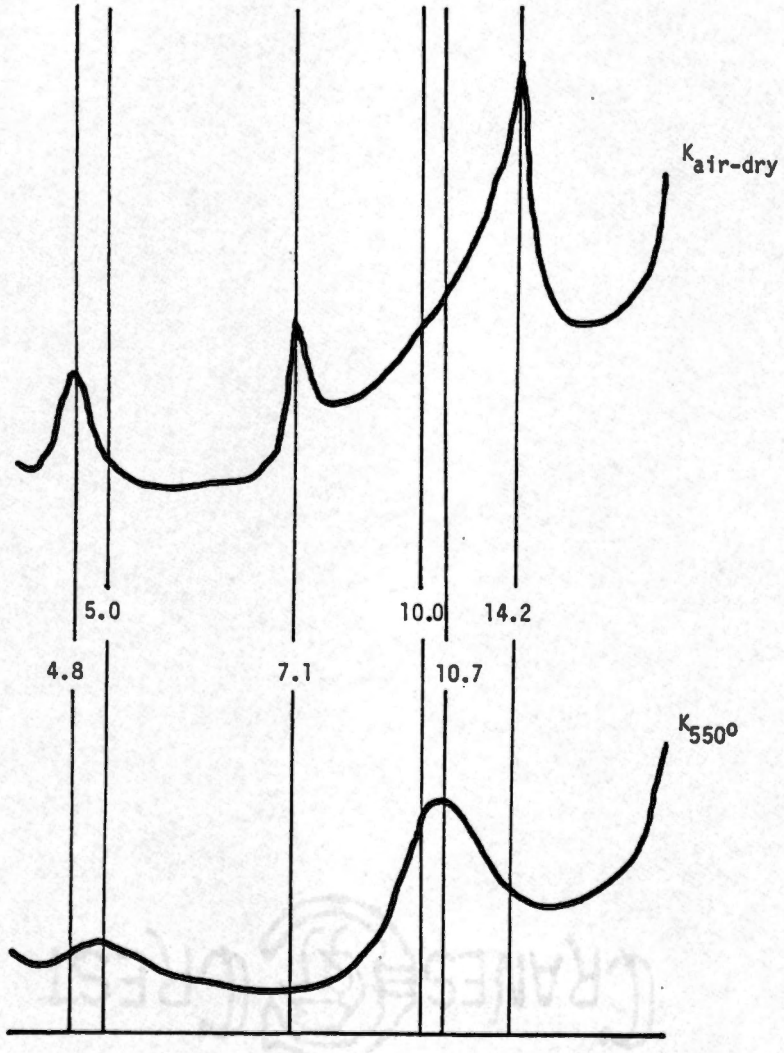


Figure 25. X-ray diffraction patterns for the control of the 60.0 g/pot $Al_2(SO_4)_3$ treatment.

up until the 550°C heat treatment. The hydroxy interlayered vermiculite was not altered until the 550°C heat treatment when it showed a partial collapse (Figure 23, 24, and 25). The 7.1A° kaolinite peak also disappeared with the 550°C heat treatment. Quartz was the dominant mineral in the silt fraction, but it was not detected in either the X-ray diffraction or DSC patterns of the clay fractions.

There are few differences in the X-ray diffraction patterns between either acidulent and the corresponding controls. The only apparent difference in elemental S treatments and the control appeared in the 550°C heat treatment where the 10.4A° peak is more symmetrical in the elemental S treatment than in the control (Figure 23). The $Al_2(SO_4)_3$ treated sample showed more resistance to collapse than the corresponding control, at the 550°C heat treatment (Figure 24 and 25).

Ca/Mg and K/NH_4 whole soil CEC values are shown in Table 9. CEC values were the highest for the 15.0 grams per pot (6000 kg/ha) application of elemental S and were slightly lower in the 7.5 grams per pot (3000 kg/ha) treatment. The lowest values were obtained in the control and in the $Al_2(SO_4)_3$ treatment.

V. Discussion

A comparison of the reported rates of elemental S and $Al_2(SO_4)_3$ necessary to cause a desired decrease in pH show considerable variability. Stoeckeler and Arnemann (59) reported that only about 1.25 times as much $(Al_2(SO_4)_3$ as elemental S was necessary to cause the same decrease in soil pH, while Chadwick (16) found that nearly 2.5 times as much $Al_2(SO_4)_3$ was needed. Ratsek (51) showed that about

Table 9. Effect of soil acidulents on CEC values.

Acidulents	Rate of Acidulent g/pot	Ca/Mg CEC meq/100 g soil	K/NH_4 CEC meq/100 g soil
None (control)	0.0	1.75	0.74
Aluminum sulfate	60.0	1.68	0.68
Elemental sulfur	7.5	1.94	0.84
Elemental sulfur	15.0	2.53	0.91

NOTE: The above CEC determinations were made on soils containing no sawdust amendment.

seven times as much $Al_2(SO_4)_3$ as elemental S was needed. In this experiment, 2.5 grams (1000 kg/ha) of elemental S per pot caused approximately the same decrease in pH as 10.0 grams $Al_2(SO_4)_3$ per pot (4000 kg/ha). However, after three months, 2.5 grams elemental S gave nearly the same pH reduction as 20 grams $Al_2(SO_4)_3$. By the end of the experiment, elemental S at 7.5 grams per pot (3000 kg/ha) caused approximately the same pH decrease as 60.0 grams $Al_2(SO_4)_3$ per pot (24,000 kg/ha). This ratio of 1:8 is closest to that reported by Ratsek, and far exceeds the reports of the others. Theoretically, on an equivalent weight basis, elemental S and $Al_2(SO_4)_3$ would be expected to produce approximately equal amounts of acidity. On a gram for gram basis, elemental S would be expected to produce approximately 7 times the acidity produced by $Al_2(SO_4)_3$. Therefore, the eight fold difference in amounts of acidulent required is very near the expected value. The lowering of pH by elemental S in this experiment was further enhanced by the release of Al, which presumably occurred with the destruction of gibbsite, kaolinite, and hydroxy interlayered vermiculite in the < 0.002 particle size fraction.

It should be pointed out that none of the researchers who studied the effects of $Al_2(SO_4)_3$ on soil pH values noted the number of H_2O molecules attached to the $Al_2(SO_4)_3$ they used. The $Al_2(SO_4)_3$ used in this experiment had 18 attached H_2O molecules. However, $Al_2(SO_4)_3$ is available with a number of different amounts of attached H_2O molecules. Such differences alter the formula weight, hence, changing the acidifying potential of the $Al_2(SO_4)_3$. This provides a possible

explanation of some of the variability in reported pH decreases with a given application rate of $Al_2(SO_4)_3$.

The increase in levels of silver-thiourea extractable Ca and Mg appear to be related to the amount of decrease in soil pH (Figure 11 and 13, pages 43 and 47). Calcium and Mg levels were nearly equal regardless of the source of acidulent, when corresponding pH values were observed (Figure 11 and 13, pages 43 and 47). Hence, there is no apparent effect of biological activity from the sulfur oxidizing microbes on these elements. Ames (2) reported that Ca levels increased much more sharply than Mg levels when elemental S was applied to several Ohio soils. In this experiment, where soil pH values were reduced to pH 4.4, extractable Ca and Mg levels approximately doubled in comparison with the controls. Past additions of dolomitic limestone ($CaMg(CO_3)_2$) to the soil represents a logical source for the observed increases in Ca and Mg levels. The acidity produced by the elemental S and $Al_2(SO_4)_3$ additions apparently increased the solubility of the limestone particles present in the soil. Crusted yellow brown deposits found on the soil surfaces and around drainage holes in the bottoms of the pots receiving the highest rates of acidulents presumably were deposits of calcium sulfate. Since these deposits around the pot bottoms resulted from leaching, this may suggest that a decrease in Ca levels may have occurred given a longer time period. The sawdust incorporated into the soil was apparently low in Mg and Ca, since sawdust content could not be related to extractable levels of either element.

In contrast to Ca and Mg, differences in extractable K levels between elemental S and $Al_2(SO_4)_3$ do not appear to be related to

changes in pH (Figure 15, page 50). There were relatively small increases of K in $Al_2(SO_4)_3$ treated soils in comparison with elemental S. Ames (2) suggested that increases in K levels observed with elemental S applications were affected by sulfur oxidizing microorganisms. An examination of DSC patterns (Figure 22, page 62) revealed an alteration of clay minerals in the elemental S treated soil. Destruction of hydroxy interlayered vermiculite in the elemental S treated soils appears to be a logical source for the increase in K extracted. A slight decrease in K levels in all treatments between February 1981 and June 1981 is probably a result of plant uptake, since blueberries were planted in the treated soils in February and grown until June. Unlike Ca and Mg, extractable K levels increased with increasing levels of sawdust, suggesting that there was a significant amount of K originally present in the sawdust.

Sodium levels increased in the $Al_2(SO_4)_3$ treated soils, but showed little change in elemental S treated soils. Increases in extractable Na were relatively linear with both rates of application of $Al_2(SO_4)_3$ and levels of sawdust, although the reason for this relationship is unknown.

Much of the increase in Al and H levels at the heaviest rates of acidification is the result of decreases in pH. It is well known that these elements increase in solubility and activity in acid soils. A comparison of corresponding pH values between acidulent treatments showed that Al levels were higher in the elemental S treatments than in the $Al_2(SO_4)_3$ treatments in February 1981, and the trend was reversed by June 1981. This may lend support to the conclusion that

heavy $Al_2(SO_4)_3$ applications may over time lead to greater Al buildups than do elemental S applications. However, it should be pointed out that in the $Al_2(SO_4)_3$ treatments, the lowest observed pH value was above 4.0. Hence, Al levels between pH 3.0 and 4.0 may be biased in the $Al_2(SO_4)_3$ treatments since they are based only on observed values between pH 4.0 and 5.0.

Thomas (60) found that KCl extractable Al levels were lower as organic matter content increased, at a given pH level. In this experiment, there was no apparent relationship between Al and sawdust levels in February. In June, however, the highest levels of Al extracted occurred at the highest levels of sawdust with both acidulents, just the opposite of what Thomas had found.

The clay minerals present in the soil used in this experiment appear to be relatively stable, except in the highest elemental S treatment. This is evidenced by few changes in X-ray diffraction patterns through the intermediate heat treatments. The hydroxy interlayered vermiculite appears to be extremely stable, showing a partial collapse only at the 550°C heat treatment. Destruction of gibbsite, which was observed in elemental S treated soils in this experiment, was also observed by Wolt et al. (69) on acid sulfate polluted soils of the Copper Basin area of Tennessee.

The concept of pH-dependent charge would lead one to believe that the highest CEC values would be obtained in the controls, where the pH was greater than 6.0. However, the highest Ca/Mg and K/NH_4 CEC values were obtained where elemental S was added at 15.0 grams per pot (6000 kg/ha). Where elemental S was added at 7.5 grams per pot

(3000 kg/ha), CEC values were also higher than the controls. The increase in Ca/Mg and K/NH_4 CEC can be attributed to the destruction of HIV. This destruction resulted in the production of more edges and/or the exposure of some interlayer, which would increase CEC values. The fact that there was no difference in the CEC values obtained from the $Al_2(SO_4)_3$ treated soil and the control is consistent with the DSC and X-ray diffraction patterns of the clay fractions, which also showed essentially no difference between them.

CHAPTER V

GENERAL SUMMARY

In the first part of this investigation, two soil acidulents were evaluated for their potential to produce optimal growth in rabbiteye blueberries (*Vaccinium ashei*) through lowering of soil pH. Aluminum sulfate was applied at rates of 7.5, 15.0, 30.0, and 60.0 grams per pot (3000, 6000, 12,000, and 24,000 kg/ha, respectively), while elemental S was added at rates of 1.9, 3.8, 7.5, and 15.0 grams per pot (750, 1500, 3000, and 6000 kg/ha, respectively). Sawdust was incorporated into the soil at rates of 0, 20, 40, and 60% by volume. The soil used in this experiment was a previously limed sandy loam surface soil having an initial pH of 6.2 to 6.5

Applications of the two smallest rates of both acidulents did not significantly increase plant weight gain of the blueberries, when compared to the controls. The greatest plant growth was achieved using elemental S at 7.5 grams per pot (3000 kg/ha) and 60% sawdust, which acidified the soil to pH 4.4. The best $Al_2(SO_4)_3$ treatment was at the rate of 30.0 grams per pot (12,000 kg/ha) and 60% sawdust, which acidified the soil to a pH of 4.8. At the highest rates of application of both acidulents, plant weight gain decreased from the best treatment considerably. Extremely high Al levels may have caused a toxicity at these high rates of application. Growth was severely restricted and chlorosis was evident across all rates of application of both acidulents where no sawdust was amended.

In addition to being more favorable for plant growth, 1 unit weight of elemental S was found to cause the same pH decrease as approximately 8 times as much $Al_2(SO_4)_3$. Sawdust levels had no significant effect on the amount of decrease in pH.

In the second part of this investigation, the acidulents were compared for their effects on several soil properties. These soil properties included silver-thiourea extractable Ca, Mg, K, Na, Al, and H, CEC, plus clay mineralogy. Magnesium and Ca levels in the most acid treatments were approximately double those of the controls and appeared to be the result of the amount of decrease of pH, rather than the source of acidulent. Potassium levels were the highest where elemental S was applied at the highest rate of application. The increase in K was thought to be the result of destruction of HIV, which would lead to the liberation of K. Sodium levels were highest in soils receiving the highest rates of application of $Al_2(SO_4)_3$. Elemental S had no apparent effect on Na levels extracted. Aluminum and H levels increased sharply only at the highest rates of application of both acidulents. Much of this effect was pH related.

Destruction of clay minerals was evident in DSC patterns at the highest rate of elemental S application. Clay minerals that showed alteration were gibbsite, kaolinite and HIV. This destruction of clay minerals, however, led to increases in Ca/Mg and K/NH_4 CEC values, when compared to the controls. These increases are thought to be a result of creation of more edges or exposure of interlayer of HIV.

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