To the Graduate Council:

I am submitting herewith a thesis written by Michael Briggs Bauman entitled "Corn Yield and Quality as Related to Sulfur Accretion on Tennessee Soils." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Plant and Soil Science.

Jeffrey D. Wolt, Major Professor

We have read this thesis and
recommend its acceptance:

Gary M. Lessman

Randall J. Miles

Accepted for the Council:

Vice Chancellor
Graduate Studies and Research

CORN YIELD AND QUALITY AS RELATED TO SULFUR ACCRETION ON TENNESSEE SOILS

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Michael Briggs Bauman

June 1983

ACKNOWLEDGEMENTS

The author wishes to express his most sincere appreciation and gratitude to the following people:

Dr. Jeffrey D. Wolt, my major professor, for his advice and assistance during this study;

Dr. Gary M. Lessman and Dr. Randall J. Miles for their helpful suggestions and cooperation as members of my graduate committee;

The Plant and Soil Science Department (Dr. Lloyd Seatz, Head) for providing financial support for this project;

Mr. David Walker and Mr. Robert Reed for technical advice and assistance in laboratory analysis;

Fellow graduate students for their friendship and support during my graduate studies;

My family and especially my wife, Beth, for their patience, encouragement, and help throughout my graduate program.

ABSTRACT

The effects of sulfur (S) fertilization and atmospheric S inputs upon extractable soil S and corn yield and S concentration were investigated in nine location-years of experimentation conducted from 1980-82 at three locations within Tennessee: Ames Plantation, Grant Junction; The Tobacco Experiment Station, Greeneville; and the Plant Science Field Laboratory, Knoxville. At each location S (as K_2SO_4) was applied at rates of 0, 17, and 34 $kg \cdot ha^{-1}$ in a replicated, randomized complete block design. The influence of S fertilization, years, and locations on grain yield, nutrient concentration of both leaf and grain samples, and soil extractable S and pH was evaluated for the data combined across years with locations nested within years. Additionally, wet/dry deposition of atmospheric S was monitored at each location throughout the study.

The analysis of data indicated that yield and S concentration of leaf and grain tissue was uninfluenced by S fertilization, suggesting that S was not limiting for corn yield in this experiment. Additionally, S fertilization and years had no ffect on extractable soil S while locations within years significantly ffected this value. The soil at Knoxville was considerably lower in extractable S than soils at either Grand Junction or Greeneville and therefore had a greater potential for S deficiency during the course of this study. An average of 16 $kg \cdot ha^{-1} yr^{-1}$ of S was contributed to these cropping systems via wet/dry deposition. It is likely that atmospheric input

may be compensating for the S removed as harvested grain and lost by leaching, thus preventing a corn response to S fertilization at these locations.

TABLE OF CONTENTS

LIST OF TABLES

CHAPTER I

INTRODUCTION

Sulfur (S) is considered by many to be the fourth most essential plant nutrient, preceded only by nitrogen (N), phosphorous (P). and potassium (K). This element is constantly being converted, transformed and transported throughout the environment. To assess the availability of S in an agricultural ecosystem, the movement and transformation of this element, in what can be referred to as the S cycle, must be considered.

There are five major avenues S can interact with a crop system: (1) soil adsorption of atmospheric sulfur dioxide (SO_2), (2) plant absorption of atmospheric SO_2 via stomatal openings, (3) sulfate ($SO_4^=$, to be subsequently abbreviated SO_4) dissolved in rainwater, (4) application, either incidentally by way of fertilizers and pesticides or directly through application of S fertilizers, and (5) release of S from soil. The first three methods are dependent upon that part of the S cycle which resides in the atmosphere.

Most S of atmospheric origin is derived from sea spray, the evolution of hydrogen sulfide from decomposing organic matter, and the burning of fossil fuels. Sulfur of anthropogenic origin has been estimated to contribute as much as 50% of the total atmospheric S. The amount of S supplied to a crop system by the atmosphere is largely unknown. It is known, however, that some crop systems can be highly dependent upon this source for their S nutrition.

In the past, significant amounts of S have been applied to crops incidentally through S-containing pesticides and low-analysis fertilizers. In many cases these materials provided adequate amounts of S for crop growth. Over the past 10-15 years, however, the trend has been to use organic pesticides and high analysis fertilizers which contain little or no S. This trend, along with higher crop yields, may be contributing to the observed increase in S deficiencies of agronomic crops.

The soil can supply S to a plant by the desorption of SO_4 from the soil, by mineralization of organic matter, and by the weathering of S-containing soil minerals. It is believed that sulfate adsorbed to soil particles can be a significant source of available S, especially if the soils are highly leached and low in organic matter. In most cases the largest amount of soil-S is contained in organic matter, with SO_4-S contributing less than 10% of the total soil S. Organic S must be mineralized before it is available to plants. It is therefore considered important in the long-term supply of S to crops. It is generally believed that the weathering of S-containing minerals contributes little to the 'available' S supply. However, in arid regions where leaching is minimal, this process can be of major importance.

The objectives of this research were to study the effect of fertilizer and atmospheric S inputs on soil S availability, corn (Zea mays L.) yields, and corn S content. This research will help to identify what components of the S cycle may best describe crop S requirements of soils at three locations in Tennessee.

CHAPTER II

LITERATURE REVIEW

Sulfur Retention by Soils

Absorption of S through the root system of plants is believed to be largely in the form of SO_4 (Ensminger and Freney, 1966). The fraction of S available for plant uptake is dependent upon the amount of soluble SO_4 present, the rate at which adsorbed SO_4 becomes soluble, and the amount of organic S which is mineralized during the growing season (Bettany et al., 1974). In humid regions, the levels of soluble SO_4 are normally below 104 $\mu mol \cdot kg^{-1}$ and are subject to considerable fluctuation. This variation can be attributed to the mineralization of organic matter, plant uptake, losses of soluble SO_4 to leaching, and S accretion from fertilizer and rainfall. In well-drained soils of humid regions, the amount of soluble SO_4 alone is generally too small to supply the S requirement of a cropping system (Williams, 1968).

Several investigators have shown that SO_4 absorbed by the soil is available for plant uptake. Experiments with soybeans (Glycine max L.), corn, cotton (Gossypium hirsutum L.), and tobacco (Nicotiana tobacum L.) have demonstrated that part of the adsorbed SO_4 in subsurface soil horizons can be utilized by these crops (Kamprath et al., 1957). Williams and Steinberg (1959) found that adsorbed SO_4 was readily available to oats (Avena sativa L.) grown in pot culture. Research has demonstrated that deep-rooted plants such as alfalfa

(Medicago sativa L.) are less likely to respond to S application when subsurface horizons are high in adsorbed SO_4 (Ensminger, 1958). It is generally accepted that adsorbed SO_4 is 'available' to plants although the degree of availability is uncertain.

Sulfate is retained to a certain extent by most soils. In most cases the subsurface horizons contain more SO_4 than do the surface horizons. However, soils which have little ability to retain SO_4, and which have a substantial amount of organic matter (4-5%), may contain the majority of their SO_4 in the surface horizons (Tabatabai and Bremner, 1972).

Sulfate retention by soils is known to be affected by the presence of iron (Fe) and aluminum (Al), soil pH, liming practices, the amount and type of clay minerals present, soil SO_4 concentration, and the presence of certain cations and anions (Harward and Reisenauer, 1966). There is a considerable amount of evidence which indicates that SO_4 retention in acid soils is largely dependent on the chemistry of Fe and Al (Chao et al., 1962 and 1964; Ensminger, 1954; Kamprath et al., 1956; MacIntire et al., 1941; Mehlich, 1964). It is believed that the hydrous oxides of these metals form coordination complexes which can be ruptured by anion penetration. This penetration is related to the ability of an anion such as SO_4 to be attracted to the metal cation (Harward and Reisenauer, 1966). This phenomena is normally referred to as anion adsorption. Although most literature refers to soil SO_4 retention as an 'anion adsorption' process, the exact mechanism for SO_4 retention is uncertain. Current research has indicated that the solubility of S-containing compounds

may be contributing to the retention of SO_4 in acid soils. This mechanism involves the precipitation of S as Fe- or Al-hydroxy sulfates (Adams and Rawajfih, 1977; Wolt, 1981; Wolt and Adams, 1979).

It is well documented that SO_4 retention in soils is strongly affected by equilibrium pH; as soil pH decreases, SO_4 retention increases (Harward and Reisenauer, 1966). In soils of pH 6.5 or greater, the retention of SO_4 apparently becomes negligible (Kamprath et al., 1956; Williams and Steinberg, 1964). This can be explained by the effect of pH on hydrous oxides. In an acid medium, Fe and Al-hydroxy groups will undergo protonation. As pH decreases the amount of protonation and positive charge of the complex will increase. This positive charge can be neutralized by anions such as SO_4 (Graham and Thomas, 1947).

Several experiments have demonstrated the effect of liming on SO_4 retention and availability. In greenhouse experiments, Williams and Steinberg (1959) observed an increased yield and SO_4 uptake of oats upon the addition of $CaCO_3$ to soil. In 1971, Elkins and Ensminger showed that increased rates of $CaCO_3$ application decreased the amount of SO_4 retained by soils. In this same work it was noted that the amount of SO_4 taken up by soybean and cotton plants was generally greater as the $CaCO_3$ rate was increased. These authors concluded that an increase in soil pH due to the addition of $CaCO_3$ may have released previously unavailable S from the soil allowing for an increase in S uptake. Others have explained this phenomena as a result of an increase in the SO_4 released from organic matter, because of a more

favorable pH for soil microbes or because of chemical hydrolysis at alkaline pH (Freney and Stevenson, 1966).

The amount and type of clay are also known to influence the retention of S in soils. Since the number of positive charges in a soil will increase with clay content, the anion 'adsorption' of SO_4 will likewise increase. Clay content, acidity, and the amount of Fe and Al hydroxides are known to increase to some degree with depth in many soil profiles which results in a similar trend for increased SO_4 'adsorption' with depth (Williams, 1975). Soils containing kaolinite have a higher adsorption capacity for SO_4 than those containing montmorillonite. This can be explained by the greater number of anion exchange sites on 1:1 type clays and the anion repulsion which is created by a high negative charge on the 2:1 type clays (Harward and Reisenauer, 1966).

Other factors which effect SO_4 retention are the amounts and types of ions present in a soil system and the SO_4 concentration. As the chemical valence of the exchangable cation increases, the magnitude of SO_4 adsorption will also increase (Chao et al., 1963; Thomas, 1960). The strength of anion retention in soils follows the order $H_2PO_4^- > SO_4^= > NO_3^- = Cl^-$ (Bohn et al., 1979). Adsorbed sulfate is readily displaced by the $H_2PO_4^-$ anion, while SO_4 has essentially no effect on $H_2PO_4^-$ (Chao et al., 1963; Kamprath et al., 1956). Several researchers have found that application of fertilizers containing monocalcium phosphate will reduce the retention of SO_4 in soils (Ensminger, 1954; Kamprath et al., 1956). It is well documented that the 'sorption' of SO_4 by soils is concentration dependent; as SO_4 concentration

increases, SO_4 'sorption' will increase (Chang and Thomas, 1963; Chao et al., 1962; Kamprath et al., 1956).

Sulfur bonded to organic compounds is the predominant form of sulfur in most soils, often making up more than 90% of the total soil sulfur. This S fraction must be mineralized to SO_4 before it can be utilized by plants (Evans, 1975). Organic S is generally grouped into two major categories: carbon-bonded S and ester-sulfates. Ester-sulfates are reduced to hydrogen sulfide by hydriodic acid and are sometimes referred to as hydriodic-acid-reducible S (Freney, 1961). Little is known about the metabolic activity of this fraction; it could be an active part of S mineralization or a stable end product of mineralization (Freney et al., 1971). Ester-sulfates are believed to be unavailable to plants, but upon drying the SO_4 linkage can break, freeing available SO_4 (Barrow, 1961; Williams, 1967).

Carbon-bonded S consists of the amino acids cystine, cysteine, and methionine. Incubation studies by Freney et al. (1975) indicate that upon mineralization, both the ester-sulfates and carbon-bonded S may be utilized by plants. These results also indicate that no single fraction comprises a major source of the available S supply of soils. Field studies by McLachlan and DeMarco (1975) and incubation studies by Freney et al. (1971) indicate that carbon-bonded S could change rapidly into the ester-sulfate form. Results of field studies by McLaren and Swift (1977) suggested that the ester-sulfate fraction, as compared to the carbon-bonded fraction, was more transitory in nature and was likely to be more important in short term mineralization of soil S. The authors indicated that carbon-bonded S was probably

passing through the ester-sulfate fraction before becoming available as inorganic SO_4. The relative contribution of carbon-bonded versus ester-sulfate S to the available S supply is difficult to establish because of the cycling of the S between these fractions (McLaren and Swift, 1977). It appears the two fractions contribute nearly equal amounts to the available S supply (Freney et al., 1975).

Since organic matter is believed to be mineralized primarily by soil microbes, any factor affecting their growth will likewise affect the mineralization of organic S. These factors include temperature, soil moisture, the C:N:S ratio, the total amount of organic matter and soil pH (Freney and Swaby, 1975). In soils the C:N:S ratio exists over a wide range and averages about 140:10:1.3 (% ratio; Buckman and Brady, 1969). Literature reviewed by Freney and Swaby (1975) indicates that direct relationships between the amount of S mineralized and either the soil type, the C:N:S ratio, or total soil C, N, or S, have not been established. Some of the S added to soils in the form of fertilizers is known to be incorporated into an organic form by microorganisms. Freney et al. (1971) found that in a 24-week period as much as 50% of total SO_4 added to a soil could be converted into organic matter.

Incubation procedures have been designed to measure the ability of organic matter to supply available SO_4 to soil. In Mississippi it was estimated that 2.6 $kg \cdot ha^{-1}$ of SO_4-S per month was being mineralized in a Grenada soil incubated at a constant temperature and moisture content (Nelson, 1964). Harward et al. (1962) found that S extracted from the soil plus S released upon incubation

could produce good correlations with yield. The success of these studies, however, are limited by differences between incubation and field conditions, and the lack of accurate detection of small releases of SO_4 (McLaren and Swift, 1977).

Studies with ^{15}N have predicted that two to three percent of the N immobilized in a soil could be released per year. If S is released at the same rate, then 3.6 kg of S $ha^{-1} \cdot yr^{-1}$ could be mineralized for each percent of organic matter contained in the soil (Terman, 1978).

Characteristics of Plant S

Plants are known to absorb and transport S as the SO_4-ion ($SO_4^{=}$). Once SO_4 is absorbed it is transported to the leaves and is either stored as SO_4 or incorporated into organic substances. Organic S is largely in the form of the amino acids methionine and cysteine. Less than 10% of organic S exists as substances other than amino acids such as thiamine, biotin, thiocitic acid, and glutathione alkaloids (Allaway and Thompson, 1966). When S is limiting, most plant S is in a protein form while SO_4-S is detectable only in small amounts. On the other hand if the S supply is more than adequate, SO_4-S will become concentrated in the plant (Ensminger and Freney, 1966).

Compared to the mobility of N and P in plants, S mobility is considered to be restricted. The relative immobility of S is expressed by the S deficiency symptoms of most plants which are characterized as chlorosis of younger leaves rather than older ones. Sulfur deficiency symptoms in corn are characterized by a slow growth rate, delayed

maturity, stunted plants and a general yellowing of the leaves (Platou and Irish, 1982).

Total N to S ratios and the concentration of total S and SO_4-S have been used as criteria for evaluating the S status of plants. Of these criteria, total S of leaf tissue has been the most common method for assessing the S status of plants (Grant and Rowell, 1978). Data on critical S levels and on N:S ratios in corn tissue are very limited, possibly because corn is a low S-accumulating crop (Table II-1).

Inconsistency of the critical S values reported for corn can be attributed to the variety of analytical procedures which are used for the separation and the determination of the S fraction. Criteria for plant sampling and differences between field and greenhouse conditions are additional factors which influence the critical S value.

Since N and S are both required for protein formation, the amounts of each element needed by the plant are closely related. Sulfur deficiency causes non-protein N to accumulate resulting in a high N:S ratio, whereas an excess S supply will result in a low N:S ratio because of the accumulation of non-protein S (Gaines and Phatak, 1982). Because of this, the N:S ratio can be used as a criteria for diagnosing S deficiencies. Yield responses to S by corn are generally greater with increasing rates of N application (Thomas, 1959; Stewart and Porter, 1969). As with S content of leaf tissue, critical values for the N:S ratio in corn are inconsistent (Table II-1). Kang and Osiname (1976) reported the N:S ratio of corn to fluctuate between 11 and 16 (percent ratio), indicating that this

Table II-1. Levels of Total S and N:S Ratios in Corn Leaf Tissue Below Which a Response to Sulfur is Likely (Critical Levels).

Method of Plant Digestion + Method of S Analysis	Part and Age of Plant Sampled	Critical Levels in Plant Tissue			Reference
		N:S		Total S	
		$\frac{\%N}{\%S}$	$\frac{mol \cdot kg^{-1} N}{mol \cdot kg^{-1} S}$	$mmol \cdot kg^{-1}$	
Nitric-perchloric acid + n.a.	10 leaves below and adjacent to ear at silking	12	27	74.9	Daigger and Fox, 1971
Sodium carbonate fusion/HCl + turbidimetric	ear leaf at tasseling	11-16	25-37	43.7	Kang and Osiname, 1976
Nitric-perchloric acid + turbidimetric	leaf opposite and below ear at silking	19	43	46.8	Reneau and Hawkins, 1980
Ashed with $NaHCO_3$ and a Ag_2O catalyst + a reduction method	ear leaves at 70 days old (greenhouse)	n.a.	n.a.	40.5	Grant and Rowell, 1978
Dry combustion + turbidimetric	tops at 35 days old (greenhouse)	12-15	27-34	31.2	Stewart and Porter, 1969
Nitric-perchloric acid + turbidimetric	leaves immediately below and opposite ear at late growth	n.a.	n.a.	59.3	Fox et al., 1964

n.a. = not available

ratio was an unsatisfactory criteria for determining S status in slightly deficient corn plants. Similarly, Daigger and Fox (1971) observed considerable variation in the N:S ratio as the S in the plant approached adequacy. These results, however, do not eliminate the usefulness of the N:S ratio as a criteria for detecting moderately severe or extreme cases of S deficiency. The N:S ratio is inadequate as a criteria for S deficiency because of the inability to distinguish between simultaneous deficiencies or excesses of both the elements (Grant and Rowell, 1978).

Sulfate-S in plant tissue has been shown to be a useful criteria for assessing the S status of many crops (Beaton et al., 1968), but research on corn and other grains is limited. Grant and Rowell (1978) concluded that the SO_4-S concentration of leaves, and the total N:S ratio of the stalks, were the best indicators of the S status of corn. Crude estimates of the S status of corn were found with total S of the stalks and leaves, and the N:S ratio of the leaves. Critical values for SO_4-S in the leaves were about 21.8 mmol $S \cdot kg^{-1}$ while the critical values for the N:S ratio of the stalk were 25 (percent ratio).

Many reports from both North America and Europe have demonstrated the ability of plants to absorb and utilize SO_2 from the atmosphere. In greenhouse conditions, Faller (1971) reported that tobacco, corn, and sunflower (Helianthus annuus L.) could obtain the majority of their S requirement from SO_2, when soil S was limiting. When adequate soil S is available to plants, lesser amounts of SO_2 are taken up from the air (Olsen, 1956; Siman and Jansson, 1976).

It is well known that high concentrations of SO_2 can damage plants by interfering with their photosynthetic process. Reports of plant damage to SO_2 in field conditions have been limited to localized areas where an industrial source has increased the SO_2 concentration of the atmosphere to abnormally high levels. Corn is considered to be a relatively tolerant species to SO_2 injury. Laurence (1979) demonstrated foliar injury to corn hybrids was minimal even at high doses of SO_2, while wheat (Triticum aestivum L.), a sensitive species, was shown to be significantly damaged at much lower SO_2 concentrations.

Contributions of Atmospheric S to a Crop System

In the southeastern part of the United States little research has dealt with the ability of the atmosphere to supply S to an agricultural system. Sulfur in rainwater has been recorded in the southeast as early as 1913 (Johnson, 1924). Although these early measurements were found to be inaccurate because of contamination of the collecting devices (Alway, 1937), they still provide useful estimates of relative S deposition at these early sites (MacIntire and Young, 1923; Johnson, 1924). More reliable tests were made from 1953-1955 when researchers in 12 states of the southeastern region investigated S content in rainwater and its influence on crop growth. Nine of these states were grouped together because of similar S contributions from rainwater (6.1 $kg \cdot ha^{-1} \cdot yr^{-1}$). In contrast, the states of Kentucky, Tennessee, and Virginia were found to have an annual average of 14.2 $kg \cdot ha^{-1}$ of S deposited by rain. Higher values of rainwater S were believed to be a consequence of the higher amount of

coal combustion in those states. In 1955 the average S input from precipitation for seven locations in Tennessee was estimated to be 14.4 $kg \cdot ha^{-1} \cdot yr^{-1}$ (Jordan et al., 1959). The value for five locations in Tennessee from 1971 to 1972 was found to be 17.1 $kg \cdot ha^{-1} \cdot yr^{-1}$ (Terman, 1978).

In 1978, wet and dry deposition of SO_4 was estimated to contribute 18.1 $kg \cdot ha^{-1} \cdot yr^{-1}$ of S to a mixed deciduous forest in eastern Tennessee. Of this amount, 11.5 $kg \cdot ha^{-1} \cdot yr^{-1}$ of S was lost in stream flow, leaving a net accumulation of 6.6 $kg \cdot ha^{-1} \cdot yr^{-1}$. Of the total input (18.1 $kg \cdot ha^{-1} \cdot yr^{-1}$ of S), only 3.3 $kg \cdot ha^{-1} \cdot yr^{-1}$ was due to dry deposition while 14.8 $kg \cdot ha^{-1} \cdot yr^{-1}$ was added by precipitation (Shriner and Henderson, 1978). Kelly (1982, unpublished results) reported an average annual input of 25.6 $kg \cdot ha^{-1} \cdot yr^{-1}$ of S from the atmosphere for three locations of eastern Tennessee in 1978-1979. Of this amount, only 3.6 $kg \cdot ha^{-1} \cdot yr^{-1}$ of S was added as particulate SO_4 while 11.4 and 10.6 $kg \cdot ha^{-1} \cdot yr^{-1}$, respectively, was added by gaseous SO_2 and SO_4 in precipitation.

Sulfur Fertility in the Southeast Region

The state of Tennessee is in a region of potential S deficiency in which soils are low in organic matter, leached and somewhat highly weathered. Jordan (1964) demonstrated that S deficiency existed in some agricultural crops throughout most of the southeastern United States. Sulfur deficiencies were not discovered in Tennessee, Kentucky and Virginia. Presently, S deficiency has not been established as a problem in Tennessee.

In the Southeastern region, S deficiency in corn has been infrequently observed until recently. Studies on Coastal Plain soils in Alabama (Marvyn loamy sand) reported that corn yield increased by .59 $Mg \cdot ha^{-1}$ upon the addition of 56 kg of S per hectare (Murdock and Lund, 1979). In Virginia, also on coarse textured Coastal Plain soils (soil series included: Slagel, Lakeland and Dragston), Reneau and Hawkins (1980) observed a 17% increase in corn yield from S application. In Darlington, South Carolina corn responded to 18 $kgS \cdot ha^{-1}$ in the years 1975-1978 and 1980 when the acetate-extractable SO_4-S level for the top 30 cm of soil (Norfolk loamy sand) was 281 $\mu mol \cdot kg^{-1}$. On the other hand, no S response occurred with corn in Columbia, South Carolina when soils (Wagram loamy sand) tested only 125 $\mu mol \cdot kg^{-1}$ in SO_4-S. Apparently, atmospheric S or subsoil S was supplying sufficient S to this crop (Suarez and Jones, 1982).

Isolation and Determination of S

Research with S as a plant nutrient has been limited because methods of S determination in soils and plants can be inaccurate, tedious and difficult. Diagnostic techniques for determining the S-supplying capacity of soils include the extraction or isolation of the desired S fraction from the plant tissue or soil, and subsequent analysis of the element. Inaccuracy results from the loss of S during isolation of the element and the lack of sensitive methods for detection of small quantities of S. Also, S analyses are largely performed by indirect methods, which are generally laborious and susceptible to interferences (Beaton et al., 1968).

When comparisons of indices of S deficiency are made, great variability is observed. This can be largely explained by the use of different methods for the isolation and analysis of S from plant and soil materials. Inconsistency can also be attributed to the age and part of a plant sampled (Ensminger and Freney, 1966).

Extractable soil S. The major objective of the soil extractant is to obtain that portion of soil S which is available to crops. The fractions of soil S which have been used to make correlations with S availability include soluble SO_4, soluble plus adsorbed SO_4, total S and organic S. It is important to note that no one extractant will perform equally well on all soils (Beaton et al., 1968).

Common extractants for soluble SO_4 have been water and a 1.35 $mol \cdot L^{-1}$ calcium chloride solution. Although soluble SO_4 is readily available to plants, these extractants have generally failed to produce good correlations with plant growth (Ensminger and Freney, 1966). Extraction with water is likely to be unsatisfactory because it does not extract adsorbed S or insoluble forms of SO_4, which may be available to plants (Williams, 1964). Calcium chloride extractants tend to overestimate S availability and do not measure 'adsorbed' SO_4 adequately (Barrow, 1961).

Solutions which extract both water-soluble SO_4 and a portion of the 'adsorbed' SO_4 have been consistent and accurate indices of S availability (Barrow, 1966). Solutions containing P (19.1 $mmol \cdot L^{-1}$) as either potassium dihydrogen phosphate (KH_2PO_4) or calcium dihydrogen phosphate (CaH_2PO_4) are commonly used to estimate available S.

The latter extractant has been more popular because the divalent Ca cation does not cause clay or organic matter to disperse as will the monovalent K ion (Ensminger and Freney, 1966). Fox et al. (1964) found that KH_2PO_4 extracted slightly more S than did $Ca(H_2PO_4)_2$; the two extractants, however, were closely correlated (r = .958). In Wisconsin, six soil extractants were tested on 49 different soils for their effectiveness in predicting the yield and S uptake of alfalfa. Extracting solutions containing P (19.1 $mmol \cdot L^{-1}$) either as $Ca(H_2PO_4)_2 \cdot H_2O$ or as $Ca(H_2PO_4)_2 \cdot HOAc$, were the most effective, but these produced poor correlations with yield or plant S uptake (r = .500) (Hoeft et al., 1973).

Since organic matter can supply S to plants, several researchers have successfully used soil extractants which recover a portion of organic S in addition to the adsorbed and soluble SO_4. These include a 0.5 $mol \cdot L^{-1}$ sodium bicarbonate solution at pH 8.5 (Kilmer and Nearpass, 1960; Bardsley and Kilmer, 1963) and hot-water extraction (Fox et al., 1964).

In general, the total S or organic S fraction of the soil has been a poor indicator of S availability (International Fertilizer Development Center, 1979). This could be explained by the inability to obtain an accurate assessment of these sulfur fractions. Organic S fractions may be poor indicators of available S because organic S is not readily available and its mineralization rate is subject to considerable fluctuation.

Soil tests of soil S status are interpreted from two standpoints: (1) by correlation of relative yield with soil test S or

(2) by the detection of a soil test S value above which S response is unlikely. The value derived from the latter method is normally referred to as the 'critical' soil test level (International Fertilizer Development Center, 1979). Little research has been performed regarding the response of corn to S. The 'critical' level for this crop would be conservatively estimated to be 300 $\mu mol \cdot kg^{-1}$ of extractable soil S (Table II-2).

Determination of SO_4-S. Analytical techniques for S determination generally involve determination of SO_4-S because it is this form which is of interest in soil extracts and S in plant tissue is frequently oxidized to SO_4 during isolation. The most widely used methods for SO_4 determination are either colorimetric, turbidimetric, titrimetric, or gravimetric. Of these methods, titrimetry and gravimetry have been the least popular. Gravimetry normally involves the addition of barium chloride ($BaCl_2$) to a sample containing sulfate, resulting in a barium sulfate ($BaSO_4$) precipitate which is dried and weighed. Titrimetric procedures which have been applied to S analysis of plant and soils include barium chloride as titrant, acidiometric titration, barium chromate as titrant, and complexometric titrations. In general, these procedures are not widely used and are both time consuming and inaccurate (Beaton et al., 1968).

Popular colorimetric procedures for SO_4 determination include barium chloranilate and methylthymol blue. Sulfate can be measured by the amount of chloranilate ion that is formed when barium

Table II-2. 'Critical' Levels of Extractable Soil S, Tested by Various Methods, for Corn Response.

Extractant Used Plus Method of Sulfate Analysis	Sampling Depth	'Critical' Level of SO_4-S in Soil	Region	Reference
	cm	$\mu mol \cdot kg^{-1}$		
$Ca(H_2PO_4)_2$ 19.1 mmol $P \cdot L^{-1}$ in 2N acetic acid + Turbidimetric with Bactogel	0-25	97	Virginia	Reneau and Hawkins, 1980
KH_2PO_4 19.1 mmol $P \cdot L^{-1}$	0-15	125†	Western Nigeria	Kang and Osiname, 1976
$Ca(H_2PO_4)_2$ 19.1 mmol $P \cdot L^{-1}$	0-15	125		
in NH_4OAc + Turbidimetric	0-15	125		
$Ca(H_2PO_4)$ 19.1 mmol $P \cdot L^{-1}$ + Turbidimetric with gum arabic	n.a.	249	Nebraska	Fox et al., 1964

n.a. = Not available.

† = Critical levels were not established but were known to be greater than 125 $\mu mol \cdot kg^{-1}$.

chloranilate is added to a solution buffered at pH 4 and containing 50% ethyl alcohol (Bertolacini and Barney, 1957). The limit of detection is .60 $\mu mol \cdot L^{-1}$ SO_4-S when measured in the ultraviolet region (Bertolacini and Barney, 1958). Measurement of SO_4 in water extracts from both plant tissue and soils have been performed successfully with this method (Beaton et al., 1968). Johnson and Nishita (1952) used a colorimetric procedure which reduced SO_4 in solution to hydrogen sulfide. The hydrogen sulfide is measured colorimetricly as methylene blue. This procedure has been found to be accurate but requires specialized equipment and is time-consuming (Tabatabai and Bremner, 1970).

Turbidimetric procedures are probably the most popular method of SO_4 determination because they do not require expensive equipment and are rapid and reproducible (Quin and Woods, 1976). Most turbidimetric procedures for SO_4 are modifications of the procedure developed by Chesnin and Yien (1950). In this method a $BaSO_4$ precipitate is formed by the addition of $BaCl_2$ to a SO_4 solution. The major limitation of this procedure has been the instability of the $BaSO_4$ precipitant. This instability can be lessened by the addition of glycerol, gum acacia, or gelatin (Beaton et al., 1968), or Tween 80 (Quin and Woods, 1976). Reproducibility of this procedure is dependent upon uniform precipitation conditions of the $BaSO_4$ seeding suspension. These conditions include acid concentration, time and speed of stirring, and volume of the reaction flask (Beaton et al., 1968). Precision in timing and mixing can be increased in turbidimetric procedures by the use of an autoanalyzer. Problems with autoanalyzers

result from baseline drift and sample carry over. These limitations, however, have been largely overcome by improved washing solutions, and results comparable to manual procedures have been demonstrated (Lea and Wells, 1980).

Other successful methods for SO_4 determination include the indirect determination of SO_4 by barium absorption spectroscopy and potentiometric titration of SO_4 using a lead electrode. The former procedure has shown greater precision as compared with turbidimetric methods and is good for detecting low concentrations of SO_4 (Hue and Adams, 1979). Goertzen and Oster (1972) determined SO_4 in soil water extracts by using a lead electrode to indicate the solution potential change which occurs when $Pb(ClO_4)_2$ is added to a SO_4-containing solution. Sulfate is detectable in solutions containing as low as 250 $\mu mols \cdot L^{-1}$.

Total S determination in plant tissue. Common methods for the determination of total S in plant tissue include dry ashing in the presence of magnesium nitrate, wet ashing in the presence of nitric and perchloric acids, combustion in a bomb, and ignition in the presence of oxygen. An extensive literature review by Beaton et al. (1968) indicated that closed systems such as ignition in the presence of oxygen and combustion in a bomb were the best procedures for obtaining accurate and absolute values for S content. On the other hand wet and dry ashing procedures were acceptable when only relative values were needed. According to Johnson and Ulrich (1959) the wet ashing procedure is superior to the dry ashing procedure for S determination because of a greater recovery of S by the former procedure. As compared to dry ashing, the perchloric acid in wet ashing procedures

keeps the boiling point below 203°C resulting in less loss of S as SO_2. Randall and Spencer (1980) found that the oxygen flask combustion method by Iismaa (1959) was superior to nitric-perchloric acid procedures with and without a catalyst. Results indicated that compared to the combustion method the wet ashing procedures underestimated the organic sulfur compounds such as cysteine and methionine by as much as 15%. This was attributed to gaseous losses during digestion when nitric acid was being driven off. For determination of total S in plant tissue, Quin and Woods (1976) found nitric-perchloric acid procedures to be superior to other methods when speed, reproducibility, and economy were considered. Disadvantages of this procedure include the explosive nature of perchloric acid and the partial loss of S in the digestion step. According to literature reviewed by the International Fertilizer Development Center (1979), the most acceptable method of oxidizing organic S was a wet ash procedure using nitric-perchloric acid plus dichromate and metavanodate. This procedure, developed by Sansum and Robinson (1974), uses a color change to indicate the digestion endpoint.

Determination of atmospheric S. In laboratory conditions several researchers have shown that soils have a high capacity to absorb SO_2 (Abeles et al., 1971; Smith et al., 1973; Bremner and Banwart, 1976). Alway et al. (1937) estimated that on an equal surface area, soil would absorb 22% of the SO_2 absorbed by a lead peroxide candle. Because of its simplicity, the lead peroxide candle has been widely used to estimate SO_2 absorption by soils.

The use of the lead peroxide candle, however, for the measurement of atmospheric S has been suggested as unsatisfactory because of non-specificity, variable reactivity, and the dependence upon air movement and humidity (Killick, 1974).

Most methods for measuring the dry deposition of SO_2 on either soils or plants are based on the product of the dry deposition rate of SO_2 and ambient SO_2 concentration at the soil or plant surface (Garland, 1978). Deposition velocities on vegetative surfaces can be influenced by wind speed, atmospheric stability, height and structure of plant, and stomatal resistence. Dry deposition of SO_2 is obviously difficult to assess and little work has been performed in this area (Sprugel and Miller, 1980).

Sulfur dioxide can be accurately measured by commercial instruments. These instruments have limited usefulness because they are costly, require a power source to operate, and require daily or hourly attention (Killick, 1976). These problems are largely overcome by the use of manual procedures, of which, the most common method involves the fixation of SO_2 as disulfitomecurate followed by a colorimetric analysis (West and Gaeke, 1956).

Dry and wet deposition of SO_4 are additional ways atmospheric S can reach a crop system. Sulfate in the form of aerosols can be sampled on surfaces such as filters or impractor plates. Deposition velocities for SO_4 aerosols have been estimated to be considerably slower than SO_2. The lifetime of SO_4 in the atmosphere is dependent on the removal by rain while dry deposition is believed to be of little consequence (Garland, 1978).

Sulfur in precipitation is in the form of SO_4 and is derived from the absorption of SO_2 with subsequent oxidation and the absorption of particulate SO_4. Collection of rainwater in a non-corrosive container with subsequent measurement of SO_4 content is the most common method for assessing this source of S. Some researchers have used a 'discrete' wet and dry collector in which a sensor for precipitation is used, allowing only wet deposition to be collected (Volchok and Graveson, 1975).

CHAPTER III

MATERIALS AND METHODS

Nine location-years of experimentation was conducted throughout Tennessee to assess the influence of crop environment (principally 'available' soil S and atmospheric S inputs) on crop response to fertilizer S application.

Field Methods

The experiment was performed from 1980-82 at three locations within Tennessee: Ames Plantation, Grand Junction; the Tobacco Experiment Station, Greeneville; and the Plant Science Field Laboratory, Knoxville. The experimental arrangement at each location consisted of a randomized complete block design, replicated three times, with fertilizer treatments of 0, 17, 34, $kg \cdot ha^{-1}$ of S applied as K_2SO_4. The test crop, corn (Zea mays L., c.v. Pioneer 3147), was planted in plots which were eight rows wide by 15.2 meters long.

Corn was produced at each location in a given year using the prevailing management practices at each location. Management practices differed principally in row spacing, rate and source of N application, and method of weed control. Row spacing was consistent among years at Greeneville (76 cm) and at Knoxville (91 cm), while Grand Junction had a row spacing of 101 cm for 1980-81 and 76 cm for 1982. Nitrogen was applied at the various locations as follows: Grand Junction, 168 kg $N \cdot ha^{-1}$ as ammonium nitrate (NH_4NO_3) broadcast

at planting; Greeneville, 168 kg $N \cdot ha^{-1}$ as urea (1980-81) or NH_4NO_3 (1982) broadcast at planting; Knoxville, 100 kg $N \cdot ha^{-1}$ as NH_4NO_3 broadcast at planting followed by 34 kg $N \cdot ha^{-1}$ as NH_4NO_3 sidedressed when corn was 30 to 45 cm tall. The methods of weed control employed are summarized in Table III-1.

Fertilizers were applied each spring prior to planting. Nitrogen was broadcast over the entire plot area while P and K were applied uniformly by hand to individual plots to provide 67 and 84 $kg \cdot ha^{-1}$ of P and K, respectively. In all situations, P was applied as monocalcium phosphate, $Ca(H_2PO_4)_2$. In 1980 the P source had a grade of 0-46-0 and was essentially S-free, while in 1981 and 1982, 0-44-0 was used to supply P and may have contained as much as 2% S contamination (Platou and Irish, 1982).

Sulfur treatments were applied incidentally as K_2SO_4 with KCl being added to satisfy the balance of the K requirement. Soils, which were slightly acid at the outset of the experiment, were limed to >pH 6 in winter 1980-81 through broadcast application of agricultural limestone.

When possible, plant populations were maintained at approximately 51,900 plants ha^{-1}. However, in many cases unfavorable weather conditions caused the plant population to be considerably less (Table III-2).

Soil types at the various experimental locations were Loring silt loam (fine-silty, mixed, thermic Typic Fragiudalfs) at Grand Junction, and Sequatchie fine sandy loam (fine-loamy, siliceous, thermic Humic Hapludults) at Knoxville. At Greeneville, soils at

Table III-1. Herbicides Applied for Weed Control According to Year and Location.

Location	Year	Herbicide Treatment		
		Atrazine[†]	Butylate[‡]	Eradicane[§]
		----kg of active ingredient·ha^{-1}----		
Grand Junction	1980	1.7	3.8	--
	1981	1.7	3.8	--
	1982	1.8	--	6.1
Greeneville	1980	2.2	--	4.5
	1981	2.2	--	4.5
	1982	2.2	--	4.5
Knoxville	1980	2.2	--	4.5
	1981	2.2	--	4.5
	1982	--	--	5.0

[†]Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine).

[‡]Butylate (S-ethyldiisobutylthiocarbamate).

[§]Eradicane (a mixture of R-25788 N-N-diallyl-2,2-dichloro-acetamide and EPTC S-ethyldiprapylthiocarbamate).

Table III-2. Plant Population According to Year and Location.

Location	Year 1980	1981	1982
		Plants·ha^{-1}	
Grand Junction	50,400	51,900	51,900
Greeneville	40,800	43,900	41,500
Knoxville	41,300	55,100	53,400

the experimental site were largely Dewey silty clay loam (clayey, kaolinitic, thermic Typic Paleudults) with significant intrusions of a more eroded Dunmore silty clay loam (clayey, kaolinitic, thermic Typic Paleudults).

Soils were sampled yearly prior to spring planting and after fall harvest. Samples taken by plot to a 45-cm depth in 15-cm increments were air-dried, screened and stored in boxes until analyzed. No precautions were taken to limit potential S mineralization in stored samples.

Sulfur inputs from precipitation and dry particulate fallout were based on the collection and analysis of samples from a wet/dry deposition collector. Two of these collectors and an electronic rain gauge were placed adjacent to the experimental site at each location. Rainwater samples, representing the wet/dry deposition, and precipitation data were collected at intervals of approximately 30 days for the duration of the experiment. Immediately following sampling, rainwater was filtered through Whatman No. 42 filter paper and was stored frozen until analyzed for SO_4-S.

Ten ear leaves were randomly sampled at mid-silking from the two center rows of each plot annually at all locations. Leaf tissue ovendried at 60^{o}C was ground to pass a 1-mm mesh screen and stored in sealed plastic bags prior to analysis.

Grain was harvested from the two center rows of each plot at each location in October of each year. Grain samples were taken at harvest by shelling grain from a representative sample of ears from each plot. Samples were stored in plastic bags until analyzed for

moisture content after which the grain was oven-dried, ground, and stored as for leaf tissue. Field weights of grain were corrected to 15.5% moisture for summarization of yields.

Laboratory Methods

Leaf tissue was digested using a binary acid mixture (Johnson and Ulrich, 1959) in which .50 g samples were first digested overnight in HNO_3 and then digested in a 10:3 mixture of HNO_3-$HClO_4$. Total S of plant digests was determined using a modification of the turbidimetric procedure of Massoumi and Cornfield (1963) (Appendix A). Potassium, Ca, and Mg in leaf tissue digests were determined via atomic absorption/emmision spectroscopy and P via phosphomolybdic acid colorimetry (Jackson, 1958). Total N in leaf tissue was determined colorimetrically via the indophenol method following H_2SO_4 digestion (Thomas et al., 1967). Sulfur and N in grain was determined as described for leaf tissue.

'Available' soil S was extracted with KH_2PO_4 (19.1 mmol $P \cdot L^{-1}$; Ensminger, 1954) and measured by the barium chloranilate procedure (Bertolacini and Barney, 1958). Soil pH was measured by pH meter using a 1:1 soil-water mixture.

Sulfate concentration in the rainwater samples was measured indirectly using barium absorption spectroscopy (Hue and Adams, 1979).

Statistical Analyses

The data were subjected to analysis of variance with treatments combined across years and locations, and with locations nested within years (Snedecor and Cochran, 1967). The partioning of degrees

of freedom for this analysis and the significance of the various effects and their interactions are summarized in Appendix B. Treatment effects which were significant at $\alpha \leq .10$ were subjected to single degree of freedom comparisons to determine whether these data were best described as linear or quadratic effects. Where appropriate, regression models were employed to evaluate the relationships among selected factors. All statistical analyses were performed with the aid of the Statistical Analysis System (SAS Institute Inc., 1982).

CHAPTER IV

RESULTS AND DISCUSSION

Corn Yield and Nutrient Content

When data were analyzed over years and locations, only grain yield and N concentration of leaf tissue demonstrated significant effects with respect to S fertilization, and even these parameters were significant only at the $\alpha = .10$ level (Table IV-1). The overall effect of S fertilization was minimal as compared to the effects of years and locations within years. These data, and the fact that the S concentration of leaf and grain tissue were uninfluenced by S fertilization, suggest that S was not limiting for corn yield in this experiment.

Generally, grain yield plus leaf and grain nutrient content varied significantly between years. Exceptions were grain N concentration and the concentrations of leaf P and K as well as leaf N:S mole ratios (Table IV-1). The effect of years was expected since climatic conditions, and to some degree, management practices varied between years.

The effects of locations within years were significant for grain yield and for most of the nutrients which were measured (Table IV-1). This variation is largely explained by the different fertility and climatic conditions between locations as well as the interaction between locations and years.

Table IV-1. Mean Grain Yield and Leaf and Grain Nutrient Content as Affected by S Fertilization, Years, and Locations.

Variable	Yield	Nutrient Concentration of Grain			Nutrient Concentration of Leaves						
		S	N	N:S	S	N	N:S	Ca	Mg	K	P
	$Mg \cdot ha^{-1}$	$mmol \cdot kg^{-1}$		mole ratio	$mmol \cdot kg^{-1}$		mole ratio	$mmol \cdot kg^{-1}$			
Rate of S Fertilization, $kg \cdot ha^{-1}$											
0	7.49	25.2	1010	40.9	38.8	1560	41.8	113	100	428	90.9
17	7.51	23.9	1000	45.2	40.5	1630	41.5	112	94.4	428	91.7
34	7.21	24.4	978	41.0	42.6	1530	37.2	110	93.2	420	88.8
Mean Square	.1392	11.21	7120	158.1	118.0	56120	194.2	.001394	.002569	.003713	.0003698
Significance of F Test†	L+	NS	NS	NS	NS	Q+	NS	NS	NS	NS	NS
Years											
80	5.24	28.3	1120	40.0	40.1	1530	39.3	121	112	399	88.4
81	9.03	23.2	873	38.7	45.4	1690	38.0	112	92.7	440	92.9
82	7.93	22.1	998	48.4	36.3	1500	43.1	101	83.0	438	90.40
Mean Square	18.71	293.2	398200	753.4	556.3	280500	200	.04321	.03564	.2246	.001184
Significance of F Test‡	**	**	NS	*	**	**	NS	**	**	NS	NS
Locations (Years)											
Grand Junction	8.08	23.9	947	42.2	38.2	1540	41.8	105	93.6	433	88.1
Knoxville	7.36	22.5	963	44.9	43.6	1650	39.3	105	73.6	420	19.5
Greeneville	6.77	27.2	1080	40.1	40.1	1530	39.1	124	120	423	83.1
Mean Square	4.087	75.34	53120	121.6	101.0	148200	119.2	.02591	.03292	.04472	.001143
Significance of F Test‡	**	*	**	NS	NS	**	NS	*	**	NS	**

†Sulfur fertilization effects were not significant (NS) or significant at the 10% (+) level, and were either linear (L) or quadratic (Q).

‡Years or locations (years) were not significant (NS) or were significant at the 5% (*) or 1% (**) level.

The average concentration of total S in leaf tissue varied between locations: Grand Junction, 38.2 $mmol \cdot kg^{-1}$; Knoxville, 43.6 $mmol \cdot kg^{-1}$; and Greeneville, 40.1 $mmol \cdot kg^{-1}$. Since a S response has not been identified, critical levels for total S in corn ear leaves would be considered to be below these values. On the other hand, these values were below the reported critical levels for total S in corn leaf tissue under field conditions (Range: 43.7 to 74.9 $mmol \cdot kg^{-1}$, Table II-1, p. 11) which suggests that these plants might be S-deficient. This appears to be contradictory since yield response to S has not been identified. An explanation for this contradiction could be the extreme variability in analytical and sampling techniques utilized by various researchers which can cause a wide range in reported values for critical S levels in plants (Sansam and Robinson, 1974). It is possible the procedure used herein for determination of total S in plant tissue resulted in some S loss in digestion, resulting in lower total S values than those reported elsewhere.

The mean values for the N:S mole ratios of each location ranged from 37 to 43 (Table IV-1), which is the upper range of the critical levels reported for this crop (mole ratios of 27-43, Table II-1, p. 11). These N:S ratios would be expected to be in this upper range, since the total S values were low as compared to reported values.

Relationship of Relative Yield and Leaf-N Concentration to the Nutrient Composition of the Leaf

Linear regression models were used to compare relative yield with leaf S concentration by location. Grand Junction was the only location which showed a significant relationship between these variables and it was weakly regressed (Appendix B).

Stepwise mutiple regression was used to identify relationships between leaf nutrient composition and relative yield or leaf-N concentration. Of the plant factors measured, N and K concentration of the leaf accounted for 98% and 0.5% respectively, of the variation in relative yield while additional plant factors had no influence on the model (Appendix B). On the other hand, variability in leaf-N concentration was accounted for by P and K concentrations of the leaf (98.5 and 0.3%, respectively; Appendix B), while additional factors had no influence.

The above models failed to support the significant effects of S-fertilization on yield and leaf-N concentration which were found in the experimental model (Table IV-1). This could be explained by the relatively low level of significance obtained for this relationship ($P \geq 90\%$). As the level of significance becomes lower, there is a greater possibility that chance alone has contributed to the observed variability. Since these models failed to identify either a significant relationship or a strong relationship between leaf-S concentration and relative yield or leaf-N concentration, they are supporting the previous conclusion that S is not limiting for corn yield in this experiment.

Soil Extractable SO_4-S

The extractable SO_4-S in these soils did not differ relative to the level of S-fertilization or years (Table IV-2), which suggests that the SO_4 added by the fertilizer is not being retained by the soil in an extractable form. If these soils were capable of retaining more extractable SO_4, then S-fertilization would be expected to cause significant differences in these values. Therefore the portion of these soils which were sampled (upper 45 cm) may be at their maximum retention level for extractable SO_4. In this case, SO_4 added by the fertilizer would be subject to leaching, crop absorption, or retention by the soil in a non-extractable S form. Immobilization of SO_4 by soil microbes into organic forms would be an example of the latter.

At Grand Junction and Greeneville the soil extractable SO_4-S was relatively high and increased considerably with depth (Table IV-2). Sulfate retention of soils is known to increase with the amount of clay and Fe- and Al-hydroxides, and the hydrogen ion concentration of the soil (Harward and Reisenauer, 1966). The soils at Greeneville (Dewey silty clay loam and Dunmore silty clay loam) are typically described as having clay textures (kaolinitic type) in their subsurface horizons (Edwards et al., 1958), which could explain the high retention of SO_4 in these soils. In contrast, the soil at Grand Junction (Loring silt loam) typically contains a silt loam texture and a fragipan in the subsurface horizons (Flowers et al., 1954). Although it is unclear why large amounts of SO_4 were retained

Table IV-2. Mean Soil Sulfur and pH as Affected by Depth, Sulfur Fertilization, Years, and Locations.

Variable	Sampling Depth 0-15 (cm) pH	0-15 (cm) Soil SO_4-S	15-30 (cm) pH	15-30 (cm) Soil SO_4-S	30-45 (cm) pH	30-45 (cm) Soil SO_4-S
		$\mu mol \cdot kg^{-1}$		$mol \cdot kg^{-1}$		$\mu mol \cdot kg^{-1}$
Rate of S Fertilization $kg \cdot ha^{-1}$						
0	5.5	290	5.6	510	5.5	1280
17	5.5	420	5.6	560	5.4	1360
34	5.4	410	5.5	590	5.4	1050
Mean Square	.06456	249900	.05346	36090	.03309	312000
Significance of F Test†	NS	NS	NS	NS	NS	NS
Years						
80	5.3	340	5.5	610	5.4	1290
81	5.5	330	5.5	510	5.3	1250
82	5.6	450	5.7	540	5.6	1140
Mean Square	1.246	144300	.1323	36610	.1075	4944
Significance of F Test†	**	NS	NS	NS	*	NS
Location (Years)						
Grand Junction	5.7	410	5.5	840	4.9	1930
Knoxville	5.5	240	5.6	230	5.8	240
Greeneville	5.2	470	5.6	600	5.6	1520
Mean Square	.6654	436900	.2497	1477000	2.476	8190000
Significance of F Test†	**	NS	+	**	**	**

†Sulfur fertilization, years, and locations (years) were not significant (NS), or were significant at the 10% (+) or 5% (*) or 1% (**) level.

by this soil type, low permeability due to the fragipan may have resulted in higher retention of Fe- and Al-hydroxides than would normally be expected. Also, a low pH (4.9) in the 30-45 cm depth could help explain this large amount of SO_4 retention.

In contrast to the soils at Greeneville and Grand Junction, the soil at Knoxville (Sequatchie fine sandy loam) had a low level of extractable SO_4-S which varied little with depth (Table IV-2). This alluvial soil typically contains a loam texture in subsurface horizons and is well drained and moderately permeable (Roberts et al., 1955). The low level of extractable SO_4-S may be due to the low clay content as well as the high leaching potential of this soil.

The SO_4-S extracted from the upper 45 cm of these soils (subsequently referred to as the pooled SO_4-S) was determined by summing the extractable SO_4-S for each depth and converting from units of $\mu mol \cdot kg^{-1}$ to units of $kg \cdot ha$ (assuming uniform bulk density of 1.4 $Mg \cdot m^{-3}$ between depths and locations). The average pooled SO_4-S of the soil at Knoxville (49.5 $kg \cdot ha^{-1}$) was considerably lower than the value at Greeneville (177.0 $kg \cdot ha^{-1}$) and Grand Junction (222.3 $kg \cdot ha^{-1}$), indicating its greater potential for S deficiency.

Soil samples were allowed to dry, which is known to release some of the S bound to the organic fraction (Williams, 1967), therefore, these extractable SO_4-S values are probably representing some of the S released by organic matter. The soils in this research contained approximately 1% organic matter, which could release 3.6 $kg \cdot ha^{-1} yr^{-1}$ of SO_4-S (Terman, 1978). The average extractable S level of the 0-15 cm depth for each location was as follows: Grand

Junction, 410 $\mu mol \cdot kg^{-1}$; Knoxville, 240 $\mu mol \cdot kg^{-1}$; and Greeneville, 470 $\mu mol \cdot kg^{-1}$. In comparison with reported 'critical' levels of surface horizons for corn (Table II-2, p. 17) only the soils at the Knoxville location appear to be potentially S deficient.

As expected, pH was not affected by S fertilization (Table IV-2). Variation in soil pH between years for the 0-15 cm depth was expected since all soils were limed in 1981 (Table IV-2). The variation in pH between years at the 30-45 cm depth is most likely a consequence of slight variations in sampling and analysis rather than an effect of years.

The Relationship of Relative Yield and Leaf-S Concentration to Soil Extractable S

To further study the relationship of soil SO_4 and the sufficiency of S for corn growth, the relationships between the following sets of variables were tested with linear and quadratic models: leaf-S concentration and relative yield versus soil extractable SO_4-S ($\mu mol \cdot kg^{-1}$) of the 0-15 cm depth and the pooled SO_4-S value ($kg \cdot ha^{-1}$). These variables were tested by locations and across locations, and only three models were significant (Appendix B). These models (none of which had an $R^2 > 0.4$) were not strongly regressed. Although these models indicate a trend of increased relative yield and leaf S concentration with increasing soil S, they are not strong enough to support such a conclusion. On the other hand, the extractable S may not be representing the available S supply. In this case, the extractable S would not be expected to

be strongly regressed on yield or on plant S concentration. Recent work by Reneau (personal communication, 1983) suggests that acid, monocalcium phosphate-extractable SO_4 is related to corn yield increases on coarse textured soils of Virginia when S was deficient (R^2 = .62). Work by Grant and Rowell (1978) demonstrated a significant relationship between KH_2PO_4-extractable SO_4 and S concentration of corn leaf tissue on a sandy loam soil (R^2 = .78). From these results, it appears that the extractable SO_4-S may be somewhat indicative of the 'availability' of S to corn, although further investigation of this extractant on soils with silt loam surface textures will be needed in order to ascertain its effectiveness as a soil test extractant for Tennessee soils.

CHAPTER V

GENERAL DISCUSSION

Estimated Gains and Losses of S in these Cropping Systems

When considering those plots which received no S treatment, the known S inputs of each experimental site were greater than the S which was lost in grain harvest (Table V-1). The average amount of S leaving the agricultural system by grain harvest for all locations was 5.9 $kg \cdot ha^{-1} yr^{-1}$. On the other hand, an average of 18.3 $kg \cdot ha^{-1} yr^{-1}$ of S was being brought into the system by wet/dry deposition and incedental sources, leaving an average excess of 12.4 $kg \cdot ha^{-1} yr^{-1}$ of S (Table V-1). The ability of this excess to supply S to the crop system is not clear, because it is not known how much S is being lost by leaching or is being fixed in unavailable forms in the upper soil profile. The loss of S from agricultural ecosystems has been measured by lysimeters and reported values range from as low as 2.2 $kg \cdot ha^{-1} yr^{-1}$ to as high as 91.8 $kg \cdot ha^{-1} yr^{-1}$ (Appendix B). A mean value for this data, 39 $kg \cdot ha^{-1} yr^{-1}$, could be used as a rough estimate for S lost to leaching under cropping conditions; but because of the wide range in reported values, this mean value must be used with caution when considering specific situations. This variation could be explained by different soil properties and types of lysimeters which were used for the leaching determination. If this mean value of 39 $kg \cdot ha^{-1} yr^{-1}$ was used to estimate the loss of S by leaching in

Table V-1. Pooled Soil S Values[†] and an Estimation of Gains and Losses of S from Those Plots Receiving No S Fertilization.

Location	Pooled Soil S	Wet/Dry[‡] Deposition	Sulfur[§] Impurities in Herbicides	Sulfur[¶] Inpurities in Fertilizers	Total[#] Known S Input	Sulfur Removed by Grain Harvest	Net[††] Gain of S in Cropping Systems
	$kg \cdot ha^{-1} yr^{-1}$						
Grand Junction	222.3	16.1	.7	1.5	18.3	6.6	11.7
Knoxville	49.5	18.8	.9	1.5	21.2	5.2	16.0
Greeneville	177.0	13.2	.8	1.5	15.4	5.8	9.6
MEAN	--	16.0	.8	1.5	18.3	5.9	12.4

[†]Sum of extractable SO_4-S in each depth (0 through 45 cm) expressed as $kg \cdot ha^{-1}$ assuming bulk density = 1.4 $Mg \cdot m^{-3}$.

[‡]Sum of monthly averages.

[§]Eradicane and butylate.

[¶]Concentrated superphosphates may contain 1.5% S (Platou and Irish, 1982).

[#]Excludes SO_2 absorbed by plant.

[††]Excludes S lost by leaching.

this study, then the average amount of known inputs (18.3 $kg \cdot ha^{-1}yr^{-1}$) would not be able to compensate for the S lost by leaching. It is therefore unlikely that this mean value is representative of the leaching losses of S in these soil systems.

The amount of S coming into these cropping systems by absorption of atmospheric SO_2 via leaf stomata is also unknown. It is known, however, that under greenhouse conditions a large percentage of a plant's S requirement can be obtained from this S source (Faller, 1971).

The most plausible explanation for the lack of a S response is that the known S inputs (principally wet/dry deposition of S) are compensating for the amount of S lost by grain harvest and by leaching. This conclusion is not clear, however, since it is unknown how much S is lost by leaching as well as how much S is gained by leaf absorption of SO_2.

If the S inputs are able to compensate for the outgo of S, it would be likely that the upper 45 cm of these soils are at or near their maximum retention level for the extractable SO_4-S. This reasoning could explain why the extractable SO_4-S was uninfluenced by S fertilization and by year.

Sulfur Status of the Cropping System at Knoxville

Since the soils at the experimental site at Knoxville have a low pooled SO_4-S value and an extractable SO_4-S level which falls into a reported 'critical range,' it could be considered a

potentially S-deficient soil. For this reason the sulfur status of this location demanded a more detailed study.

The soils at Knoxville consisted of a Sequatchie fine sandy loam. This soil typically contains a loam texture throughout the soil profile (Roberts et al., 1955). An illuvial horizon is present, but contains only a small percentage of clay (≃ 14%) and therefore has little capacity to retain large amounts of S. The 30-45 cm depth of this soil, which includes part of the illuvial horizon, only showed a small increase in extractable S (15 $\mu mol \cdot kg^{-1}$; Table IV-2). Since this soil is not capable of retaining large amounts of S and the extractable SO_4 level was not affected by S treatments, it is highly possible that the soil is retaining the maximum amount of SO_4 possible.

At Knoxville the total amount of S input, 21.2 $kg \cdot ha^{-1}yr^{-1}$, minus the S lost by crop removal, 5.2 $kg \cdot ha^{-1}$, would leave an excess of 16 $kg \cdot ha^{-1}yr^{-1}$ of S (Figure IV-1). During the growing season for corn (May-October) only 6.1 $kg \cdot ha^{-1}yr^{-1}$ of S would be brought into the system by wet/dry deposition making a total known S input of 8.5 $kg \cdot ha^{-1}$. If this soil system is at its maximum retention level for SO_4, then the wet/dry deposition for the eight months during which the corn is not grown would be subject to leaching or would be retained in some unavailable form. If S is retained in organic matter, and mineralization of S occurs at the same rate as predicted for N, then these soils (which contain approximately 1% organic matter) would release only 3.6 $kg \cdot ha^{-1}yr^{-1}$ of S (Terman, 1978). Equally low levels of S release would be expected if S is retained

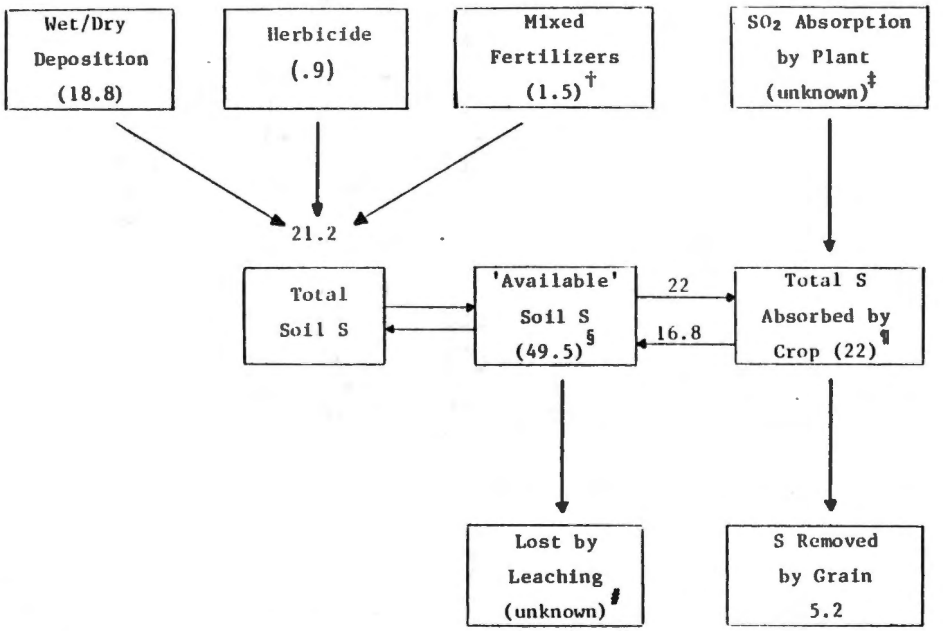

Figure IV-1. Sulfur Status of the Cropping System at Knoxville ($kg \cdot ha^{-1} yr^{-1}$).

†Estimated to be 1.5% S impurities in concentrated superphosphates (Platou and Irish, 1982).

‡Largely unknown value; possible range could be minimal to 10 $kg \cdot ha^{-1} yr^{-1}$ (Fox, 1976 and Kelly, personal communication).

§Represents the extractable SO_4-S of the upper 45 cm of the soil assuming bulk density = 1.4 $Mg \cdot m^{-3}$.

¶Estimated from Terman, 1978 assuming a grain yield of 7.4 $kg \cdot ha^{-1}$.

#Largely unknown value; estimates via lysimeters range from 2.2 to 91.8 $kg \cdot ha^{-1} yr^{-1}$ (Appendix, Table A-3).

in these systems as Al-hydroxy sulfate mineral (Wolt and Adams, 1979). Average corn yield at Knoxville (7.4 $Mg \cdot ha^{-1}$) requires about 22 $kg \cdot ha^{-1}$ of S for normal growth, of which 5.2 $kg \cdot ha^{-1}$ is lost in grain harvest and 16.8 $kg \cdot ha^{-1}$ would be retained in organic residues (Figure IV-1). Total known S inputs during the growing season for corn, 8.5 $kg \cdot ha^{-1}$, could partially supply the demand for S by this crop.

If the extractable soil SO_4 is representing the available S supply, then the S pool (49.5 $kg \cdot ha^{-1}$; Table IV-3) could easily meet this crop's demand for S (22 $kg \cdot ha^{-1}$). Because the extractable SO_4 level is approximately twice the amount of S needed by this crop, it seems possible that this soil is capable of supplying the crop demand for S.

In contrast to the results from the experimental site at Knoxville, several researchers have reported S deficiencies in corn on soils of a loamy sand texture having extractable SO_4-S levels which were slightly higher than those found at Knoxville (Fox et al., 1964; Suarez and Jones, 1982). This could be explained by the large contribution of S to the cropping system at Knoxville via wet/dry deposition (18.8 $kg \cdot ha^{-1} yr^{-1}$) which could be compensating for the low level of SO_4 in this soil, thus preventing a S response. Another explanation could be the fact that the texture of the soil at Knoxville (sandy loam) is less coarse than the soils mentioned above, and therefore may be retaining more available SO_4 in the subsurface horizons.

Future Trends Affecting the S Status of a Cropping System

If the S inputs into a soil system, containing small amounts of available S, were significantly reduced or if the crop demand for S was increased, then the likelihood of a S deficiency would also increase. Presently the U.S. E.P.A. is enforcing the reduction of SO_2 emissions, which could significantly change the atmospheric contribution to the available S supply of a crop system. The evidence indicates that in modern times wet-dry deposition of S has been relatively constant with time in the state of Tennessee (Appendix B). On a seasonal and yearly basis, wet/dry deposition of S was found to fluctuate considerably at the individual sites of this experiment (Appendix C). No seasonal or yearly patterns were identifiable in the relatively short term of this investigation. The present trend toward the use of high analysis fertilizers and organic pesticides, both of which contain little or no S, is another factor which can affect the S input into a crop system. At the same time, higher crop yields resulting from improved farming practices and increased fertilizer use, are increasing the crop demand for S. It is evident from this discussion that these factors must be evaluated from time to time in order to assess the potential for S deficiency in a crop system.

CHAPTER VI

SUMMARY

Nine location-years of experimentation were conducted throughout Tennessee to assess the influence of S fertilization and atmospheric S inputs upon extractable soil S and corn yield and S concentration.

When data were analyzed over years and locations, only grain yield and N concentration of the leaf tissue demonstrated significant effects with respect to S fertilization (α = .10 level). The overall effect of S fertilization, however, was minimal when compared to years and locations within years, suggesting that S was not limiting for corn yield in this experiment. This conclusion was also supported by regression models which indicated that of the plant factors measured, yield was largely a function of leaf-N concentration, while leaf-N concentration was largely a function of leaf-P concentration (R^2 = .980 and .985, respectively).

Additionally, S fertilization and years had no affect on extractable soil S while locations within years significantly affected this value. The soil at Knoxville was considerably lower in extractable S than soils at either Grand Junction or Greeneville and therefore had a greater potential for S deficiency. Regression models failed to identify a strong relationship between the extractable SO_4 level and yield or leaf-S concentration ($R^2 \leq .4$). An average of 16 $kg \cdot ha^{-1} yr^{-1}$ of S was contributed to these cropping

systems via wet/dry deposition. It is likely that atmospheric input may be compensating for the S removed by harvested grain and lost by leaching, thus preventing a corn response to S fertilization at these locations.

A more complete understanding of the S status of these cropping systems could be accomplished with the clarification of the following factors: the degree to which the soil extractable SO_4 is related to the available S supply; the ability of this crop to utilize atmospheric SO_2 for its S requirement, and the amount of S which is lost from these systems via leaching.

LITERATURE CITED

LITERATURE CITED

Abeles, F. B., L. E. Craker, L. E. Forrence, and G. R. Leather. 1971. Fate of air pollutants: Removal of ethylene, sulfur dioxide, and nitrogen dioxide by soil. Science. 173:914-916.

Adams, Fred and Zahir Rawajfih. 1977. Basaluminite and alunite: a possible cause of sulfate retention by acid soils. Soil Sci. Soc. Am. J. 41:686-692.

Allaway, W. H. and J. F. Thompson. 1966. Sulfur in the nutrition of plants and animals. Soil Sci. 101:240-247.

Alway, F. J., A. W. Marsh, and W. J. Methley. 1937. Sufficiency of atmospheric sulfur for maximum crop yields. Soil Sci. Soc. Am. Proc. 2:229-238.

Bardsley, C. D. and V. J. Kilmer. 1963. Sulfur supply of soils and crop yields in the Southeastern United States. Soil Sci. Soc. Am. Proc. 27:197-199.

Barrow, N. J. 1961. Studies on mineralization of sulfur from soil organic matter. Australian J. Agr. Res. 12:306-319.

Barrow, N. J. 1966. Studies on extraction and on availability to plants on adsorbed plus soluble sulfate. Soil Sci. 104:242-249.

Beaton, J. D., G. R. Burns, and J. Platou. 1968. Determination of sulfur in soils and plant material. The Sulfur Institute Tech. Bull. 14.

Bertolacini, R. J. and J. E. Barney. 1957. Colorimetric determination of sulfate with barium chloranilate. Analytical Chem. 29:281-283.

Bertolacini, R. J. and J. E. Barney. 1958. Ultraviolet spectrophotometric determination of sulfate, chloride, and fluoride with chloranilic acid. Analytical Chem. 30:202-205.

Bettany, J. R., J. W. B. Stewart, and E. H. Halstead. 1974. Assessment of the available soil sulfur in an ^{35}S growth chamber experiment. Can. J. Soil Sci. 54:390-315.

Bohn, Hinrich L., Brian L. McNeal, and George A. O'Conner. 1979. Soil Chemistry. John Wiley and Sons, N. Y.

Bremner, J. M. and W. L. Banwart. 1976. Sorption of sulfur gases by soils. Soil Biol. Biochem. 8:79-83.

Buckman, H. O., and N. C. Brady. 1969. The nature and properties of soils. 7th Ed. The Macmillan Co., New York.

Chang, M. L. and G. W. Thomas. 1963. A suggested mechanism for sulfate adsorption by soils. Soil Sci. Soc. Am. Proc. 27-281-283.

Chao, T. T., M. E. Harward, and S. C. Fang. 1962. Soil constituents and properties in the adsorption of sulfate ions. Soil Sci. 94:276-283.

Chao, T. T., M. E. Harward, and S. C. Fang. 1963. Cationic effects on sulfate adsorption by soils. Soil Sci. Soc. Am. Proc. 27:35-38.

Chesnin, Leon and C. H. Yien. 1950. Turbidimetric determination of available sulfates. Soil Sci. Soc. Am. Proc. 15:149-151.

Daigger, L. A. and R. L. Fox. 1971. Nitrogen and sulfur nutrition of sweet corn in relation to fertilization and water composition. Agron. J. 63:729-730.

Driebelbis, F. R. 1947. Some plant nutrient losses in gravitational water from monolith lysimeters at Coshocton, Ohio. Soil Sci. Soc. Am. Proc. 11:182-188.

Edwards, Max J., Ben L. Matzek, F. R. Austin, S. R. Bacon, A. C. Anderson, and Robert Wildermath. 1958. Soil Survey of Green County, Tennessee. U. S. Government Printing Office, Washington, D. C.

Elkins, D. M. and L. E. Ensminger. 1971. Effect of soil pH on the availability of adsorbed sulfate. Soil Sci. Soc. Am. Proc. 35:931-934.

Ensminger, L. E. 1954. Some factors affecting the adsorption of sulfate by Alabama soils. Soil Sci. Soc. Am. Proc. 18:259-364.

Ensminger, L. E. 1958. Sulfur in relation to soil fertility. Auburn (AL) Agr. Expt. Sta. Bull. 312.

Ensminger, L. E. and J. R. Freney. 1966. Diagnostic techniques for determining sulfur deficiencies in crops and soils. Soil Sci. 101:283-290.

Evans, L. T. 1975. Sulfur in Agriculture. p. 3-8. K. D. McIachlan (ed.). Sulfur in Australaian agriculture. Sydeny University Press. Sydney, Australia.

Faller, N. 1971. Effects of atmospheric SO_2 on plants. Sulfur Institute J. 6(4):5-7.

Flowers, Robbie L., Joseph A. Phillips, Wiley C. Mangrum, Roy K. Moore, and Lewis A. Dungan. 1954. Soil Survey of Fayette County, Tennessee. U. S. Government Printing Office, Washington, D. C.

Fox, D. G. 1976. Modeling atmospheric effects--an assessment of the problem. Water, Air, and Soil Pollut. 6:173-198.

Fox, R. L., R. A. Olson, and H. F. Rhoades. 1964. Evaluating the sulfur status of soils by plant and soil tests. Soil Sci. Soc. Am. Proc. 28:243-246.

Freney, J. R. 1961. Some observations on the nature of organic sulfur compounds in soil. Aust. J. Agr. Res. 12:424-432.

Freney, J. R., G. E. Melville, and C. H. Williams. 1971. Organic sulfur fractions labelled by addition of ^{35}S-sulfate to soil. Soil Biol. Biochem. 3:133-41.

Freney, J. R., G. E. Melville, and C. H. Williams. 1975. Soil organic fractions as sources of plant available sulfur. Soil Biol. Biochem. 7:217-21.

Freney, J. R. and F. J. Stevenson. 1966. Organic sulfur transformations in soils. Soil Sci. 101:307-316.

Freney, J. R. and R. J. Swaby. 1975. Sulfur transformation in soils. p. 31-39. In K. D. McIachlan (ed), Sulfur in Australian agriculture. Sydney University Press. Sydney, Australia.

Gaines, T. P. and S. C. Phatak. 1982. Sulfur fertilization effects on the constancy of the protein N:S ratio in low and high sulfur accumulating crops. Agron. J. 74:415-418.

Garland, J. A. 1978. Dry and wet removal of sulfur from the atmosphere. Atmos. Environment 12:349-361.

Goertzen, J. O., and J. D. Oster. 1972. Potentiometric titration of sulfate in water and soil extracts using a lead electrode. Soil Sci. Soc. Am. Proc. 36:691-693.

Graham, R. P. and A. W. Thomas. 1947. The reactivity of hydrous alumina towards acids. Am. Chem. Soc. 69:816-821.

Grant, P. M. and A. W. G. Rowell. 1978. The distribution of sulfate and total sulfur in maize plants (Zea mays L.) in relation to the diagnosis of deficiency. Rhod. J. Agr. Res. 16:43-59.

Harward, M. E., T. T. Chao, and S. C. Fang. 1962. The sulfur status and sulfur supplying power of Oregon soils. Agron. J. 54:101-106.

Harward, M. E. and H. M. Reisenauer. 1966. Reactions and movements of inorganic soil sulfur. Soil Sci. 101:326-335.

Hoeft, R. G., L. M. Walsh, and D. R. Keeney. 1973. Evaluation of various extractants for available soil sulfur. Soil Sci. Soc. Am. Proc. 37:401-404.

Hue, N. V. and Fred Adams. 1979. Indirect determination of mircograms of sulfate by barium absorption spectroscopy. Commun. Soil Sci. Pl. Anal. 10:841-851.

Iismaa, O. 1959. Micro determination of sulfur in plant material. J. Aust. Inst. Agr. Sci. 25:136-138.

International Fertilizer Development Center. 1979. Sulfur in the tropics. IFDC Tech. Bull. T-12.

Jackson, M. L. 1958. Soil chemical analysis. Prentice Hall, Inc. Englewood Cliffs, N. J.

Joffe, J. S. 1933. Lysimeter studies: II. Soil Sci. 35:239-257.

Johnson, C. M. and Hideo Nishita. 1952. Microestimation of sulfur. Anal. Chem. 24:736-742.

Johnson, C. M. and A. Ulrich. 1959. Analytical methods for use in plant analysis. Calif. Agr. Exp. Sta. Bull. 766.

Johnson, E. M. 1924. Sulfur in rainfall in Kentucky. Am. Soc. Agron. J. 16:353-356.

Jones, H. C. 1974. Pre-operational atmospheric monitoring in the Cumberland Steam Plant area: The pH and sulfate content of precipitation. T.V.A. Report E-EB-74-1.

Jordan, H. V. 1964. Sulfur as a plant nutrient in the Southern United States. U.S.D.A. Tech. Bull. 1297.

Jordan, H. V., C. E. Bardsley, L. E. Ensminger, and J. A. Lutz. 1959. Sulfur content of rainwater and atmosphere in southern states as related to crop needs. U.S.D.A. Tech. Bull. 1196.

Kamprath, E. J., W. L. Nelson, and J. W. Fitts. 1956. The effect of pH, sulfate and phosphate concentrations on the adsorption of sulfate by soils. Soil Sci. Soc. Am. Proc. 20:463-466.

Kamprath, E. J., W. L. Nelson, and J. W. Fitts. 1957. Sulfur removed from soils in field crops. Agron. J. 49:289-293.

Kang, B. T. and O. A. Osiname. 1976. Sulfur response of maize in Western Nigeria. Agron. J. 68:333-336.

Killick, Colin M. 1976. Test of a permeating sampling device for integrated sulfur dioxide concentrations in ambient air. Envir. Sci. Tech. 10:473-476.

Kilmer, V. J., Orville E. Hays, and J. Muchenhirn. 1944. Plant nutrient and water losses from Fayette silt loam as measured by monolith lysimeter. Agron. J. 36:249-263.

Kilmer, Victor J. and D. C. Nearpass. 1960. The determination of available sulfur in soils. Soil Sci. Soc. Am. Proc. 24:337-340.

Laurence, J. A. 1979. Response of maize and wheat to sulfur dioxide. Plt. Disease Rept. 63:468-471.

Lea, R. and C. G. Wells. 1980. Determination of extractable sulfate and total sulfur from plant and soil material by an auto-analyzer. Commun. Soil Sci. Pl. Anal. 11:507-516.

Lipman, J. G. and A. B. Conybeare. 1936. Preliminary notes on the inventory and balance sheet of plant nutrients in the United States. New Jersey Agr. Expt. Sta. Bull. 607.

Lyon, T. L. and J. S. Bizzell. 1936. Lysimeter experiments: IV. Cornell Univ., Agr. Expt. Sta. Memoir. 194.

MacIntire, W. H., W. M. Shaw, and B. Robinson. 1941. Influence of limestone and dolomite upon sulfate retention from annual additions of potassium sulfate. Soil Sci. 51:73-84.

MacIntire, W. H. and J. B. Young. 1923. Sulfur, calcium, magnesium and potassium content and reaction of rainfall at different points in Tennessee. Soil Sci. 15:205-227.

McLachlan, K. D. and D. G. DeMarco. 1975. Changes in soil sulfur fractions with fertilizer additions and cropping treatments. Aust. J. Soil Res. 13:169-176.

McLaren, R. G. and R. S. Swift. 1977. Changes in soil organic sulfur fractions due to the long term cultivation of soil. Soil Sci. 28:445-453.

Massoumi, A. and A. H. Cornfield. 1963. A rapid method for determining sulfate in water extracts of soils. Analyst 88:321-322.

Mehlich, A. 1964. Influence of sorbed hydroxyl and sulfate on neutralization of soil acidity. Soil Sci. Soc. Am. Proc. 28:492-496.

Murdock, Lloyd W. and Jane F. Lund. 1979. Corn response to sulfur on Coastal Plain soils. Sulfur in Agriculture. 3:4-11.

Nelson, L. E. 1964. Status and transformation of sulfur in Mississippi soils. Soil Sci. 97:300-306.

Olsen, R. A. 1957. Absorption of sulfur dioxide from the atmosphere by cotton plants. Soil Sci. 84:107-111.

Platou, J. S. and Roberta Irish. 1982. The fourth major nutrient. The Sulfur Institute, Washington, D. C. p. 31.

Quin, B. F. and P. H. Woods. 1976. Rapid manual determination of sulfur and phosphorus in plant material. Commun. Soil Sci. Pl. Anal. 7:415-426.

Randall, P. J. and K. Spencer. 1980. Sulfur content of plant material: A comparison of methods of oxidation prior to determination. Commun. Soil Sci. Pl. Anal. 11:257-266.

Reneau, R. B. and G. W. Hawkins. 1980. Corn and soybeans respond to sulfur in Virginia. Sulfur in Agriculture. 4:7-11.

Roberts, Wallace, B. C. Nichols, J. N. Odom, M. H. Gallatin, L. E. Odom, and T. E. Beesley. 1955. Soil Survey of Knox County, Tennessee. U. S. Government Printing Office, Washington, D. C.

SAS Institute Inc. 1982. SAS User's Guide: Statistics, 1982 Ed. Alice A. Ray (ed.). SAS Institute, Inc. Cary, N. C.

Sansum, L. L. and J. B. D. Robinson. 1974. Wet digestion, manual and automated analysis of total sulfur in plant material. Commun. Soil Sci. Pl. Anal. 5:365-383.

Shriner, D. S. and G. S. Henderson. 1978. Sulfur distribution and cycling in a deciduous forest watershed. J. Environ. Quality 7:392-396.

Siman, G. and S. L. Jansson. 1976. Sulfur exchange between soil and atmosphere, with special attention to sulfur release directly to the atmosphere. 1.) Formation of gaseous sulfur compounds in the soil. 2.) The role of vegetation in sulfur exchange between soil and atmosphere. Swedish J. Agr. Res. 6:37-45; 135-144.

Smith, K. A., J. M. Bremner, and M. A. Tabatabai. 1973. Sorption of gaseous atmosphere pollutants by soil. Soil Sci. 116:313-319.

Snedecor, G. W. and W. C. Cochran. 1967. Statistical Methods. 6th Ed. The Iowa State University Press, Ames, Iowa.

Sprugel, D. G. and J. E. Miller. 1980. A field estimate of sulfur dioxide deposition velocities to rapidly growing soybeans. Water, Air, and Soil Pollut. 12:233-236.

Stauffer, R. S. and R. H. Rust. 1954. Leaching losses, rainfall, and percolation from eight Illinois soils. Agron. J. 47:207-211.

Stewart, B. A. and L. K. Porter. 1969. Nitrogen-sulfur relationships in wheat (Triticum aestivum L.), corn (Zea mays L.) and beans (Phaseolus vulgaris). Agron. J. 61:267-271.

Suarez, E. L. and U. S. Jones. 1982. Atmospheric sulfur as related to acid precipitation and soil fertility. Soil Sci. Soc. Am. J. 46:976-980.

Tabatabai, M. A. and J. M. Bremner. 1970. A simple turbidimetric method of determining total sulfur in plant materials. Agron. J. 62:805-806.

Tobatabai, M. A. and J. M. Bremner. 1972. Distribution of total and available sulfur in selected soils and soil profiles. Agron. J. 64:40-43.

Terman, G. L. 1978. Atmospheric sulfur--the agronomic aspects. The Sulfur Institute Tech. Bull. No. 23.

Thomas, W. 1959. Effects of applied nitrogen and sulfur on yield and protein content of corn. Agron. J. 51:572-573.

Thomas, W. 1960. Effects of electrolyte imbibition upon cation-exchange behavior of soils. Soil Sci. Soc. Am. Proc. 24:329-332.

Thomas, R. L., R. W. Sheard, and J. R. Moyer. 1967. Comparison of conventional and automated procedures for nitrogen, phosphorus, and potassium analysis of plant materials using a single digestion. Agron. J. 59:240-243.

Volchok, H. L. and R. T. Graveson. 1975. Wet/dry fallout collection. Proc. 2nd Federal Conf. on the Great Lakes. ICMSE-Fed. Council for Science and Technology, Washington, D. C.

Williams, C. H. 1967. Some factors affecting the mineralization of organic sulfur in soils. Plant and Soil. 26:205-223.

Williams, C. H. 1968. Seasonal fluctuations in mineral sulfur under subterranean clover posture in Southern New South Wales. Aust. J. Soil Res. 6:131-139.

Williams, C. H. 1975. The chemical nature of sulfur compounds in soils. p. 21-31. In K. D. McLachlan (ed) Sulfur in Australaian Agriculture. Sydney University Press. Sydney, Australia.

Williams, C. H. and A. Steinbergs. 1959. Soil sulfur fractions as chemical indices of available sulfur in some Australian soils. Aust. J. Agr. Res. 10:340-352.

Williams, C. H. and A. Steinbergs. 1964. The evalution of plant available sulfur in soils: II. Plant and Soil. 21:50-62.

West, P. W. and G. C. Gaeke. 1956. Fixation of sulfur dioxide as disulfilomercurate (II) and subsequent colorimetric estimation. Anal. Chem. 28:1816.

Wolt, J. D. 1981. Sulfate retention by acid sulfate-polluted soils in the Copper Basin Area of Tennessee. Soil Sci. Soc. Am. J. 45:283-287.

Wolt, J. D. and Fred Adams. 1979. The release of sulfate from soil-applied basaluminute and alunite. Soil Sci. Soc. Am. J. 43:118-121.

APPENDICES

APPENDIX A

SULFATE DETERMINATION BY TURBIDIMETRY

(Modified Procedure of Massoumi and Cornfield, 1963)

Procedure

Reagents: As outlined in reference

Standard curve:

Place 0, 1, 2, 3, 4, and 5 ml of the working standard sulfate solution (20 µgS/ml) in separate 50 ml Erlenmeyer flasks. Add distilled water to bring total volume in each flask to 20 ml. Add 2.5 ml of 25% NHO_3, then 2 ml of the HOAc-H_3PO_4 mixture. Swirl flasks gently by hand in a circular motion. The diameter of the swirling circle should be about 1 foot and the solution must not be agitated. Swirl each flask five circles. After swirling each flask, as described above, repeat the swirling procedure. Add 0.5 ml of $BaSO_4$ seed-suspension, then 5 ml of $BaCl_2$ solution: swirl flasks as described above. Add 1 ml of gum acacia-acetic acid solution, and swirl again. Allow solutions to stand for 1 hour before reading. To read, place a piece of Parafilm on the flask's opening and hold down with thumb and invert flask ten times without agitating the solution vigorously. Then pour the solution gently into the turbidimeter glass vial and read. If a

turbidimeter is not available, a colorimeter with blue filter (440 nm) can be used. Readings will be lower if a colorimeter is used and hence accuracy is decreased.

Samples:

An aliquot of not more than 20 ml and containing between 0.02 and 0.01 mg S is placed in a 50 ml Erlenmeyer flask. Then, the same procedure as for the standard curve is followed. A standard curve is necessary for each set of samples analyzed.

Comments:

1) A set of Repipets was found to speed up the procedure and improves the reproducibility of results greatly. Each of the reagents (except for the $BaSO_4$ seed-suspension which has to be prepared fresh daily before use) is placed in a Repipet bottle and the Repipet is set to deliver the required volume of the reagent.

2) Standards and samples are placed side by side after making to 20 ml and each reagent is added to all samples successively. Do not add all reagents to one sample before going to the next sample.

3) Temperature is very critical and can greatly affect readings. A temperature of 23-25^{o}C is very desirable. Because of the temperature effect, standard curves will not be always the same. Standard curves may often result in S-shaped curves.

4) Generally, the 0 mg S point on the curve does not follow the curve of the other points. It will be advisable to neglect it. However, to be sure that reagents or glassware are not contaminated, a 0 mg S sample is included every time and its reading recorded.

APPENDIX B

Table B-1. Statistical Analyses of Data Using A Nested Design.

	Source of Variation with their Respective Degrees of Freedom†					
	TRT (df) 2	YRS 2	LOC(YRS) 6	TRT X YRS 4	TRT X LOC(YRS) 12	BKS X (YRS X LOC) 18
Yield	+‡	**	**	NS	NS	NS
Nutrient Concentration of Leaves						
S	NS	**	NS	NS	NS	NS
N	+	**	**	NS	NS	NS
N:S	NS	NS	NS	NS	NS	NS
P	NS	NS	**	NS	NS	NS
Ca	NS	*	*	NS	NS	NS
Mg	NS	**	**	NS	NS	*
K	NS	*	NS	NS	NS	NS
Nutrient Concentration of Grain						
S	NS	**	*	NS	+	*
N	NS	**	*	NS	NS	NS
N:S	NS	*	NS	NS	+	*
Soil SO_4-S and pH by Depth						
0-15 cm						
SO_4	NS	NS	NS	+	+	NS
pH	NS	**	**	NS	NS	NS
15-30 cm						
SO_4	NS	NS	**	NS	NS	NS
pH	NS	NS	*	NS	*	**
30-45 cm						
SO_4	NS	NS	**	NS	NS	NS
pH	NS	*	**	NS	NS	*
Pooled Soil SO_4-S[3]						

†The following are abbreviations: TRT (Treatment), YRS (Years), LOC (Locations), BKS (Blocks). The mean squares of TRT, YRS, and LOC(YRS) were tested against the mean square of TRT X LOC(YRS), while other mean squares were tested against the pooled error (residual term).

‡Effects of independent variables were not significant (NS) or were significant at the 10% (+), or 5% (*) or 1% (**) level.

§Sum of extractable SO_4-S in each depth 0 through 45 cm expressed as $kg \cdot ha^{-1}$ assuming bulk density = 1.4 $Mg \cdot m^{-3}$.

APPENDIX C

Table B-2. Relationships Between Relative Yield, Nutrient Composition of Leaf and Soil S as Explained by Regression Models.

(Y =)	(X =)	Equation	Significance[†] of F-Test		C.V. %
relative yield	leaf-N concentration	$y = .05321(x)$	**	.980	—
relative yield	leaf-N concentration (Z = leaf-K concentration)	$y = .02829(x) + .090443(z)$	**	.985	—
leaf-N concentration	leaf-P concentration	$y = 17.37(x)$	**	.985	—
leaf-N concentration	leaf-P concentration (Z = leaf-K concentration)	$y = 11.04(x) + 1.374(z)$	**	.988	—
leaf-S concentration (at Knoxville)	Soil S of the 0-15 cm depth ($kg \cdot ha^{-1}$)	$y = .2355(x) - .0005611(x)^2 + 21.778$	**	.340	15.8
relative yield (at Grand Junction)	leaf-S concentration leaf-S co	$y = .4579(x) + 73.41$	**	.265	7.01
relative yield (at Grand Junction)	pooled soil S[§]	$y = -.04303(x) + 5.983 \times 10^{-6}(x^2) + 163.9$	**	.372	6.48
leaf-S concentration (at Greeneville)	pooled soil S	$y = .008757(x) - 1.223 \times 10^{-6}(x)^2 + 29.34$	+	.183	17.9

[†]F test was not significant (NS) or was significant at the 10% (+), or 5% (*) or 1% (**) level.

[‡]All nutrient concentrations are in $mmol \cdot kg$.

[§]Sum of extractable SO_4-S in each depth 0 through 45 cm expressed as $kg \cdot ha^{-1}$ assuming bulk density = 1.4 $Mg \cdot m^{-3}$.

Table B-3. Rate of S Lost by Leaching Under Cropping Conditions as Measured by Lysimeters.

Lysimeter	Amount of SO_4-S Leached	No. of Years Studied	Soil Type	Reference
	$kg \cdot ha^{-1} yr^{-1}$			
erosion type	33.6	10	silt loam	Stauffer and Rust, 1954
monolith	39.6	5	silt loam	Driebelbis, 1947
monolith	4.3	5	silt loam	Driebelbis, 1947
monolith	2.2	2	silt loam	Kilmer, et al., 1944
filled-in	91.8	10	silt loam	MacIntire, et al., 1941
funnel type	44.8	2	A_1 horizon	Joffe, 1936
type unknown	44.8	3	variation of soil types	Lipman and Conybeare, 1936
filled-in	50.4	1	sandy loam	Lyon and Bizzell, 1936

Table B-4. Wet/Dry Deposition in Tennessee.

Year(s)	No. of Locations	Average Wet/Dry Deposition	Reference
		$kg \cdot ha^{-1} yr^{-1}$	
1955	7	14.2	Jordan, et al., 1959
1971 to 1972	5	17.1	Jones, 1974
1973 to 1976	1	18.1	Shriner and Henderson, 1978
1978 to 1980	3	14.2	J. M. Kelly, personal communication
1980 to 1983	3	16.0	this research

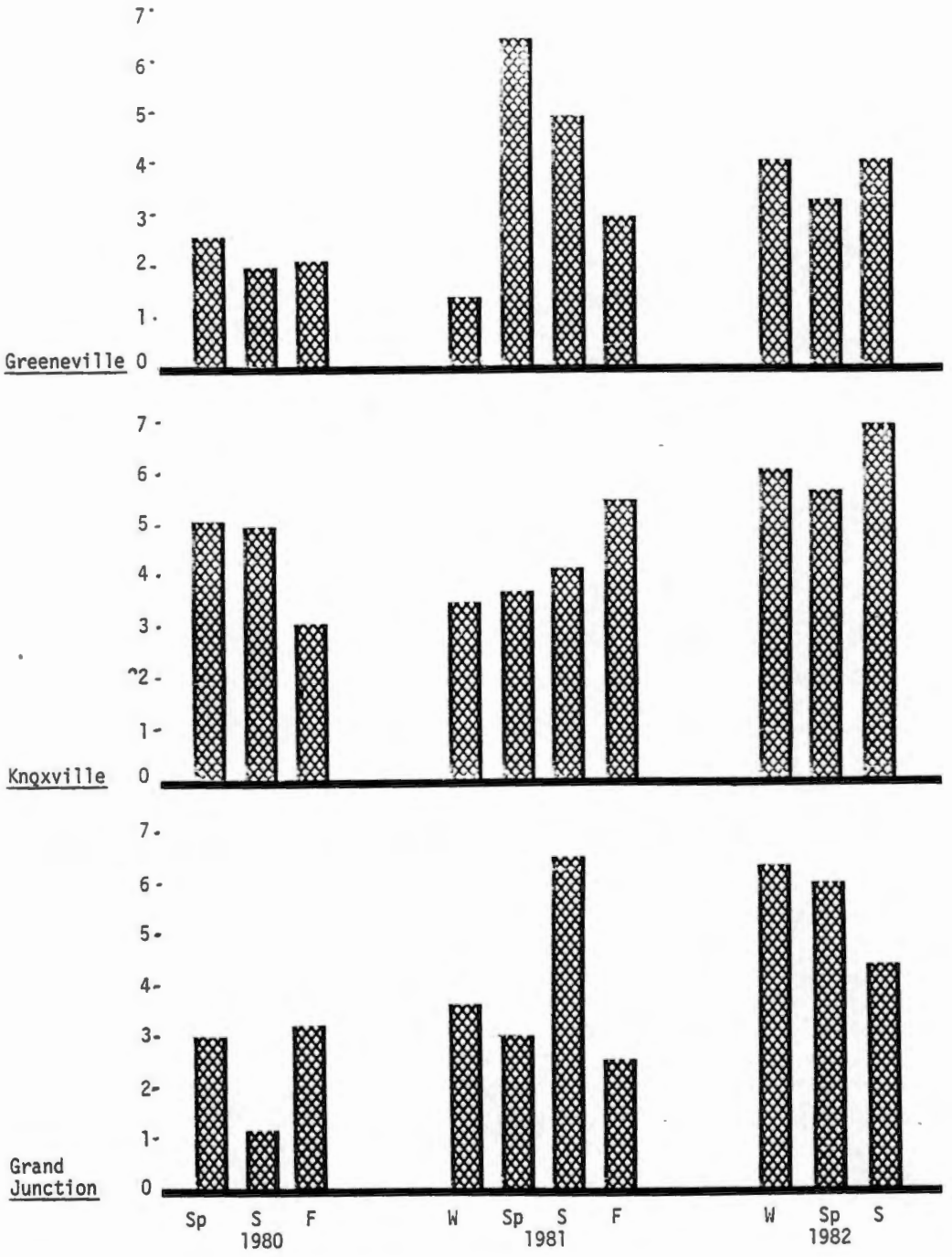

Figure A-1. Variation in Wet/Dry Deposition of S by Season, Year and Location ($kg \cdot ha^{-1} qtr^{-1}$).

APPENDIX D

Table B-5. Conversion Table of SI Units Used in the Thesis.

SI Unit	Equivalence
$\mu mol\ S\ kg^{-1}$	.3206 ppm
$mmol\ S\ kg^{-1}$	3.2×10^{-3} % S
$mmol\ N\ kg^{-1}$	1.4×10^{-3} % N
$mmol\ P\ kg^{-1}$	3.1×10^{-3} % P
$mmol\ K\ kg^{-1}$	3.9×10^{-3} % K
$mmol\ Ca\ kg^{-1}$	4.0×10^{-3} % Ca
$mmol\ Mg\ kg^{-1}$	2.4×10^{-3} % Mg
$\frac{mol \cdot kg^{-1} N}{mol \cdot kg^{-1} S}$	$.444\ \frac{\%N}{\%S}$
$Mg\ ha^{-1}$	15.95 bu/acre
$Mg \cdot m^{-3}$	$g \cdot cm^{3}$

VITA

Michael Briggs Bauman was born in Galax, Virginia on September 16, 1956. In June 1975, he graduated from Marion High School in Marion, Virginia. In May 1979, he received a Bachelor of Arts degree from Emory and Henry College, Emory, Virginia with a major in Biology. In January 1980, he enrolled at Virginia Polytechnic Institute, Blacksburg, to pursue a Bachelor of Science degree in Agronomy, which was awarded in March 1981. He received his Master of Science degree from The University of Tennessee, Knoxville in June 1983 with a major in Plant and Soil Science.

He is married to the former Elizabeth Duval Wiekel of Johnson City, Tennessee.